New Approaches to Surface Structure Determinations

P. Eisenberger and L. C. Feldman

Summary. Progress in understanding the many scientifically interesting and technologically important processes that occur at surfaces has been slowed by the absence of basic structural information. A variety of new techniques are being developed to attack this central problem in surface science. With the new surface probes it is now possible to quantitatively determine the arrangement of atoms in the first monolayers of a solid. This provides the basis for exciting advances in surface science.

Surface scientists have been studying the physical and chemical phenomena that occur at the surfaces and interfaces of materials for more than 25 years. These phenomena include many of great technological and scientific interest such as catalysis and electrolysis, as well as those in the unusual world of two-dimensional solid structures, where the reduced dimensionality can significantly alter the nature of physical processes. The most avid surface scientist might claim that everything interacts through its surfaces. In spite of the many workers who have been attracted to the field by its exciting potential and the large expenditures of money and resources that have been made, progress has been difficult. There have been many reasons for this, not the least being the complexity of the phenomena that occur at surfaces. Initially, a great difficulty was the development of ultrahigh-vacuum (UHV) techniques (pressures of 10^{-10} to 10^{-11} torr) and surface characterization tools so that clean, stable surfaces could be reliably prepared. A major current impediment to progress is lack of structural information.

Until recently, surface scientists have depended on low-energy electron diffraction (LEED) for structural information. Although LEED has provided significant information about the symmetry of ordered surface structures, it has been less successful in providing quantitative information about the local atomic structure. To quantitatively characterize a surface structure it is necessary to determine the coordinates of all the surface atoms. In principle, such information is contained in the intensity of the backscattered electrons that form the electron diffraction (LEED) patterns. While such intensity analyses have been pursued for many years, it appears that the complex scattering calculations required for the local structure determination cannot be carried out unambiguously. Hence new surface structure probes have been sought.

In science there have been many instances in which an understanding of structure has led to an understanding of function. The search for structure has successfully been pursued by the biophysicist for complex enzymes and proteins and, of course, by the solid-state physicist and chemist for the many ordered materials. These fields and their applications have blossomed as new structural pictures have emerged. It is for this kind of reasoning that there is excitement among surface scientists as they observe the development of a great many new techniques for determining the structure of ordered and disordered surfaces.

In this article we concentrate on the major new techniques, their recent accomplishments, and their potential for solving surface structures. We wish to show that the surface scientist does now finally possess an impressive array of techniques that are capable of providing highly accurate surface structural information.

New Techniques

With some oversimplification, one can say that in the past several years scientists have turned all their available structural probes to the problem of determining surface structures. Photons, ions, atoms, positrons, and neutrons are joining electrons in the new techniques. At this level of generality the new surface structure experiment can be schematically illustrated as in Fig. 1. The main components are a source of probing particles or radiation whose energy and momentum can be selected by a monochromator, an apparatus for preparing and characterizing the surface, and detection equipment for evaluating the interaction of the probing particles with the surface atoms or electrons. In many of these new techniques the source of radiation is a large, complicated apparatus, such as a synchrotron, that is shared by many users. Together with the already expensive surface preparation apparatus, this results in costly and intricate equipment. Furthermore, the stability of the surface puts limits on the duration of experiments, resulting in a new mode of operation for the materials scientist who is used to smaller and more conventional laboratory experiments.

Each type of probe has a different interaction strength, which affects its surface sensitivity. The stronger the interaction, the fewer atomic planes are penetrated and the greater the surface sensitivity. In addition, surface sensitivity may be enhanced by the geometry of the experiment. If the probing particle enters or the scattered or ejected particle leaves nearly parallel to the surface, the surface sensitivity will be increased. While surface sensitivity is helpful, too strong an interaction can result in the probe interacting more than once with the material, which may make interpretation difficult. Multiple scattering effects are largely responsible for the difficulty of interpreting the results from LEED.

Each probe can be used to study structure through elastic scattering of the incident radiation by surface atoms or through spectroscopic techniques such as x-ray absorption and photoemission which involve elastic scattering of excited electrons. In addition, inelastic techniques such as electron loss spectroscopy are being developed to study the vibrations of atoms on surfaces. These techniques and probes are summarized

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in Table 1, where their characteristic surface sensitivities are indicated. If we attempted to describe all these techniques in this article we could do justice to none of them, hence we have limited ourselves here to static structural determinations and do not consider the inelastic techniques. Furthermore, we do not review the established techniques of LEED, low-energy ion scattering, and neutron scattering; the latter requires samples with high surface areas, such as atoms and molecules adsorbed on graphite, to obtain surface sensitivity. We also do not review recent LEED developments such as the quantitative analysis of surface defects (steps and vacancy clusters) or applications of the principles of LEED to the electron microscope, which permits the analysis of surface domains of less than 1000 angstroms. Positron-based techniques are yielding fascinating results in atomic physics, but little information in a surface structural sense, and they are not included here. We do discuss new techniques based on the use of photons, high-energy ions, and atoms and attempt to describe them in a manner that illustrates the character of the measurement and thus ultimately its strength and weaknesses for a particular type of surface structural problem.

The gross features that distinguish surface structures are their atomic composition (which elements are present and to what extent) and the positions of the atoms. One is also interested in the degree of structural order (extent of periodicity) and chemical order (uniqueness of adsorbate binding site). Structural order is usually characterized in terms of the symmetry of the surface structure as deduced from a diffraction experiment. For adsorbates, atomic positions are measured relative to substrate sites or other surface atoms to yield the (chemical) bond length and the adsorbate sites (Fig. 2, b and c). In general, layers of atoms below the first monolayer may also be displaced, and a full characterization requires their site determination as well (Fig. 2, a and c). In this article we emphasize the techniques that can give quantitative information about the coordinates of the surface atoms.

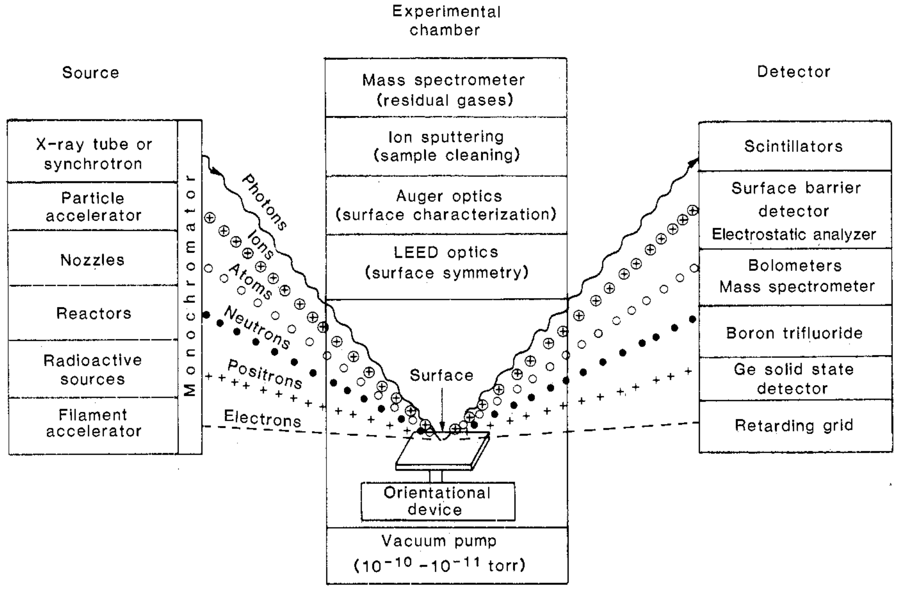

Fig. 1. Main components in a surface structure experiment: source of radiation, experimental vacuum chamber containing surface cleaning and characterization equipment, and radiation detector.

Photons

There has been a rush of new techniques based on photons because of the development of storage ring sources of synchrotron radiation, which have provided an approximately 10^6-fold enhancement in available fluxes (*1*). Photons can be used to determine structure either directly through elastic scattering processes or indirectly through the elastic scattering of the photon-generated excited electrons.

One of the most generally applicable techniques for bond distance determination is the surface version of the x-ray absorption fine structure method, or SEXAFS. The basic EXAFS phenomena have been extensively reviewed (*1*). Consider the simple case of atoms of type A (adsorbed) on a surface containing atoms of type S (surface atoms of the substrate). If one measures the energy dependence of the x-ray absorption of atom A in the energy region above its excitation threshold, one finds oscillations in the absorption probability. Those oscillations, which produce the fine structure in the x-ray absorption spectra, arise from interference with the elastic scattering of the ejected photoelectron by the surrounding atoms. The period of the oscillations is related to the distance between A and its neighboring A or S atoms (Fig. 2). The magnitude of the oscillations contains information about the number of atomic species and distribution of bond lengths of the surrounding atoms. In SEXAFS, the surface sensitivity is greatly enhanced by using secondary electron detection schemes to measure the absorption. The emission of a photoelectron in the absorption process leaves the atom in an excited state; relaxation from the excited state yields a secondary (or Auger) electron which is characteristic of the atomic species (Fig. 3d) and whose intensity is proportional to the absorption probability of the exciting atom. Detection of the secondary electrons enhances the surface sensitivity because the escape depth of the electrons is much shorter than the penetration depth of the incident photons.

Due to the polarization of the photon beam and dipole selection rules, the outgoing photoelectrons are ejected in well-defined directions. By rotating the surface with respect to the direction of polarization one can obtain geometric information. This technique was first proposed in 1976 (*2, 3*) and has been made experimentally feasible with the advent of synchrotron radiation. Since the initial study of one-third of a monolayer, ~ 3 × 10^{14} atoms of iodine per square centimeter on an Ag (111) (*4*) surface, many studies have been performed. It appears that all elements from carbon on (elements heavier than boron in the periodic table) can be studied (*5*). Bond distances can be determined to 0.01 Å and the coordination geometry can, in simple cases, be determined reliably by use of both amplitude and polarization dependences. Extended periodicity in the absorbate atomic arrangement is not required since this is a local probe. The signal is sufficiently strong that fractions of a monolayer can be studied.

The structure of either an incommensurate overlayer or a surface with more than one binding site would be difficult to determine with this technique. The requirement for a unique threshold value of atom A to distinguish it from the substrate, implies that a structure determination for a clean surface (no absorbate) would be difficult since the EXAFS spectra would contain information from

Table 1. Surface structure probes and techniques.

Probe	Technique	Acronym or descriptive term*	Monolayers sampled
Photons	Absorption spectroscopy	SEXAFS	1 to 5
	Photoemission	PHD	1 to 5
	Elastic scattering	Bragg reflection diffraction	30
	Interferometry	Standing waves	1000
	Inelastic light scattering	Raman	1000
	Photon-stimulated desorption	PSD	1
Ions	Elastic scattering	Shadowing and blocking	1 to 10
	Secondary ion emission	SIMS	~ 1
Atoms	Elastic scattering	Helium diffraction	1
	Inelastic scattering		1
Neutrons	Elastic scattering	Neutron diffraction	Bulk
	Inelastic scattering		Bulk
Positrons	Elastic scattering		1 to 5
	Inelastic scattering		
Electrons	Elastic scattering	LEED	1 to 5
	Inelastic scattering	ELS	1 to 5
	Electron stimulated desorption	ESDIAD	1
	Inner shell excitation	EAPFS	1

*SEXAFS, surface x-ray absorption fine structure; PHD, photoelectron diffraction; LEED, low-energy electron diffraction; ELS, electron loss spectroscopy; ESDIAD, electron-stimulated desorption ion angular distributions; EAPFS, electron appearance potential fine structure.

both the top substrate layer and one to five layers of bulk structure below. It may be possible to overcome this difficulty in the future by utilizing the small electron binding energy shifts of the surface atoms compared to the bulk. In addition to the use of total yield or Auger electrons to measure the energy-dependent absorption, there has been success in using ions that are ejected when the photon absorbed at site A breaks the bond with atom S, yielding S or A ions or both. This photon-stimulated desorption process holds considerable promise for extending the technique to hydrogen binding and for obtaining other interesting chemical information (*6*). EXAFS-type behavior can also be found near the threshold for electron bombardment excitation of core holes (*7*).

Another spectroscopic technique based on the use of photons is the direct detection of outgoing ejected photoelectrons rather than measurement of photon absorption (*8*). The main difference is that in the SEXAFS case the electron must scatter back onto the absorption site in order to modify the absorption probability, while in the electron technique it scatters away from the absorbing site into the detector (Fig. 3d). The quantitative interpretation of the photoelectron-based measurements is more complicated because of the need for multiple scattering corrections. They are, in fact, very similar to those required in LEED, and this technique has many of the strengths and weaknesses of LEED. Interpretation of SEXAFS measurements is simplified by the absence of multiple scattering for the first coordination shell because the electron must scatter back onto the original absorbing site. The two strengths of the photoelectron techniques are that the spatial symmetry of the ejected scattered photoelectrons can be used very quickly to determine the symmetry of the site of the adsorption (*8*), and an ordered arrangement of A atoms is not required. The energy dependence of the ejected photoelectrons in a given direction has oscillations similar to those in SEXAFS, but they are not as simple to interpret (*9*). Site symmetry and bond angles can also be determined by measuring the angular distribution of a surface species ejected by electron (*10*), photon (*11*), or ion (*12*) collisions.

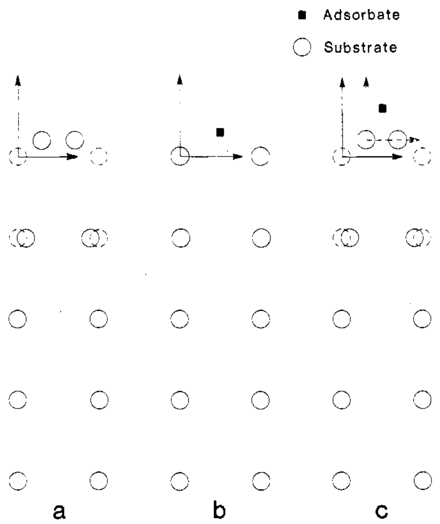

Fig. 2. Schematic of the surface structure problem, namely, determining the position of substrate atoms relative to their bulklike site and determining the position of an adsorbate relative to the substrate atoms. (a) Reconstructed clean surface, (b) adsorbate on bulklike surface, (c) adsorbate on reconstructed surface. The axes indicate the reference point for measuring the surface atomic coordinates.

Bragg diffraction, in which the location of the peaks determines symmetry and the intensity determines the atomic coordinates, has been the basis for elucidating the structures of almost all three-dimensional solids. Thus, in principle, it should be straightforward to determine the structure of an ordered first layer of a solid or an ordered overlayer of adsorbate atoms by elastic Bragg diffraction. Until recently it was thought that the signal would be too weak to see the scattering from a single layer; however, experiments on the reconstructed Ge (100) surface have shown that this is not the case (*13*). (A surface is termed reconstructed if it has an atomic arrangement different from that expected from simple termination of a bulklike crystal.) The weakness of the atomic scattering cross section of the photon was partially compensated for by having the incident and exit beams directed nearly parallel to the surface (Fig. 3a). If the incident x-ray beam enters at a sufficiently glancing angle—less than 1°—then total external reflection of the beam will occur and the penetration depth of the x-rays will be limited to 25 to 50 Å from the surface. The weak coupling makes the interpretation of the intensities of Bragg peaks relatively straightforward. Two-dimensional features of the scattering arise from the existence of long-range order only in the plane of the surface. Thus instead of Bragg peaks one has Bragg rods, which extend in the direction perpendicular to the surface. Scattering in the plane of the surface will only provide information about the coordinates of the surface atom in that plane. One must examine the intensity dependence of the rods to determine the coordinates perpendicular to the surface. The measurement and interpretation of those intensities are expected to be problematic, but they have not yet been attempted.

Both ordered adsorbed overlayers and clean surfaces can be studied, especially if their symmetry is different from that of the bulk itself. Structurally disordered surfaces, which lack the sharp peaks characteristic of long-range periodicity, would give too small a signal to be studied by this technique. With the development of more intense synchrotron sources it may be possible to study disordered surfaces in the future.

Another photon-based technique which has recently emerged utilizes the standing wave pattern created by a Bragg reflection from the substrate to determine adsorbate structures (*14*). As one rotates a perfect crystal through a

Bragg peak, the interference pattern above the surface produced by the incident and scattered waves has its maxima and minima shifted with respect to the surface in a continuous and predictable way (Fig. 3c). One can determine the surface coordinates of atom A by measuring the intensity of a fluorescent photon or Auger electron as a function of the position of the electric field maximum. This is also a local structural technique and does not require an ordered array of A atoms. Note that the reference position for this technique is the bulk lattice, so that if the surface structure is altered for several layers into the medium it could be difficult to interpret the results in terms of local bonding. As with SEXAFS, the determination of the structure of a clean surface would be difficult. Signal strengths are adequate for the study of fractions of a monolayer. Again as in SEXAFS, the information content is limited and multiple site structures would be difficult. The most serious drawback of the technique, however, is the need for a nearly perfect crystal substrate, which currently limits its application to semiconductor crystals. In these cases site determination to ~ 0.04 Å is possible.

Atom (Helium) Scattering

The basic approach of elastic atom (helium) scattering is the same as that of x-ray diffraction or LEED (Fig. 3b) and it therefore has some of the same general features. The intensities of Bragg peaks are used to evaluate the surface structure. The technique can be used to study periodic structures in both substrate and adsorbate layers (*15*).

The intensity provided by modern atomic beam sources, together with the extremely high interaction strengths, gives this technique more than adequate surface sensitivity. In fact, it is probably capable of probing disordered surfaces. The surface sensitivity of this approach is so great that the low-energy helium atoms only come within 3 to 4 Å of the surface. At such large distances, it is the outer electrons that dominate the scattering potential and, as one might imagine, the potential of the surface atoms is hard to specify. The extremely strong coupling results in multiple scattering complications as in LEED, with one important difference: the interaction is so great that only the top layer is probed. This should simplify the interpretation of the scattering results provided the difficulties with determining the true potential are resolved. Because of the interaction strength, referencing the structure measured to the substrate may be impossible, although relative parallel and perpendicular displacements within the first layer may be measured.

Ion Scattering

Charged particle accelerators produce energetic ion beams which undergo Rutherford scattering from surface atoms. The repulsive potential produces a shadow behind the scattering atom (Fig. 3e) which reduces the scattering yield from the underlying atoms. In this case the wavelength of the incident radiation (0.1- to 3.0-MeV He$^+$ and H$^+$ are usually used) is much smaller than the crystal lattice spacing and the interactions are viewed as billiard ball collisions rather than diffraction phenomena. The energy and mass of the probing ions and scattering atoms, together with the known loss of energy of an ion as it passes through a condensed medium, are used to identify the type and mass of the atoms and the depth at which scattering occurs. A model of the interaction shows that the displacements of the first layer can be determined by measuring the scattering from atoms in the shadow region (*16*).

The variation of the shadow size allows a determination of the magnitude of the displacement; the scattering intensity permits a determination of the number of atoms displaced. These determinations depend on a knowledge of the ratio of the interaction parameter to the thermal displacements of the atoms. The former is relatively easily learned, but the latter may present significant problems and can limit the accuracy of the determinations in some cases. Alternatively, in the case of a known structure the thermal displacements of surface atoms can be found (*16*).

The ability of the technique to determine surface structure is significantly increased by the blocking of large-angle scattered beams (Fig. 3f). For example, if atom S scatters a particle back toward

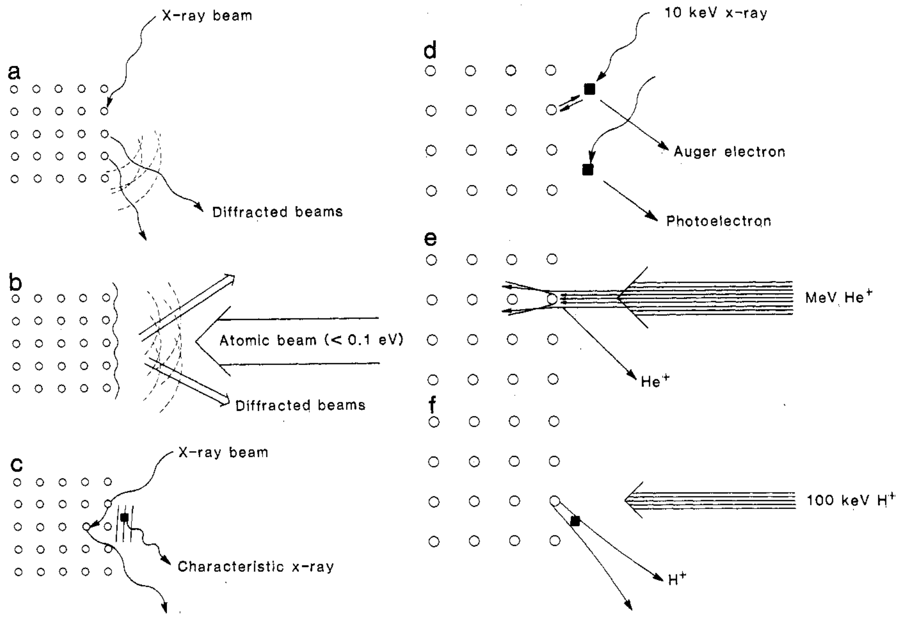

Fig. 3. Schematics of some of the new surface structure techniques. (a) X-ray diffraction at a surface. The angle between the incident beam and the surface plane is small to confine the interaction to the surface region of the solid. (b) Atomic beam diffraction. The interaction occurs 3 to 4 Å from the surface and the diffraction process senses the "corrugation" in the potential at this large distance. (c) Standing wave technique. The pattern of interference between incident and outgoing x-rays builds a standing wave outside the surface of the solid with nodes and antinodes at known distances. The standing wave can induce fluorescence in the adsorbate; the relative intensity of the adsorbate signal as a function of nodal distance gives the adsorbate site. (d) Surface x-ray absorption fine structure. Incident radiation creates a photoelectron which scatters from a neighboring atom, modifying the cross section for absorption and permitting extraction of the substrate-adsorbate distance. The intensity of the outgoing secondary (Auger) electron is used as a measure of the process. This geometry is also used in the photoelectron diffraction process, in which case the angular distribution of the photoelectron is measured directly. (e) Ion shadowing. The flux distribution of an incident ion beam is modified at the surface of a solid to form a shadow cone. Suppression of the intensity of He$^+$ ions backscattered from the underlying atoms is used to determine the coordinates of the surface atoms. (f) Ion shadowing and blocking. Particles scattered from the first monolayer of the solid are blocked in their outward path by a surface adsorbate. The angular distribution of the outgoing particles yields the coordinates of the adsorbate and surface substrate atoms.

the detector but atom A is in the way, one will see a reduction in the intensity of the scattered beam. By combining the angular dependence and magnitude of the shadowing associated with S atoms and studying the angular dependence of the blocking (of S atom scattering) by A atoms, one can uniquely define the local geometry in terms of distances and angles. The blocking technique is attractive; in simple cases analysis of the magnitude of the effects is not necessary—surface parameters are determined from purely geometric considerations (*17*). Another ion scattering geometry recently proposed makes use of grazing incidence along a low-index direction in the surface. The strong variations in ion flux density due to surface channeling are used to deduce adsorption sites (*18*).

A particular strength of these ion scattering techniques is that the atomic positions of an adsorbate and a substrate can be determined separately. Thus adsorbate-induced substrate reordering (Fig. 2) can be established by this technique. Positions of atoms can be determined relative to their bulklike sites to a few hundredths of an angstrom. The technique is local and long-range periodicity is not required.

Radiation damage problems, particularly in the blocking technique, which requires large exposures, have been overcome by use of efficient counting apparatus and other experimental techniques. As with other local techniques, the information content is somewhat limited, and complex structures will require measurement in many crystallographic directions. Ions with lower energies (< 5 keV) have been used for surface structure determinations for some time and continue to supply useful information. The interaction is still phenomenologically described by a billiard ball model, but the interaction is so strong that only the first layers are seen and it is difficult to interpret the intensities without a detailed model of the potential. Significant progress has been made recently with this technique through the incorporation of new detection schemes such as time-of-flight spectrometry (*19*).

Accomplishments

The conceptual development of techniques such as those described above is, of course, followed by actual trial (and error) so that their usefulness can be established. Although these experiments are still on the "learning curve," recent accomplishments have enabled a preliminary evaluation of the ability of the new techniques to determine surface structure. In some cases different approaches have been applied to similar problems, permitting interesting comparisons.

Reconstructed surfaces. Low-energy electron diffraction has shown that clean semiconductor surfaces are usually reconstructed into an ordered array (Fig. 2). The determination of the positions of the surface atoms in these systems has defied solution and is a goal for all new techniques.

The glancing incidence x-ray diffraction probe was first applied to Ge (001) and demonstrated that the surface had 2 × 1 periodicity—that is, the repeat distance in one direction was twice what it would be in a perfect crystal, while the repeat distance in the other direction was the same as that in a perfect crystal. Conventional x-ray diffraction techniques were used to analyze the scattering intensity and determine the surface atom coordinates. The measurements provided direct evidence for subsurface strain and determined the atomic positions parallel to the surface in the first two monolayers of the solid (*13*). The atomic displacements were close to theoretical values.

The atomic diffraction technique has been applied to the Si (001) (*20*), Si (111) (*21*), and GaAs (110) (*22*) surfaces. Studies of the GaAs (110) surface yielded atom coordinates in quantitative agreement with a reconstruction model originally proposed on the basis of LEED analyses (*23*). The results show a tilting of the Ga-As bond by 30° ± 5° out of the surface plane.

Energetic ion scattering studies of the Si (001) 2 × 1 surface yielded direct evidence of subsurface strain (*24*). Displacements in the plane of the surface in the first four monolayers of the solid were characterized and different surface reconstruction models tested (*25*). Studies of the Si (111) 7 × 7 surface showed substantial atomic displacements (0.4 ± 0.1 Å) perpendicular to the plane of the surface (*26*).

In some cases, the surfaces of clean metals may also be reconstructed. Ion scattering techniques were applied to the W (001) surface (*27*) and demonstrated the reconstruction originally reported on the basis of LEED; the ion scattering data also yielded the number of surface atoms displaced and their "in-plane" displacement (0.23 ± 0.05 Å). The spacing of the first two monolayers of Pt (111) was studied in detail by ion scattering techniques (*28–30*), which showed an outward relaxation of ~ 1 percent (of the bulk spacing) in this system.

Adsorbate-covered surface. Another class of surface structure problems concerns the atomic location of an adsorbate on a surface (Fig. 2b) and the structural effects of its interaction with the substrate (Fig. 2c). The SEXAFS technique has now been applied to a number of adsorbate site determinations. By use of the total yield method the iodine-copper bond length on Cu (111) was determined within 0.02 Å (*31*). The polarization of the synchrotron beam may permit a site determination based simply on symmetry considerations; this approach was employed in the case of iodine on Cu (001) (*31*) and sulfur on Ni (001) (*32*) and a fourfold site was found in both cases. No systematic differences from the bond lengths in bulk structures have been reported so far. A recent study of iodine and tellurium adsorption on a variety of silicon and germanium surfaces indicated that the adsorption site depends on the nature of the adsorbate (*33*). Study of the interesting system of oxygen on aluminum yielded an O-Al bond distance of 1.79 ± 0.05 Å (*5*)—one of the few results obtained by these new techniques that is grossly different from the LEED result (2.12 ± 0.05Å) (*34*).

The combined channeling and blocking technique has been applied to the system of sulfur on Ni (110) (*17*). The sulfur was found to be 0.87 ± 0.03 Å above the Ni, in agreement with a previous LEED result; however, it was also shown that the Ni surface itself undergoes an expansion in this case—that is, the substrate is not inert in the adsorption. Adsorbate-induced substrate rearrangements have been observed in hydrogen on W (001) (*27*) and Pt (001) (*35*) and oxygen on Ni (111) (*36*) by ion scattering techniques. In the latter case the Ni atomic positions have been determined within ~ 0.05 Å. The direct observation of adsorbate-induced reconstruction of a substrate is particularly significant; it shows that one cannot think of an adsorbate simply sitting on an inactive substrate.

Hydrogen has a special place among adsorbates, since it is most accessible to theoretical analysis but is difficult to detect experimentally. Atomic beam scattering has been used to study hydrogen adsorbed on Ni (110) (*37*). The extracted corrugation functions for the H + Ni (110) system was matched against calculations as a function of the hydrogen position (*38*). This resulted in the first direct determination of the site of hydrogen.

The standing wave method has been applied to determine the site of bromine on Si (001) (*14*) at a unique surface, namely a crystal-liquid boundary. It was found that 30 percent of the bromine was 1.73 ± 0.07 Å from the surface and 70 percent at undefined sites. Although not directly comparable with conventional surface experiments, these results have indicated the possible use of this technique for structure determination.

The case of the metal adsorbate Au on the metal substrate Ag (111) has been investigated by ion scattering techniques. The Au atoms were found to reside within 0.1 Å of the next crystal site, both vertically and horizontally. Such studies of the initial stage of epitaxy are useful in crystal growth physics and various technologies (*39*).

As the results above indicate, these new techniques have the ability to obtain accurate structural information. However, while these results are impressive, they are meager compared to what will be learned in the future. Systematic studies with these techniques will provide insights into important questions concerning surface-bonding structures and surface reconstruction.

Perspectives

On the basis of these preliminary results, we can try to predict which of these new techniques will prove useful for different types of surface structure problems (Fig. 2). Undoubtedly, LEED will continue to provide a measure of the overall symmetry of surfaces and will be a common element connecting various experiments on ordered substrates (Fig. 1). The extreme surface sensitivity of atomic beam diffraction makes it an important supplement in surface symmetry determinations. However, it is still not clear that atomic beam diffraction can yield the actual coordinates or atomic positions of surface atoms without major advances in the theoretical treatment of this process.

Reconstructed surfaces, as shown in Fig. 2a, will be explored through x-ray diffraction and ion scattering techniques. Both methods can yield the atomic coordinates associated with the reconstructed surface. X-ray diffraction is most easily applied in the case of a reconstructed surface that yields superlattice reflections, such as the reconstructed Ge (001) 2 × 1 surface. Ion scattering can be applied to that case, as well as to a relaxed surface with a 1 × 1 periodicity; an example of such a structure occurs when there are only vertical displacements of the surface atoms.

The position of an adsorbate on an unreconstructed surface (Fig. 2b) can be determined by fine-structure techniques (photon- and electron-induced), photoelectron diffraction, channeling and blocking, x-ray diffraction, the standing wave method, and atomic diffraction. SEXAFS will probably make a major contribution because of its ability to measure bond lengths and sites for structurally ordered and disordered systems and for adsorbates with low and high atomic numbers. The channeling and blocking method will also contribute significantly; its only additional limitation is difficulties with adsorbates of low atomic number. X-ray diffraction requires structurally ordered adsorbates, and the standing wave technique requires a perfect substrate. Photoelectron diffraction methods will have considerable difficulty in quantitatively determining surface coordinates but should contribute to site identification. The same is true for atomic diffraction, although it could be important for studying adsorbates with very low atomic numbers, particularly hydrogen.

The structure in Fig. 2c consists of an adsorbate on a reconstructed surface. It can result from either adsorption on an already reconstructed surface or can be produced as a result of the substrate-adsorbate interaction. These two possibilities are most easily distinguished through the ion scattering techniques, in which a change in substrate structure shows up as a change in the substrate surface peak. The substrate and adsorbate atomic coordinates can be determined by the channeling and blocking technique. Alternatively, the substrate-adsorbate bond distance could be determined by SEXAFS and the adsorbate distance (from the unreconstructed substrate) measured by the standing wave method; the two measurements would characterize this complicated structure.

We hope that this article has conveyed the great surge in the development of new surface structure techniques. Although no single method can answer all the questions, these techniques together have the the potential for solving almost any surface structure problem. This raises the exciting possibility that the decade of the 1980's will see significant progress in surface science. However, a cautionary word would be appropriate. The techniques being developed come mainly from the fields of physics and in many cases involve big machines such as synchrotrons and accelerators. Surfaces have been prepared and characterized at pressures of 10^{-10} to 10^{-11} torr, and the interpretations of the data can be subtle and complicated. For these techniques to realize their full potential, the surface chemist and the surface physicist must work together to adapt them to the real conditions under which chemical reactions occur on surfaces. For, in addition to the wonders of the two-dimensional world that will be opened up by the new techniques, an increase in our understanding of such processes as catalysis, electrolysis, and epitaxy would be of great importance.

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