Reconstruction of two gallium arsenide surfaces. The upper diagram shows the structure of the (110) surface; the lower diagram shows the (111) surface. The GaAs–vacuum interface is at the top of each diagram. The bulk bonds are tetrahedral, whereas the surface bonds are planar for gallium atoms (green) and prismatic for arsenic atoms (red). The computer drawings are the work of Marcos Puga of the University of Wisconsin, Milwaukee. Figure 1

Exploring surface structure

A host of very new microscopies and spectroscopies, using photons, electrons, ions, atoms and molecules as probes, are answering technologically important questions about how surface atoms are arranged.

Shuk Y. Tong

Over the past seven or eight years, we have witnessed the development of a host of new tools for analyzing the atomic structures of surfaces. The quantitative structural information provided by these new tools has already contributed greatly to our understanding of the electronic, vibrational and chemical properties of surfaces. Through the continuing innovation of surface scientists all over the world, new and improved spectroscopies and microscopies are being invented and brought on line every year. The scanning tunneling microscope, which has an unprecedented ability to map the three-dimensional topography of surfaces, is just one recent example. (See PHYSICS TODAY, April 1982, page 21.)

Shuk Y. Tong is professor of physics and director of the Laboratory for Surface Studies at the University of Wisconsin, Milwaukee. He is visiting investigator at the University of Wisconsin, Madison, Synchrotron Radiation Center, located in Stoughton, Wisconsin.

In the early 1970s, when we had only one or two surface-structural techniques, new structural models had to wait many years to be tested, and even then the results were often inconclusive. Now, in 1984, we have ten or more analytical techniques for measuring the structure of surfaces directly, using probes such as synchrotron radiation, electrons, ions, atoms and molecules.[1] In addition, there are accurate spectroscopic techniques for measuring the electronic and vibrational properties of surfaces, thus providing complementary information.

Throughout this period of rapid growth, the surface-equipment industry has maintained a close working relationship with research scientists. Many of the technical workers and consultants in the industry are university-trained scientists with higher degrees. The close coupling between university research laboratories and the surface-equipment industry has played an important role in the remarkable recent growth of surface analysis.

In this article, I assess the status of the analytical tools used to determine surface structure. After discussing the many techniques and giving some meaning to the acronyms listed in the table on page 56, I will look at some of the recent—and unexpected—findings on surface structure.

The important parameters

The coordination of atoms and the distribution of electrons are different near the surface of a crystal than in the bulk of the crystal. If we picture a crystal as an array of steel balls tied together by springs, and if we cut the springs along a plane to form a surface, then it is not difficult to understand why surface atoms would move away from their bulk positions, as they have in the crystal represented in figure 1. The structural change that occurs in the surface region may involve atoms in one or more surface layers.

Although most semiconductors used

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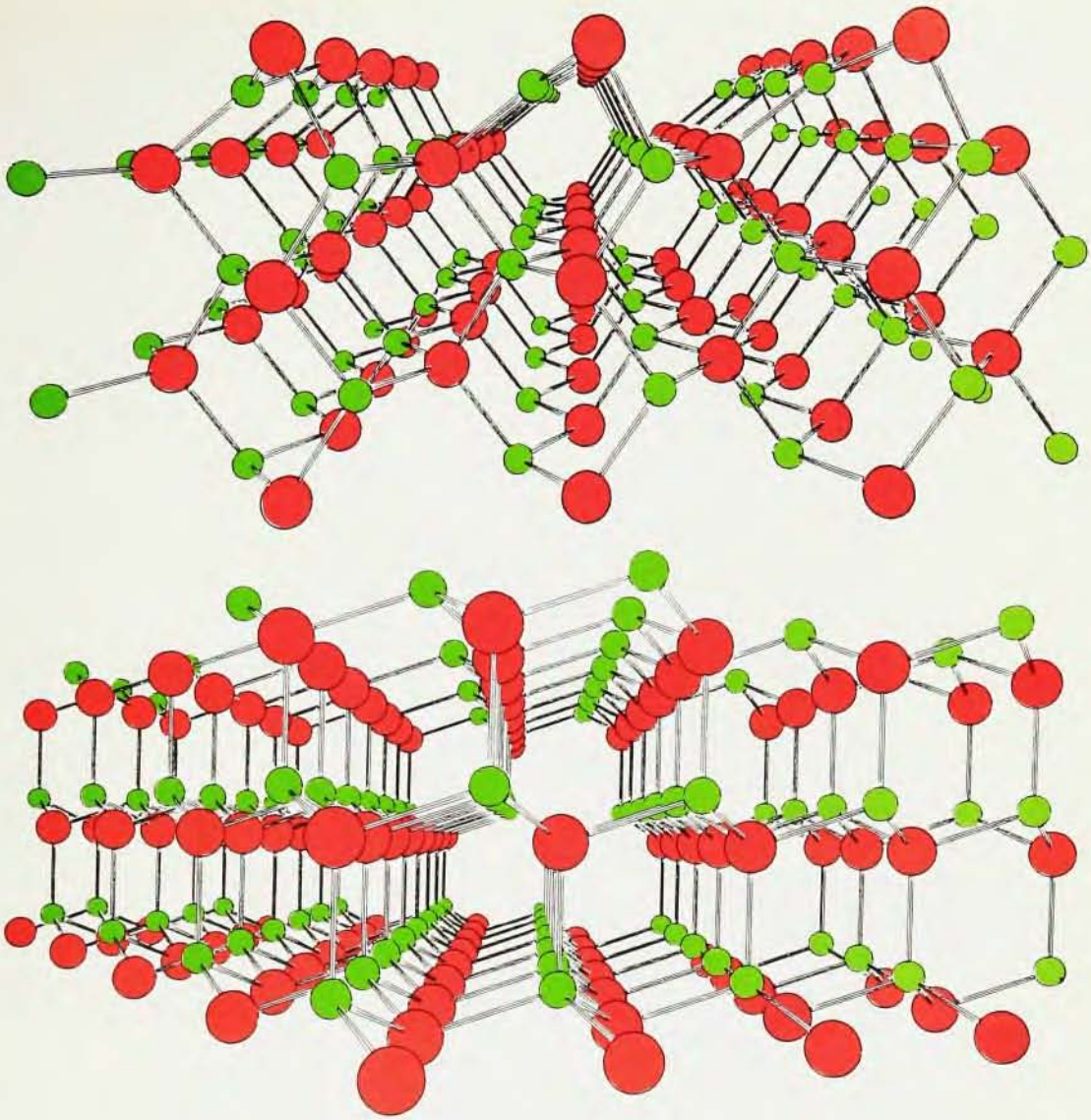


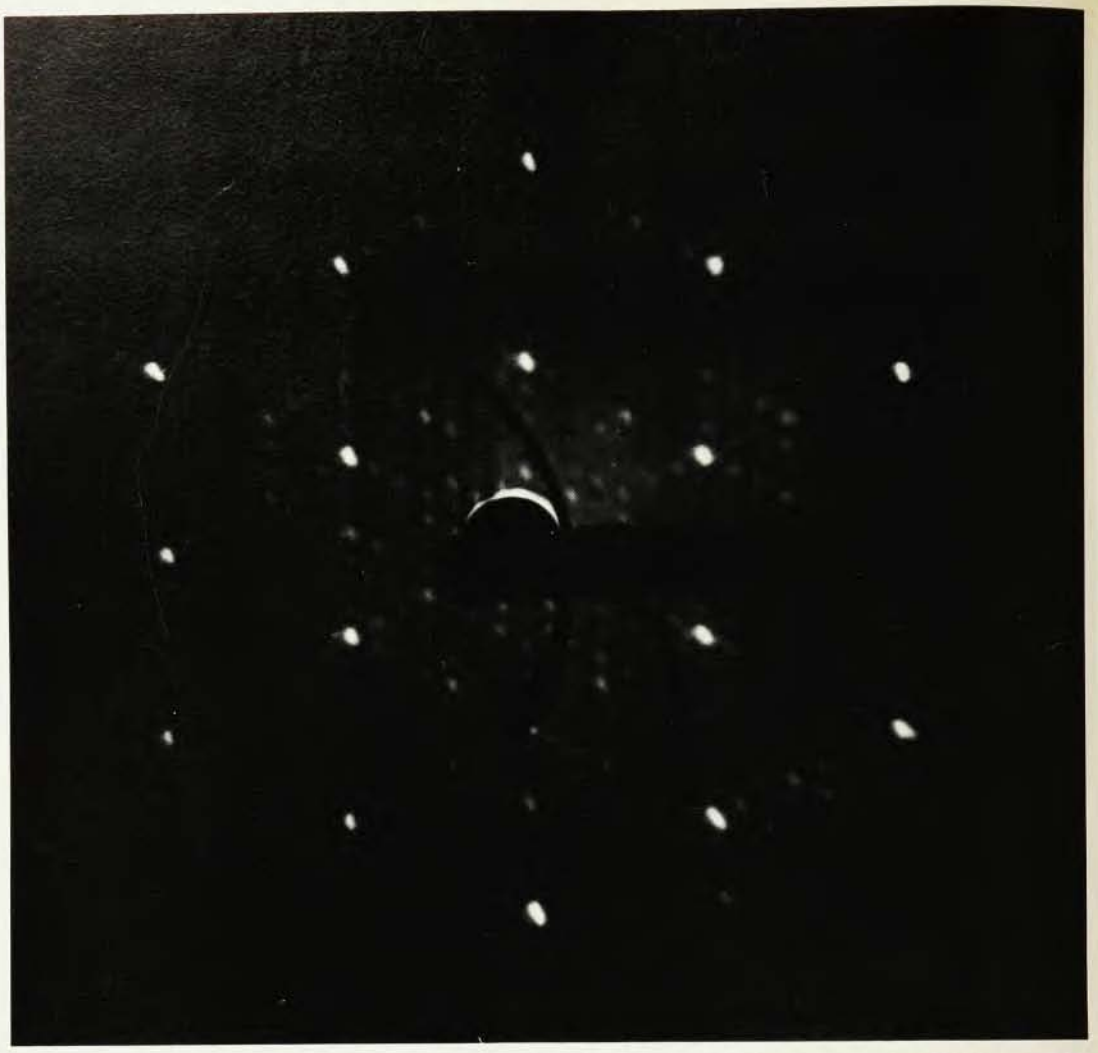
in modern technology are single crystals, most metals in everyday use are polycrystalline, so their surfaces are made up of a variety of crystal planes. However, researchers in the laboratory can grow single crystals and cut them to expose individual crystal planes. Some crystals can be grown through a layer-by-layer deposition from the gas phase.

The surface of a single crystal has two-dimensional periodicity. If a change results in a new structure with the same periodicity, we call this change a *surface relaxation*. For example, the (100) surface of copper is relaxed. If a structural change results in a different periodicity, we call it an $n\times m$–θ *surface reconstruction*, indicating a new unit cell n and m times larger than that of the bulk and rotated by an angle θ. For example, the (111) surface of silicon, annealed after cleaning by ion bombardment, exhibits a (7×7) reconstruction: The surface unit cell has basis vectors parallel to but 7 times longer than those of the bulk, forming a new unit cell 49 times bigger.

It is important to determine accurately the structure of surfaces. Without knowledge of the structure, there can be no real understanding of the electronic (valence band), vibrational (phonon dispersion) and chemical (binding) properties of the surface region. The current state of surface studies is analogous to that of bulk studies after the 1912 development of x-ray crystallography, which led to descriptions of lattice dynamics (1935), band structure (1937), electron–lattice interactions, superconductivity, electronic transport and so on, a body of physical phenomena known as condensed-matter physics.

The surface unit cell. It is possible to determine the size and shape of the surface unit cell accurately by low-energy electron diffraction, a technique that uses electrons with energies from 20 eV to 500 eV. Here one directs at a surface an electron beam of well defined energy and momentum. The elastically back-scattered electrons, which are concentrated along specific directions because of simple wave interference, appear as spots on a fluorescent screen. The collection of spots maps out the two-dimensional reciprocal lattice vector space of the surface, from which one can determine the real space unit cell. Figure 2 shows the LEED spot pattern of the (111) surface of silicon. The (7×7) surface reconstruction increases the number of spots on the screen by a factor of 49.

Low-energy electron diffraction and a technique known as Auger electron spectroscopy are the two analytical tools largely responsible for the everyday characterization of surfaces. To monitor surface order, one uses LEED or a high-energy version of it known as reflection high-energy electron diffraction. A disordered surface, for example, produces no LEED spots because it back-scatters electrons throughout the hemisphere. To determine surface



Spot pattern from the diffraction of low-energy electrons by the (111) surface of silicon. The 7×7 reconstruction of this surface increases the number of spots by a factor of 49. Figure 2

composition, one uses AES, which is able to detect the presence of a surface species to a concentration of 1 in 10^3 atoms.

Low-energy electron diffraction has other applications. At the University of Wisconsin, Madison, Max Lagally uses a high-angular-resolution version of the technique to study the sizes and distribution of steps and overlayer domains on surfaces, gaining information important for understanding the kinetics of crystal growth. At Brown University, Peder Estrup uses LEED to monitor surface phase transitions. He has found that the (100) surfaces of molybdenum and tungsten go through reversible order–disorder transitions in the 200–300-K temperature range.

Distances between surface atoms. There is, of course, more to the structure of surfaces than simply the size and shape of the unit cell. The distances between atoms *within* each unit cell and the distance between surface layers are also important. On the (7×7) reconstructed surface of silicon, for example, we would like to know the location of each silicon atom.

One source of information on the distances between surface atoms is the intensity variation of a LEED beam as a function of incident energy—an "IV profile." The intensity is maximum in a given direction if the waves scattered in that direction by different surface atoms interfere constructively. By measuring peak positions in IV profiles, it is possible to determine which structural arrangement best fits the data. Because an atom scatters a low-energy electron strongly—approximately a million times more strongly than it scatters an x ray—one must use a multiple-scattering diffraction theory to calculate the peak positions in an IV profile.

The first successful determinations of surface structure were made in the early 1970s, as the result of experimental work and the development of LEED theory (Thor Rhodin and I describe this in our article, PHYSICS TODAY, October 1975, page 23). The first structure determined was that of a clean metal surface, in 1972–73. This was followed by determination of the structure of ordered atomic overlayers on metals, in 1973–75. The first molecular adsorbate system analyzed was an overlayer of carbon monoxide on the (100) surface of nickel; and the structure of the (110) surface of the compound semiconductor gallium arsenide was solved in 1978.

Synchrotron-radiation techniques

An important development in the 1970s for surface analytical tools was the use of synchrotron radiation for condensed-matter and surface physics research. The synchrotron sources give experimenters a highly collimated, continuous spectrum of light that includes wavelengths not available from other sources. The synchrotron radiation is extremely bright, that is, a large number of photons per unit time enter a unit solid angle from a unit

source area. By way of comparison, the most powerful commercially available x-ray generator, a 60-kW rotating-anode tube, delivers to an experiment about 10^8 photons/sec, whereas a synchrotron source can deliver a thousand times that amount, and the light it produces is a hundred times better collimated. This dramatic difference in brightness makes the development of many new surface probes possible.

Three surface-structural techniques emerged as a direct result of the high brightness and continuous spectrum of synchrotron radiation: surface extended x-ray absorption fine structure, energy- or angle-dependent photoelectron diffraction, and x-ray diffraction by surfaces.

SEXAFS, is based on measurement of an atom's absorption coefficient as a function of the energy of incident photons. When the energy of an incident photon exceeds the threshold for exciting a core electron of an atom, a photoelectron is emitted. The absorption coefficient of a particular shell—K, L, M or whatever—is defined as the probability of exciting a photoelectron from that shell. For an isolated atom, the absorption coefficient above the absorption edge, or threshold of absorption, is a smooth function of energy, determined by the overlap of the wavefunction of the core state and the wavefunction of the photoelectron. If the absorbing atom is bonded to any neighbors, the photoelectron's wavefunction goes through a series of maximum and minimum amplitudes near the absorbing atom due to interference between its outgoing and backscattered waves. By measuring the modulation in the absorption coefficient and determining the wavelengths at which turning points occur, one can determine the distance between the absorbing atom and its neighbors. This surface technique is an analog of EXAFS, a bulk technique developed during the early 1970s.

It is generally posible to divide the data into two energy regimes: from 0 to 50 eV, where multiple scattering is important, and from 50 to 500 eV, where only single scattering is important. In the lower energy range, the technique is known as NEXAFS, near edge x-ray absorption fine structure, while the term SEXAFS is usually reserved for the higher energy range.

The first structure determined by SEXAFS was that of an overlayer of iodine on the (111) surface of silver.[2] That 1978 experiment found the shortest iodine–silver bond lengths in a $\sqrt{3}\times\sqrt{3}$–30° overlayer system to be 2.87 ± 0.03 Å, in good agreement with a 1973 LEED result of 2.80 ± 0.14 Å.

Joachim Stöhr and his coworkers at Exxon have used NEXAFS to study the adsorption of atoms, diatomic molecules, aromatic (ring-like) and other polyatomic molecules on metal surfaces. They find that for molecular adsorption systems, NEXAFS results are dominated by large peaks related to intramolecular resonances. These resonances can be understood as transitions into molecular orbital states such as σ^* and π^*, where wavefunctions have amplitudes that are largely localized within the molecule. As a result, NEXAFS is particularly sensitive to the intramolecular bond length and the orientation of these bonds relative to the surface. In the case of atomic adsorbates, the wavefunction of the final state is spread out among substrate atoms that are within a radius equal to the photoelectron's mean free path. Hence, NEXAFS spectra of atomic adsorbates reflect more than just nearest-neighbor substrate atoms.

Neither SEXAFS nor NEXAFS require long-range order, and therefore both techniques are used to study surfaces where the only order is local, that is, where any order is no more than about 10 Å in extent. Neither technique is suitable for studying clean surfaces, because the signal from the surface layer would be overwhelmed by signals coming from deeper layers.

Energy-dependent and angular-dependent photoelectron diffraction—EDPD and ADPD—are techniques closely related to SEXAFS and NEXAFS. Here one directly measures the number of photoelectrons emitted from a given core level as a function of photon energy or photon angle. By measuring the photoelectrons coming from a specific level, one avoids the interfering absorption edges seen in SEXAFS.

Early ADPD work focused on layer compounds and atomic overlayers on metals. More recent ADPD experiments have focused on molecular overlayers on metals and materials such as Sb_2Te_2Se. The first EDPD measurements were made in 1978, on selenium overlayers on nickel. Measurements of molecular and atomic adsorbates such as carbon monoxide, sulfur, iodine, sodium and tellurium on the surfaces of metals such as nickel, copper and silver have followed.

Recently, John Barton and his coworkers at the University of California, Berkeley, used Fourier transformations to analyze EDPD data taken along the directions of adsorbate–substrate nearest-neighbor bonds. Three groups, including Barton's and my own, are persuing this analytical technique, which is known as angle-resolved photoemission extended fine structure, or ARPEFS.

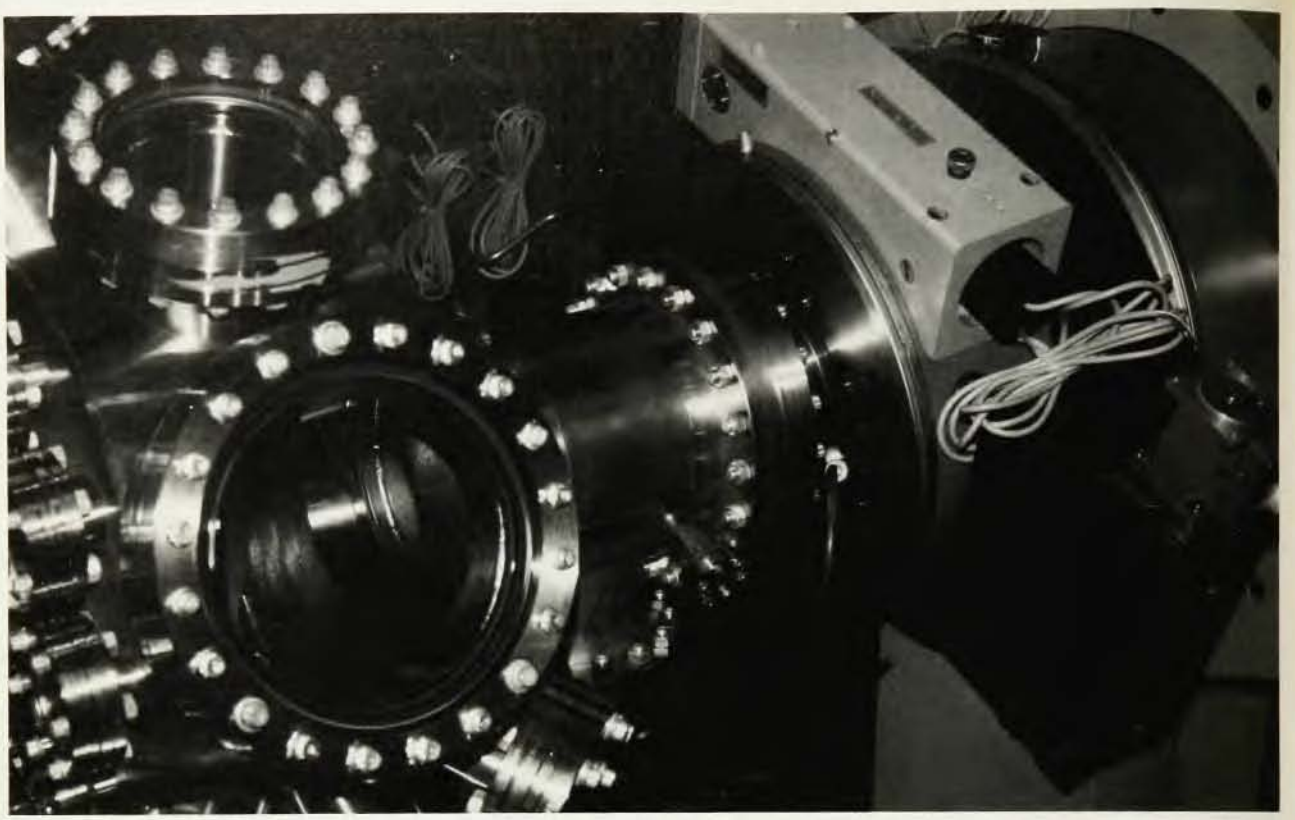
Diffraction of x rays is a well-known technique with which one can determine bulk lattice constants to an accuracy better than 0.01 Å. Recent progress toward applying this technique to the study of single-crystal surfaces is very encouraging. There are two basic requirements for success in this application. First, because the number of atoms in a surface is far less than that in the bulk, one must use a very bright x-ray source. This calls for synchrotron radiation sources, although, for heavy elements such as gold, a high-powered rotating-anode source will suffice. Second, because the sample is in an ultra-high-vacuum chamber, one must install a window material transparent to x rays. Beryllium windows, like the one shown in figure 3, are the most common, in spite of their brittleness and toxicity.

Because an x ray penetrates deep into a solid, the surface signal is superimposed on a large signal from the bulk. Thus, x-ray diffraction is most suitable for analyzing $(n\times m)$ reconstructed surfaces, where the surface periodicity is different from that of the bulk. In a reconstructed material, atoms in the surface layers that have the new periodicity scatter x rays into *new* diffraction spots. The deeper layers, with their (1×1) periodicity, do not contribute to the extra spots. The great power of the x-ray technique is that the diffraction is kinematical, that is, each atom scatters an x-ray photon only once, making the analysis straightforward.

Only a relatively small number of surface problems have been examined with the technique. The earliest work, in 1980, showed[3] large pairwise displacements of 0.92 Å in the top layer of atoms on the (2×1) reconstructed (100) surface of germanium. More recently, Ian Robinson of Bell Laboratories studied the (2×1) reconstructed (110) surface of gold, and found[4] that alternate rows of atoms in the top layer are removed—a "missing-row" structure. He also found that atoms in the top and second layers undergo large displacements both perpendicular and parallel to the surface.

Now that researchers have demonstrated that x-ray diffraction is a useful technique for studying certain surface problems, there is a considerable effort underway to apply it. Progress is being made in conjunction with the development of storage-ring x-ray sources at Brookhaven, Cornell and Stanford, as well as at Orsay, Hamburg and Daresbury. The potential of the x-ray technique is limited at present by the availability and power of such sources.

One can use electron beams to study absorption fine structure in a manner somewhat analogous to the way photons are used in SEXAFS. Researchers currently follow two general approaches. The first, extended x-ray-edge energy-loss fine structure, uses electrons of energy around 10^5 eV. The second, extended appearance potential



Apparatus for making x-ray diffraction measurements in an ultrahigh vacuum. A four-circle diffractometer (right) couples precision motions into a vacuum chamber (left) in which samples are prepared and characterized. The x rays pass into the chamber through a beryllium window (the cylindrical structure at the center of the photograph, just to the right of the large glass window), and after diffraction travel back out through the window to a scintillation detector. Paul Fuoss and Ian Robinson use this instrument at AT&T Bell Labs. Figure 3

fine structure,[5] uses a lower-energy beam of about 10^3 eV.

Ion-beam scattering

We now turn to another important class of techniques, which use ion beams to probe surface structure. These techniques typically use beams of H^+ or He^+ in the energy range of 100 eV to 2 MeV. It is useful to divide the energy into low and high regions characterized by ion velocities below and above the Bohr velocity of 2.2×10^6 m/sec. In the high-energy region, the ions cast a very narrow shadow cone of radius about 0.1 Å, and the ions have a negligible probability of being neutralized. In the low-energy region, the shadow cone has a radius of about 1 Å, and for inert gas ions, the probability of neutralization is very high. High-energy ion scattering is commonly known as Rutherford back scattering. Here a beam of ions incident on an aligned single crystal scatters, showing an energy peak that corresponds to the contribution from the exposed monolayers of the surface. Scattering from underlying atoms is suppressed due to the shadowing of the beam by the first layer of atoms. If the surface atoms are displaced from their bulk-like sites, they do not shadow the underlying atoms, and the surface scattering peak increases. Accurate measurements of the surface peak intensity then yield information on the positions of the surface atoms.

Further detailed information on the structure of the surface comes from *angle-resolved* ion scattering, where one measures the angular distribution of the ions scattered from the surface. Particles scattered from the second and deeper layers are blocked in their outward trajectories by surface atoms; the blocking angles yield the coordinates of surface atoms or adsorbates.

Low-energy ion scattering uses ions of energy about 1 keV. Here, the shadow cone has a large radius and the technique is sensitive to the exposed atoms only. In 1981, Masakazu Aono in Ibaraki, Japan, introduced a special version of LEIS; he and his coworkers measured ions in the back-scattering direction only, that is, they measured ions with a scattering angle of 180°. This version of low-energy ion scattering, which they named impact collision ion-scattering spectroscopy, eliminates blocking effects and allows one to deduce the distance between surface atoms from the shadowing effect alone.

High-energy and low-energy ion scattering have now been applied to a wide range of surface problems, including adsorbate–substrate systems and the relaxation and reconstruction of clean surfaces.[6] Later I will discuss some of the structures determined by ion scattering.

One can also probe surfaces by using atoms with low energies—helium at 10 to 200 millielectron volts, for example. In a technique known as helium-atom diffraction, the measurement of the angular distribution of backscattered helium atoms reveals the two-dimensional corrugation of the potential between the helium atoms and the surface.

Two structural techniques developed in the late 1970s are based on the desorption of neutral[7] or ionized atoms from surfaces. The techniques, electron-stimulated desorption and photon-stimulated desorption, allow one to break surface bonds selectively and identify binding sites and bond angles (see PHYSICS TODAY, November 1980, page 17). Both ESD and PSD are sensitive to the local geometry and promise to provide information on the orientation of adsorbed molecules and the angles of surface bonds. When the

angles of desorption are taken into account, the technique is known as electron-stimulated desorption ion angular distribution.[8] Measurements with this technique show, for example, that oxygen ions leave different faces of tungsten at different angles, and that these angles have the same symmetry as the substrate lattice. The desorption angles give information on the orientation of the bonds that bind the adsorbate to the surface.

Pictures of surfaces

None of the above techniques gives the actual morphology of the surface. For example, a surface defect such as a vacancy or step shows up in an x-ray or LEED pattern as an increase in the general background. It is possible to tell if a surface has many steps, but none of the methods tells us *where* the steps or defects are.

Perhaps a stronger reason for developing surface imaging techniques is that nothing satisfies a person's curiosity better than a "picture," in which one can actually "see" the assembly of atoms, the spaces between, the steps and terraces.

Since 1958 we have had field ion microscope images[9] of surface atoms under applied electric fields of 2 to 5 volts/angstrom. The best available resolution of FIM is less than 3 Å. Images of surfaces not under a strong external field are now available by the methods described below.

In 1982, a group at the IBM Zurich Research Laboratory developed scanning tunneling microscopy. In this technique, one brings a small metal tip within about 5 Å of the surface being studied, so that electrons can tunnel through the vacuum between surface and tip. At that distance, a potential difference of a hundredth of a volt gives a tunneling current of about one nanoamp. The tip is mounted on three piezoelectric arms meeting at right angles, which can move the tip in three dimensions with remarkably precise control. Control of the position of the tip is typically limited by thermal drift and by vibrations, not by the piezodrives.

The tunneling current is extraordinarily sensitive to the height of the tip above the surface; a 1 Å change in tip height changes the current by an order of magnitude. The tip scans the surface, while an electronic feedback loop adjusts its height to maintain a constant current. The resulting trace of height versus lateral position is, in effect, a contour map of the surface.

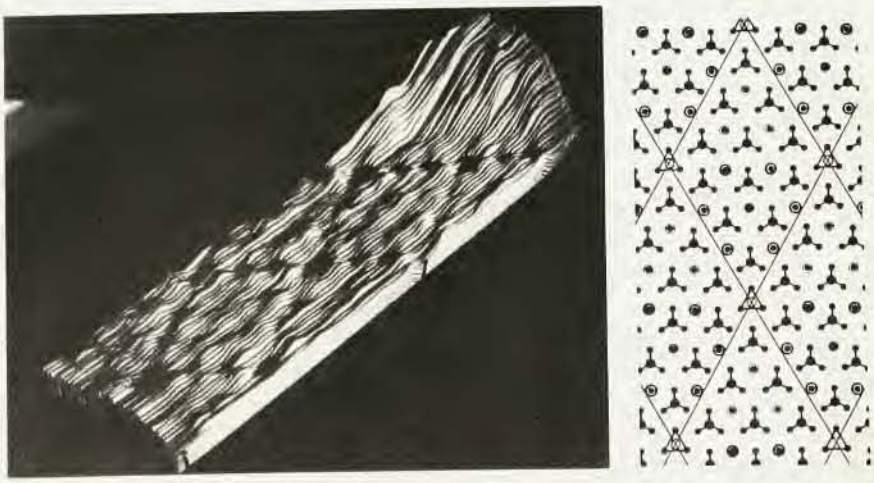
There are two points to bear in mind about surface images. First, it is not yet possible to obtain a clear view of individual surface atoms. For that, we will have to resolve the full three-dimensional topology of the surface with a resolution of better than 2 Å. The best resolution of scanning tunneling microscopy is about 5 Å, while transmission electron microscopy gives a two-dimensional *projected* image of atoms with a resolution of 2–3 Å. Second, in STM, the image is a contour map of constant electron distribution, from which one can deduce the positions of atomic cores with a proper theory. In TEM, we *are* looking at atomic cores. However, remembering that even a simple photographic picture can distort an object, one should resist the obvious temptation to measure distances between bright dots to deduce distances between atoms on the surface. Distances between atoms are better deduced from models, by using computer simulations to select the model that produces images most like the measured ones. Nevertheless, both TEM and STM now have the resolution to provide a great deal of information on the topographic features of surfaces.

Figure 4 shows an STM image of silicon's 7×7 reconstructed (111) surface. A theory developed by Jerry Tersoff and Donald R. Hamann of Bell Laboratories indicates that the STM image corresponds to a contour of constant "local density of states" of the bare surface. Reducing the tip radius or the tunneling resistance picks out contours closer to the surface, giving better resolution.

The greatest single bottleneck in the development of STM so far has been the tip. The lack of detailed information on the microscopic structure of the tip has impeded the quantitative understanding of STM. More important, the inability to prepare high-resolution tips reproducibly has been a major obstacle to carrying out extensive experimental studies. The unique advantage of STM, however, is its ability to resolve the three-dimensional topography of the surface, including nonperiodic structures that are often inaccessible by other techniques.

In the last few years, there has also been substantial progress in the use of electron-microscope imaging techniques for surface analysis. A method called high-resolution imaging transmission electron microscopy employs low-order diffracted beams to produce an interference image of the material under investigation; the principle is similar to that of a light microscope, but here electrons are the imaging particles. A transmission electron microscope developed at Cambridge University takes advantage of recent technical progress in electron optics and stability, and can achieve a lateral resolution of 2 Å. Figure 5 shows an image from that machine. Here we are looking at the reconstructed (110) surface of gold. The image was produced by orienting the surface of a 100-Å-thick gold specimen parallel to the electron beam, resulting in a profile of the surface. Inset is an image simulation with a 23.5% outward relaxation at the top of the serrated structure.

Electron microscopes of a second class are currently being tested for use to study surfaces. These instruments use a 5-Å-wide beam of electrons in a technique known as scanning transmission electron microscopy. By scanning this very fine probe across a specimen



Scanning tunneling microscope data, plotted in three dimensions, and model of surface. The STM plot (left) is of the 7×7 reconstructed (111) surface of silicon at 300 °C. The adatom model at the right has a periodicity consistent with the plot. The plot and model are the work of Gerd Binnig, Heinrich Rohrer, Christoph Gerber and Edmund Weibel of IBM, Zurich. Figure 4

and collecting, for instance, Auger electrons, one can form a surface image. The scanning principle is similar to that used to produce a television image. An important potential use of STEM is the analysis of chemical inhomogeneities on surfaces. Do foreign chemicals adsorb preferentially at surface steps? This is the type of question that STEM may be particularly adept at answering.

Properties related to structure

Besides the techniques whose primary purpose is determining surface structure, there are techniques that measure surface dynamical properties that also give us distinct information on the structure. One such technique is angle-resolved ultraviolet photoemission spectroscopy.[10] Using symmetry and polarization properties, one can use ARUPS to determine the tilt angle of, for example, adsorbed carbon monoxide on transition-metal surfaces.[11] This technique also gives other important structural information. On semiconductor surfaces, for example, geometric rearrangement can push surface electronic states away from the band gap, as was found by ARUPS on the (110) surface of gallium arsenide. Thus, ARUPS measurements of surface states provide important information on surface reconstruction.

Spectroscopists have long used the vibrational modes of molecules to study molecular structure. Three methods have recently been developed to study vibrational modes of clean or adsorbate-covered surfaces.

The first of these is called reflection–absorption infrared spectroscopy. In an RAIRS experiment, infrared radiation is reflected at a high angle of incidence from a metal surface that bears adsorbed molecules. The infrared excitation of a vibrational mode of a molecule requires that the vibration has associated with it an oscillating dipole moment in the direction normal to the surface. At the University of Wisconsin, Milwaukee, Robert Greenler has determined the optimal angle of incidence for the infrared radiation; he has found the relation between the angle and the absorbance of radiation by a thin layer of molecules on a surface. Researchers have used RAIRS to study the adsorption of carbon monoxide on various crystal faces of copper, nickel, palladium and platinum.

The second technique for studying the vibrational modes of clean or adsorbate-covered surfaces is high-resolution electron energy-loss spectroscopy. An important feature of HREELS is that at off-specular directions, it measures all the vibrational modes of a system, both perpendicular and parallel to the surface. This is an important advantage over optical spectroscopic techniques such as RAIRS, which are blind to modes where the dipole oscillation is parallel to the surface.

Harald Ibach and his coworkers at KFA in Jülich, West Germany, have used HREELS to study clean surfaces and surfaces with atomic and molecular adsorbates, at specular and off-specular directions. In collaboration with Talat Rahman of Kansas State University, Douglas Mills of the University of California at Irvine and John Black of Brock University in Canada,[12] Ibach's group recently mapped out the entire dispersion relation of surface phonons on the clean (100) surface of nickel and on the (100) surface of nickel covered with a $c(2\times2)$ overlayer of oxygen.

An important recent experimental innovation is the use of incident electrons with energies higher than 50 eV. Recent experiments on the (100) surface of nickel by Ibach's group, and calculations by Burl Hall, Mu L. Xu and myself, have determined the off-specular inelastic cross-section as a function of electron energy over the wide energy range of 50 to 260 eV. Figure 6 is a photograph of an HREELS lens system.

A third method for studying vibrational modes of clean surfaces is known as inelastic atom scattering spectroscopy. Here one uses atoms of energies 10 to 200 meV as probes. The technique has a fine spectral resolution of 0.5 to 4 meV, and can be used to study very-low-frequency vibrational modes of surfaces.

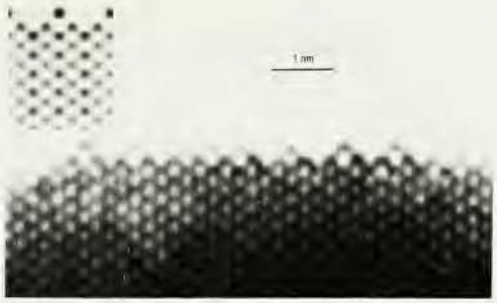
Surface theory

An obvious but major goal of theory is to calculate the total energy of different atomic arrangements with sufficient accuracy to say which configuration has the lowest energy. This is a difficult task because in many cases the energy differences are as small as 0.1 eV per atom. However, major advances made since 1978 allow one to predict, with some confidence, structures for a few metal and semiconductor surfaces.

In 1959, James Phillips, now at Bell Laboratories, and Leonard Kleinman, now at the University of Texas, intro-

Techniques and their characteristics

Acronym	Technique	Probe particle	Measured particle
ADPD	Angular-dependent photoelectron diffraction	Photon	Electron
AES	Auger-electron spectroscopy	Electron	Electron
ARPEFS	Angle-resolved photoemission extended fine structure	Photon	Electron
ARUPS	Angle-resolved ultraviolet photoemission spectroscopy	Photon	Electron
EAPFS	Extended appearance potential fine structure	Electron	Electron
EDPD	Energy-dependent photoelectron diffraction	Photon	Electron
ESD	Electron-stimulated desorption	Electron	Ion, atom
ESDIAD	Electron-stimulated desorption ion angular distribution	Electron	Ion
EXAFS	Extended x-ray absorption fine structure	Photon	Electron, photon
EXELFS	Extended x-ray-edge energy-loss fine structure	Electron	Electron
FIM	Field ion microscopy	Atom	Ion
HEAD	Helium-atom diffraction	Atom	Atom
HREELS	High-resolution electron-energy-loss spectroscopy	Electron	Electron
IAS	Inelastic atom scattering	Atom	Atom
ICISS	Impact collision ion-scattering spectroscopy	Ion	Ion
LEED	Low-energy electron diffraction	Electron	Electron
LEIS	Low-energy ion scattering	Ion	Ion
NEXAFS	Near-edge x-ray absorption fine structure	Photon	Electron, photon
PSD	Photon-stimulated desorption	Photon	Ion, atom
RAIRS	Reflection–absorption infrared spectroscopy	Photon	Photon
RBS	Rutherford back scattering	Ion	Ion
RHEED	Reflection high-energy electron diffraction	Electron	Electron
SEXAFS	Surface extended x-ray absorption fine structure	Photon	Electron, photon
STEM	Scanning transmission electron microscopy	Electron	Electron
STM	Scanning tunneling microscopy	(Needle)	Electron
TEM	Transmission electron microscopy	Electron	Electron



Transmission electron microscope image of the (110) surface of gold, showing a region with a partial 2×1 reconstruction. Inset is a simulation of the image. The image and simulation are the work of Laurence Marks of Arizona State University. Figure 5

duced pseudopotentials for calculating electronic properties of nonmetals. What began as an almost empirical technique for keeping valence electrons from interacting with the strong potential near the core, has become a very accurate self-consistent theory. In 1978, James Chadi of Xerox and others showed[13] that minimizing the total energy is an effective way to determine surface structure. Modern pseudopotential calculations claim an accuracy of 0.02 eV per atom on many systems.[14]

A milestone in calculating the bulk structure of metals was reached in 1978 with the work of Arthur Williams, Victor Moruzzi and James Janak of IBM. They used the Korringa–Kohn–Rostoker method to evaluate the bulk lattice constant, cohesive energy and bulk modulus for a series of metals, and were able to determine which metals have a face-centered cubic lattice and which have a body-centered cubic structure. In 1981, Arthur Freeman and his group at Northwestern University introduced a more accurate technique known as the full-potential linearized augmented-plane-wave method. At about the same time, J. Sam Faulkner of Oak Ridge National Laboratory improved upon the Korringa–Kohn–Rostoker method for nonspherical potentials. Theorists are using these general potential techniques to determine surface structure.

We now have the encouraging situation that electronic calculations and total-energy calculations are sufficiently precise that the difference between methods for metals and nonmetals is diminishing. However, one should bear in mind that total-energy calculations can only determine local minima and compare these minima for a predetermined number of configurations. Theory can *not* start with 10^{16} atoms and consider all possible configurations to find the atomic arrangement that has the lowest energy.

What have we learned?

Before 1972, we knew very little about surface structure. There was practically no information on the distances between surface atoms. Calculations of dynamical properties such as surface phonons and surface states used bulk terminated surfaces.

In the dozen years since then, researchers have amassed a large body of information on surface structure. We now have a much more realistic and quantitative view of surface atomic arrangement, adsorbate binding sites and even the distribution of steps on surfaces. We are at the threshold of actually being able to look at a surface at the atomic level through the new imaging techniques. Looking back at the development of the field, we see achievements beyond the most optimistic expectation of many researchers.

The contribution of theory to this development, particularly through its close coupling to the experimental effort, could hardly be over-emphasized. The combination of theory and experiment is telling us not only *how* surface atoms are arranged, but also, in many cases, *why* such arrangements occur.

What follows is a very brief sample of information gathered on surface structure.

Clean-surface relaxation. It has long been suspected that the spacing between layers near a metal's surface would relax to values different from those in the bulk. Early theoretical models using pair potentials considered only the change in the atomic coordination. These calculations almost universally predicted that the spacing between the first and second atomic layers would be larger than it is in the bulk.

The first structural results from LEED, in 1972–73, were on surface relaxation, and showed that the spacing between layers is usually *less* than it is in the bulk. Within a year, theorists found that this result is consistent with models that take into account the electronic forces on surface atoms due to the need for surface electrons to redistribute. Recent calculations[15] that allow the participation of several layers in the relaxation process indicate that multilayer relaxation is a common phenomenon on many metal surfaces.

Measurements of multilayer relaxation are carried out mainly by LEED and RBS, and results from the two techniques usually agree to about 0.05 Å. The measurements and analyses to date have determined multilayer relaxations for various surfaces of metals such as copper,[16] silver,[17] aluminum and nickel.

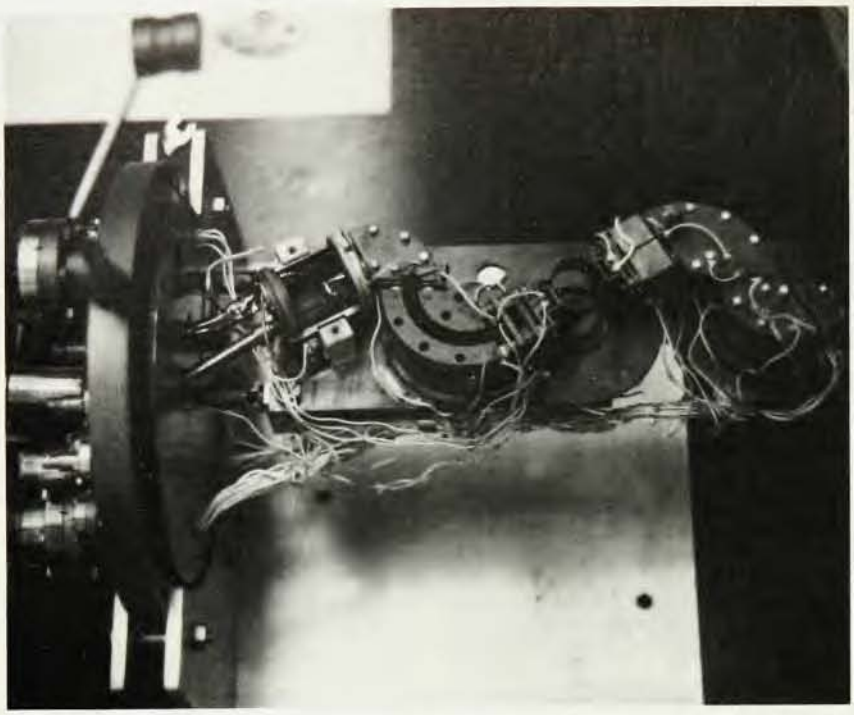
Various open faces of iron show multilayer relaxation in directions both normal to and parallel to the surface.[18]

Clean-surface reconstruction. The $(n\times m)$ reconstructions of clean metal surfaces have long intrigued surface scientists. Although these occur in lighter metals, they are most common in 4d and 5d metals. A 1977 LEED experiment showed[19] that in the reconstruction of the (100) surface of tungsten, adjacent rows of surface atoms move in opposite directions along [110], forming a $c(2\times2)$ superlattice. The (2×1) missing-row structure of gold's reconstructed (110) surface, mentioned earlier, was determined by x-ray diffraction, TEM, STM and RBS. The x-ray and RBS techniques also determined that the second layer must have a lateral displacement of about 0.12 Å.

Other surfaces of 5d metals, such as Ir(110) and Pt(110), also exhibit the (2×1) reconstruction. The (100) faces of these metals show a variety of structures. Determining in detail the positions of atoms on the reconstructed surfaces of these metals, and doing the same for reconstructed semiconductor surfaces such as Si(111), Si(100) and GaAs(100), remains the most challenging problem in surface structural analysis.

Atomic overlayers. Since the early LEED studies of chalcogen overlayers on nickel in 1973–75, the structures of chemisorbed layers of atoms on metal surfaces have received a great deal of attention, because they provide a first view of the solid–solid interface and crystal growth. Binding sites and bond distances are the most important parameters. From the 80 or so overlayer–substrate systems studied, some general patterns emerged. One of these is that the chemisorption site is usually where atoms are removed when the surface is formed. In other words, chemisorption generally fills "bulk defects" and heals a surface of broken bonds. Using ICISS, Aono has determined that these sites usually correspond to locations of high surface electronic density.

Exceptions to this behavior occur for the smaller and more reactive adsor-



Optics of an instrument for high-resolution electron-energy-loss spectroscopy. This HREELS device, which can take spectra at 5 meV resolution, is used by James Erskine and his coworkers at the University of Texas, Austin. Figure 6

bates hydrogen, carbon and oxygen. These smaller atoms often form bonds on top of surface atoms, as well as inside or below the surface layer. The structures of oxygen overlayers on Cu(110), Ni(110) and Ni(100) are unresolved, and very few cases of hydrogen or carbon adsorption structures have been solved. For the c(2×2) overlayer of O on Ni(001), some data indicate that the oxygen atom occupies an off-center site, although the majority of theoretical and experimental results show it sitting at the centered site. Details of this structure, such as a lateral shift of about 0.3 Å, remain unresolved.

Molecular overlayers. Molecules adsorbed on metal surfaces have been studied mainly by HREELS, NEXAFS and LEED.[20] Researchers have used these techniques to analyze the structures of carbon monoxide, straight-chain hydrocarbons such as C_2H_2 and aromatic hydrocarbons such as C_6H_6 that are adsorbed on nickel, rhodium and platinum surfaces. These complicated systems illustrate the value of using more than one surface technique. A good example is the structure of the ethylidyne species (CH_3–C<) on the (111) surface of platinum, first determined[21] by dynamical LEED analysis. The structure was confirmed by HREELS, NEXAFS and other measurements, which also cleared up confusion created by earlier experiments.

Clean semiconductor surfaces. The structure of the technologically most important single-crystal surface, the (7×7) reconstructed (111) surface of silicon, remains unknown, although many models have been proposed. (See, for example, the model in figure 4.)

However, we now understand much about this surface. For example, there is strong evidence to suggest that the (7×7) structure is made up of smaller units and that vertices play an important role in the long-range order of these units. If one cleaves a silicon crystal to form a (111) surface, there is a (2×1) surface reconstruction. A mechanism involving π bonds seems to be an important factor in this process.[22] However, there seem to occur large, multilayer atomic displacements, and the detailed atomic positions have not yet been determined. None of the many proposed models has yet received acceptance by all techniques.

The situation is much better for the structure of the III–V compound semiconductors. As early as 1964, solid-state physicists Alfred MacRae and Garth Gobeli pointed out that the (110) face of gallium arsenide must have a different geometric structure than that of a bulk-terminated face. In 1978, dynamical LEED analysis[23] determined that the gallium atoms in the surface layer recede toward the bulk, and that the arsenic atoms rotate outward, with an angle of tilt of $27° \pm 2°$. Total-energy calculations, ARUPS, and other measurements later confirmed this structure. A similar "buckling" reconstruction occurs on the (111) face, forming a (2×2) structure with a quarter monolayer of vacancies.[24]

Theory has contributed to our understanding of the "buckling" reconstruction mechanism. Dangling bonds of the sp^3-type are unstable on the surfaces of III–V compound semiconductors. Theory shows that to lower the electronic energy, orbital rehybridizations of the $sp^3 \rightarrow sp^2$ type for group III atoms, and of the $sp^3 \rightarrow s,p_{x,y,z}$ type for group-V atoms, take place on the (110) and (111) surfaces, accompanied by atomic displacements. Calculations also show that the rehybridization lowers the energy of the group-V dangling bonds, which are doubly occupied, and raises the energy of the group-III dangling bonds, which are empty. Hence, buckling is energetically favorable. Figure 1 shows computer drawings of the reconstructed (110) and (111) faces of gallium arsenide.

Outlook. Diffraction probes such as LEED and x-ray scattering tell us the average positions of atoms that have long-range periodicity. Short-range probes such as SEXAFS, EDPD, ADPD, RBS and ICISS determine the local geometry of surface atoms and their neighbors. Imaging techniques provide important information on surface morphology. When we apply different techniques to the same problem, not only do we get a useful cross check, but more importantly, we get a new level of information that individual techniques alone can not provide. We now have a host of surface techniques as well as a quantitative theory that is rapidly advancing both in accuracy and sophistication, fueled in part by the availability of powerful computers. If the last 12 years provide any indication, then the next decade promises to be a most exciting period, and will likely mark the golden age of surface science.

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