

Surface spectroscopy

Analyzing the energies of x-ray and uv photoexcited electrons, of Auger electrons and of inelastically scattered electrons, among others, has provided much new and practical information about surfaces.

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In the last 15 years there has been a tremendous growth in the field of surface science, all largely made possible by the development and application of various surface spectroscopies. In this article we hope to provide a picture of a few of the principal surface spectroscopic methods and how they are applied to answer important questions in surface science.^{1,2} In particular, we hope to provide the reader with a perspective of the unique considerations and technical problems associated with applying spectroscopic methods to surfaces. While the particular examples we discuss are the results of colleagues and coworkers at the Thomas J. Watson IBM laboratories, we believe they are representative of the types of surface studies and spectroscopies performed in the field in general.

Although a surface is defined by the boundary between any two different states of matter, most activities in surface science are related to studies of solid surfaces. Surfaces of crystalline solids are the most widely studied because they offer the greatest opportunity for understanding the many complex phenomena that occur at surfaces. The atoms at a crystal surface are not bonded to as many neighbors as atoms in the bulk; they may also have a different geometric arrangement than in the bulk. As there are impurities and defects in the bulk, there may also be foreign atoms or molecules, new compounds or altered arrangements on the surface. All of these may alter both the microscopic and macroscopic properties of the surface and affect the many processes that take place there—such as catalysis, crystal growth, oxida-

tion, corrosion and embrittlement. Not only are surface properties important in the electronics industry because of the thinness of integrated circuits, but almost all device fabrication steps make use of several physical and chemical processes that occur at surfaces and interfaces.

Thus, both physical properties (such as structure and electronic states) as well as chemical properties of surfaces are of interest. One needs to learn, for example, what elements exist on the surface, what their chemical forms are, how they are bound to the surface and so forth. The progress made in recent years is enormous: just 15 years ago few surface studies could answer the most elementary question of whether a surface was atomically clean, and certainly not what foreign atoms might be there. With devices such as the electron spectrometer shown on the cover and in figure 1, we can now answer these and more detailed questions for a large number of surfaces and a wide variety of potential adsorbates.

Several aspects of surface spectroscopic methods still have limitations on what questions we can address with them and under what conditions we can apply them. To understand these constraints, let us first consider some of the general principles and requirements of surface spectroscopy.

As is true of all spectroscopies, our aim is to probe the quantum states of a system—in this case, a surface. The simple energy-level diagram in figure 2 shows schematically a set of electronic energy levels and transitions for a free atom and for the corresponding solid. The higher valence levels of an atom interact strongly in the solid, forming bands of energies, some filled, some empty; the overall reduction in the potential energy for all electrons in the solid keeps the electrons more tightly bound. For the sketch, we have assumed that these atoms form a metal

when brought together. At the surface, the reduced coordination of the atoms changes the width of the valence band and may produce new localized states, referred to as surface states. In the case of covalently bonded materials (such as silicon or germanium), one generally thinks of these as unsatisfied valence bonds or "dangling" bond states at the surfaces. The lower, more localized core levels of the atoms are not as sensitive to the details of bonding or geometry at the surface as are the valence levels; their energies do, however, differ slightly from the corresponding levels for interior atoms. In addition to these states derived from the electronic states of the atoms, there are also surface collective excitations, such as surface phonons and plasmons. Adsorbed molecules on the surface also have their own set of electronic energy levels as well as internal vibrations or vibrations against the surface.

One of the necessities of any viable "surface" spectroscopy is to have sufficient surface sensitivity to delineate the energy states or transitions of the surface from those in the bulk. For adsorbed atoms, this is clearly easier if the adsorbate transitions are well-separated or distinguishable from those of the bulk or surface, than if the adsorbed atoms behave like these of the substrate. The distinguishability thus depends not only on the spectroscopic technique but also on the properties of the atoms involved.

Of the wide variety of methods used to probe the energy levels and transitions at the surface, we shall discuss three widely-practiced methods: Photoemission spectroscopy, Auger electron spectroscopy and electron energy-loss spectroscopy. Figure 2 also illustrates schematically the excitation mechanics involved in each. Both photoemission and Auger spectroscopies involve ionization: core or valence electrons are ejected out of the sample.

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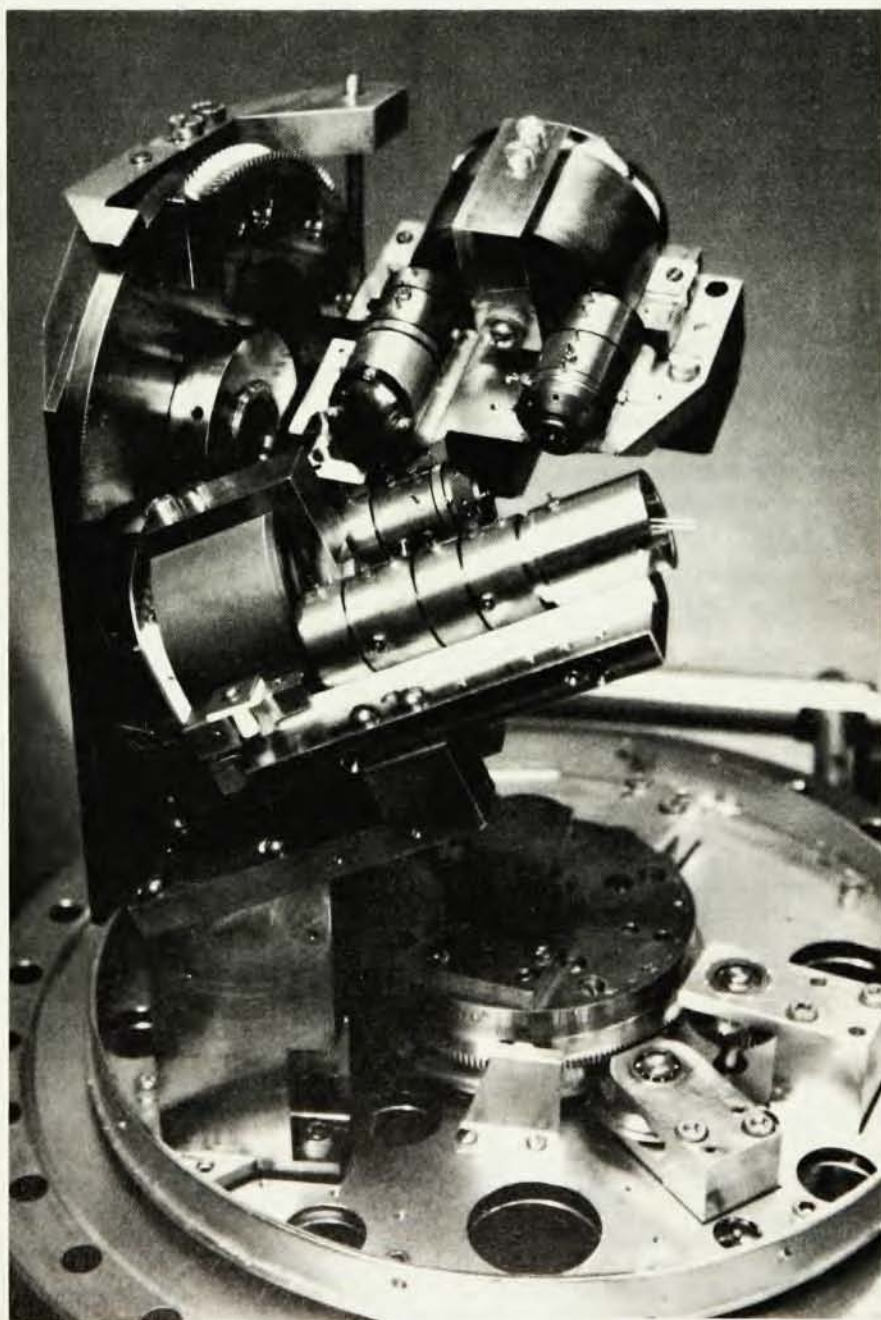
In photoemission spectroscopy, an energetic photon transfers its energy to excite and eject an electron from either a core or valence level, while in Auger electron spectroscopy a less tightly bound electron drops in energy to fill a vacant core level (initially produced by a high-energy photon or electron) and simultaneously ejects a second electron. In contrast, electron energy-loss spectroscopy involves excitation of the sample but not ionization: An incident electron scatters inelastically, losing energy to excite electronic transitions or vibrations at the surface. We shall return to discuss these processes in more detail later.

In general, one measures the energy of electrons emitted or scattered from the surface. The specific type of energy analyzer for each spectroscopic technique is determined by the energy resolution and the collection angle required. Figure 1 shows a high-resolution, variable-acceptance-angle, angle-dependent electron spectrometer built in our lab and used for both photoemission and energy-loss spectroscopy. The analyzer is mounted on a stainless-steel vacuum flange, so that one can use it in an ultrahigh-vacuum chamber. Even though the sample resides in an ultrahigh-vacuum environment, typically 10^{-13} atmospheres, residual contamination can occur within tens of minutes. Unlike many other spectroscopic measurements, one cannot indefinitely collect experimental data from a surface, and one must usually make a compromise—for example, with resolution—to obtain sufficient data before the sample becomes contaminated. The vacuum conditions required to maintain the clean surface are also just those required to perform electron spectroscopy; without a good vacuum, electrons are scattered by atoms in the ambient gas or on top of the sample. To achieve the required ultrahigh vacuum the spectrometers must have vacuum

flanges with metal seals—instead of elastometer seals—as well as special vacuum pumps. The internal walls of the chamber must also be specially processed to remove residual contaminants—usually by heating the vacuum chamber to about 150°–200°C for 10–24 hours while pumping to remove the contaminants as they are desorbed.

It is the interactions of electrons with atoms or solids that provide the limited escape depth and inherent surface sensitivity of these electron spectroscopies. For example, electrons emitted from the solid with kinetic energies of 10 eV,

100 eV or 1000 eV will have typical escape depths of about 20 Å, 5 Å or 50 Å, respectively. For comparison, the penetration depth for both visible and infrared radiation is on the order of microns, 10^4 Å. Although the precise values of the electron escape depths depend on the nature of the material, the variations are rather small, and, in general, an electron energy near 100 eV provides the maximum sensitivity to the surface. This energy dependence of the escape depth of the electrons also permits one to use emitted electrons of different energies to gain information



Variable-angle spectrometer for high-resolution uv photoelectron spectroscopy and electron energy-loss spectroscopy. The spectrometer has been mounted on its vacuum flange but has not yet been electrically wired. The electron monochromator rests on the bottom flange facing up, while the electron energy analyzer is mounted on a double-angle goniometer and faces down. For photoelectron spectroscopy, uv light irradiates the sample through a side port. The sample sits on the axis of the flange between the analyzer and monochromator lens elements. The vacuum flange is about 1 foot in diameter. Figure 1

regarding the variation of properties with depth.

Of course, because of the strong electron-matter interaction, the surface-spectroscopic techniques we have described cannot be applied in cases where vacuum conditions cannot be maintained, as in studies in a liquid or gaseous environment or of a solid-solid interface. Although these types of conditions pose many additional challenges for future surface spectroscopic studies, the electron spectroscopies have nevertheless been invaluable. We now turn to some specific techniques and examples.

Photoemission spectroscopy

In photoemission spectroscopy—referred to as PES in the jargon—either high-energy photons, such as x rays, or low-energy photons, such as ultraviolet rays, excite electrons directly out of the valence band or core levels; these electrons are then detected and their energy analyzed. The maximum kinetic energy of the emitted electron, equals the photon energy, $h\nu$, less the sum of the work function and the electron binding energy relative to the Fermi level. A typical photoemission spectrum thus consists of peaks due to photoelectrons, which escape from various levels in the sample with no subsequent inelastic collisions, together with a continuous low background from electrons that undergo inelastic scattering before leaving the sample. The photoexcitation of core levels requires photons of relatively large energies, typically in the x-ray range. This type of spectroscopy is frequently referred to as x-ray photoemission spec-

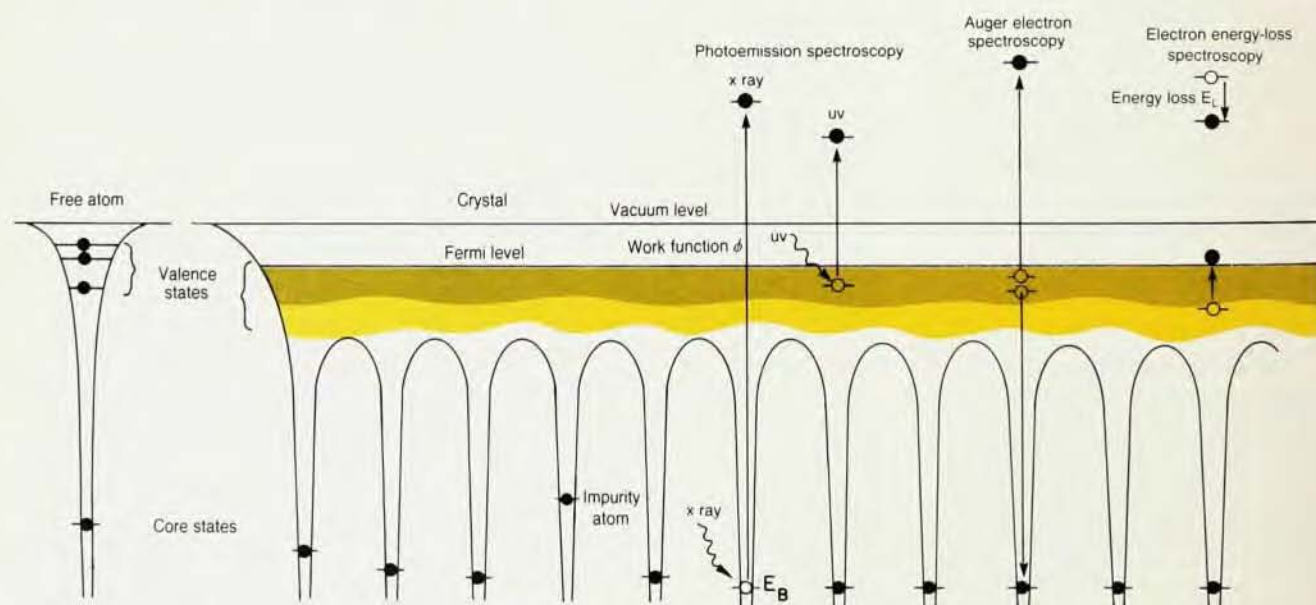
troscopy, or XPS. If one is interested in studying only the valence states, uv photons result in lower electron kinetic energies, which generally allows both higher signal levels and greater resolution. Such studies are usually referred to as ultraviolet photoemission spectroscopy or UPS.

The x rays for spectroscopic studies have traditionally been provided by the K_{α} radiation from magnesium (1253.6 eV) or aluminum (1486.6 eV), which is reasonably intense and quite monochromatic. The uv sources used in UPS have generally been rare-gas-discharge lamps. In recent years, synchrotron radiation from electron storage rings has become useful as a light source for both x-ray and uv spectroscopic studies. (See, for example, the article by Arthur Bienenstock and Herman Winick, June, page 48). Monochromatized synchrotron radiation is intense, collimated, polarized and available over a broad spectral range—up to 10 keV at some sources. This availability of a single source for XPS and UPS has reduced the distinction between them. One useful feature of sources of polarized light is that polarized photons can provide information about the symmetry of the electronic states being probed.

One can use x-ray photoemission spectroscopy for quantitative elemental analysis because the core-level binding energies are unique to each atom (hence the name "electron spectroscopy for chemical analysis," commonly referred to as ESCA). Kai Siegbahn, working with x-ray sources over the last three decades, received the Nobel Prize in Physics for 1981 for his pion-

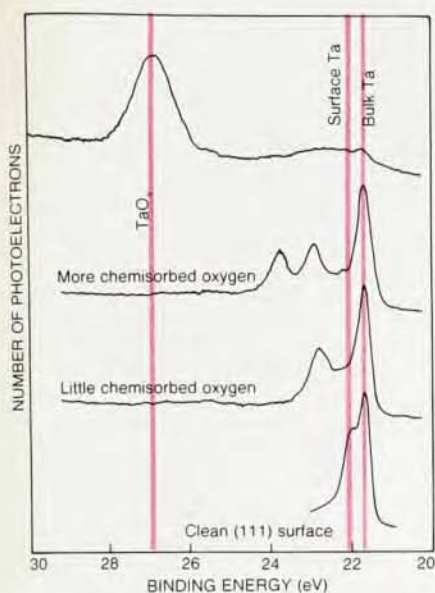
eering work in this field. Recent advances in photoemission spectroscopy—such as intense synchrotron light sources, high-resolution optical monochromators and large-collection-angle electron spectrometers—have allowed measurements of greater detail, and have thereby allowed us to apply x-ray techniques to problems in surface science.

In figure 3 we show the photoemission spectra of the 4f levels of the (111) surface of tantalum, taken with 66-eV photons from a storage ring at the University of Wisconsin.³ The graph shows only the $7/2$ spin-orbit component of the 4f levels. These levels are not, strictly speaking, core states, although they are fairly well localized and serve to illustrate some of the principles of XPS. For the clean surface (bottom graph) one observes photoemission peaks from both the surface and bulk atoms. The small difference in binding energy between surface and bulk atoms—referred to as a chemical shift—arises from the differences in the local environment of bulk and surface atoms: The change in coordination at the surface affects the screening of these localized states by the valence electron density and changes the core electron binding energy of the surface atoms. The direction of the chemical shift in any particular case depends on the details of charge transfer in the surface region. With sufficient resolution, one should also be able to distinguish differences in binding energies for the 2nd and 3rd layer of tantalum atoms. Chemical changes at the surface that modify the valence charge on the surface atoms also produce chemi-



Energy levels for the electronic structure of a free atom and a solid with respect to the vacuum. The valence states and, to a lesser extent, the core states are modified from their free-atom values and differ slightly for surface and bulk atoms. The electron density for the

valence states is schematically shown by the degree of shading. The figure also shows processes involved in three spectroscopic methods—x-ray and uv photoemission, Auger electron and electron energy loss—used to investigate these electronic states. Figure 2



Photoemission spectra for the 4f level of tantalum for an incident photon energy of 66 eV, showing only the $1/2$ spin-orbit component. When the surface is exposed to oxygen, the oxygen bonds to surface atoms, thus changing their binding energies. As more oxygen bonds to the surface two different Ta-O configurations appear. When the oxidation is complete, the oxide suppresses the emission from the bulk Ta levels. Figure 3

cal shifts—as the spectra for tantalum in the presence of oxygen show. Oxygen atoms bond to the tantalum surface, redistributing the valence electron charge, and reduces the electrostatic potential around each surface atom. One of the attractive features of photoemission spectroscopy is that a simple, usually linear relationship exists between the amount of charge transfer (that is, the state of oxidation) and the measured binding energies of core electrons. Thus for low oxygen exposures we see only one new peak, while for higher exposures we see two peaks; the second peak can be attributed to a second phase having more oxygen atoms bonded to each tantalum surface atom. Some of these oxygen atoms perhaps lie beneath the surface tantalum atoms. Finally, at very high oxygen exposures, the tantalum emission is attenuated and a characteristic emission band of tantalum oxide appears.

Because the parallel component of momentum is conserved in the photoemission process, one can determine the momentum distribution of the valence states in a crystal or periodic surface. Angle-resolved photoemission is the only surface technique actually capable of measuring both the energy and momentum of the delocalized valence states. Such angle-resolved measurements provide detailed information about the nature of these two-dimensional states.

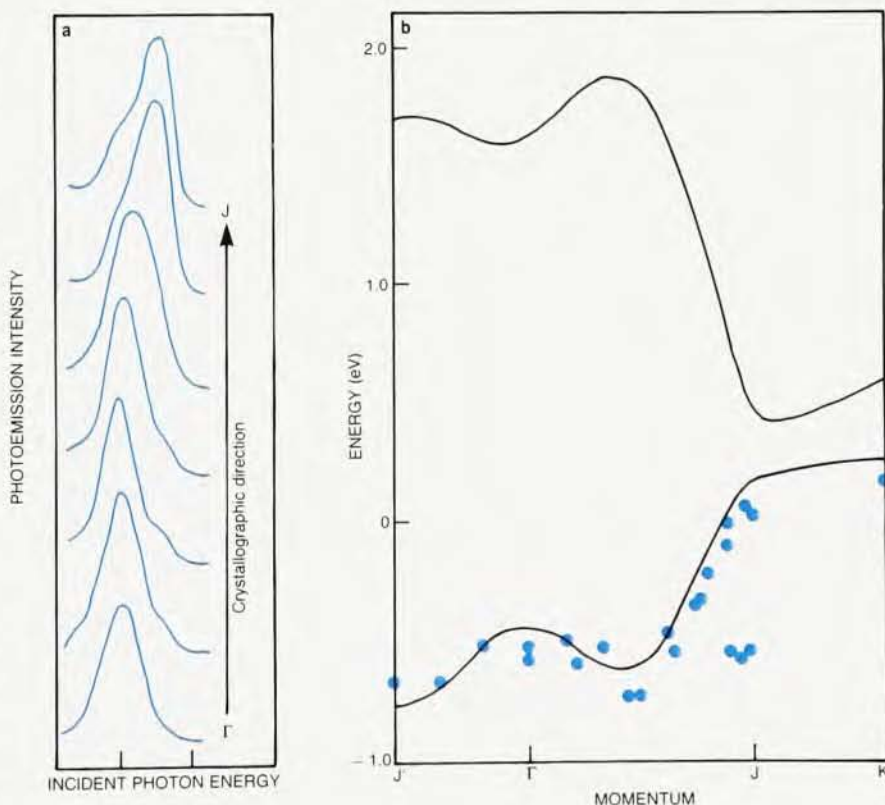
Figure 4 shows some results of angle-dependent uv photoemission measurements⁴ for one of the surface states of a cleaved Si(111) 2×1 surface whose atomic structure has been the subject of much controversy. The variation with crystallographic direction of the energy of emitted electrons is clear in the graphs. As we mentioned, this variation allows one to construct an energy-momentum (or band-dispersion) diagram for these states, as shown in the right-hand part of figure 4. These experimental data have helped to clarify the structure of the Si(111) surface: Of the many models proposed over the last 20 years to describe the structure of this surface, only a recently proposed π -bonding model successfully describes the experimental dispersion curve, in addition to describing successfully most other experimentally determined features of this surface.⁵

The π bonding that apparently occurs on this silicon surface arises because it is energetically more favorable for the valence electrons of the surface atoms to rehybridize rather than remain as dangling bonds on the surface. To allow the π bonding to occur, the surface atoms from zig-zag chains on top of the surface. Total-energy calcu-

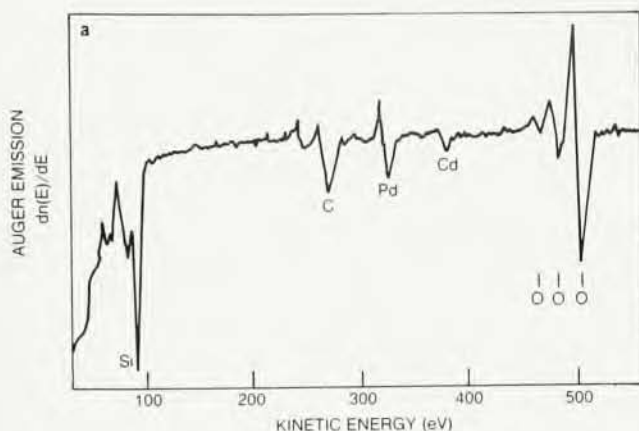
lations favor this type of bonding, and several different experimental results now also support the model.

Photoemission spectroscopy has also been successfully applied to the study of adsorbed atoms and molecules on surfaces. Here, the binding energies of valence electrons can serve as a "chemical fingerprint" of the adsorbed species, so that one can use the photoemission spectrum to follow chemical reactions on the surface. Polarization-dependent studies can again provide information on the symmetry and orientation of the adsorbed species. To interpret such valence levels or their surface dispersion quantitatively—in terms of the nature of bonding or the detailed geometry on the surface, for example—requires detailed theoretical calculations, as we mentioned for the case of the Si(111) 2×1 surface. Such calculations unfortunately become very complex and time-consuming for anything but simple adsorbed atoms.

Although we have presented a simple one-electron picture of photoemission spectroscopy, in reality, more is involved than just exciting an electron: The remaining ion, for example, can interact strongly with the surrounding electrons, thus introducing complex

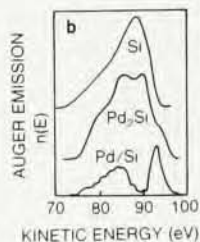


Angular variation of the photoemission spectrum of the Si(111) 2×1 surface. Each graph represents a different collection angle; The symbols Γ and J represent directions where specific electron momenta are collected. The shifts in peak positions are used to determine the energy-momentum relationship for the dispersion curve shown in **b** (dots). The theoretical curves are from a π -bonding model for the structure of this surface. Such dispersion curves are very sensitive to the detailed geometry and nature of bonding. Figure 4



Auger spectra of Pd on a Si(111) surface. We plot the derivative of the emitted electron current produced by a 5-keV electron beam incident on the sample; the Auger transitions are clearly visible. The Palladium transition has a relatively low cross section, and one can see electrons from other contaminants such as oxygen, cadmium and carbon. Graph **b** shows the direct emitted Auger signal for the LVV silicon transition for clean Si, Pd₂Si and an additional form of silicon that exists near the Si-Pd₂Si interface.

Figure 5



many-body effects. Such effects are particularly important for localized states at surfaces, and they must always be considered when examining absolute binding energies and photoemission lineshapes. These many-body effects, of course, complicate the quantitative application of photoemission spectroscopy as well as many of the other spectroscopic methods we describe.

Auger electron spectroscopy

After an atomic core level is ionized by an energetic electron or photon, the hole in the inner shell can be filled by an electron from a less tightly bound level with the simultaneous emission of a photon or of a second electron that carries off the energy gained by the first. The latter, non-radiative, decay process is referred to as an Auger process, after Pierre Auger who first identified the process back in 1925. In the case of light elements (Z less than 20), Auger emission is more probable than photon emission (x-ray fluorescence) when the initial hole is in the K shell. In heavier elements, Auger processes can still dominate for initial holes in outer electron shells. Thus, when the excitation energy is below 1 keV, Auger processes generally predominate over radiative transitions.

The kinetic energy of the ejected electron is the energy gained by the filling of the core hole minus the binding energy (with respect to vacuum) of the ejected electron in the presence of a hole in the atom. The Auger electrons with the largest energy provide information about the initial core states and, like x-ray photoe-

mission spectra, can thus be used for elemental analysis. Because each element gives rise to many different Auger transitions, one must in most cases consider several transitions for elemental analysis. Figure 5 shows Auger spectra of several monolayers of palladium on a contaminated silicon (111) surface. Here we plot, as one generally does, the derivative of the Auger electron energy distribution to enhance the features and to allow one to detect small concentrations. The Auger signal also depends on the matrix elements of the particular Auger transition and, for example, as a result the palladium signal is smaller than that from silicon. The other Auger signals in figure 5a correspond to carbon, cadmium and oxygen contaminants.

Changes in the valence electron densities will also markedly change the energy distribution of the emitted Auger electrons—in other words, Auger chemical shifts are large. However, because Auger emission involves three different levels, these shifts are difficult to predict or interpret theoretically. One can, nevertheless, use the Auger spectra to provide important qualitative information. For example, in figure 5b we show⁶ the Auger electron energy distribution for the LVV Auger transitions (these involve a hole in an L-shell core state and two valence electrons) of a clean silicon surface and for the same surface covered by various amounts of palladium. The formation of palladium silicide changes the valence states of the silicon atom and gives rise to a new pattern in the Auger spectrum. The main features shown in

the spectra can be successfully explained⁷ on the basis of the known valence-band density of states of Pd₂Si. For low coverages of Pd, one observes Auger electrons characteristic of another form of silicon not related to known Pd-Si compounds. It appears that Pd reacts on Si to form Pd₂Si with small amounts of a nonstoichiometric Pd-Si alloy formed at the Pd₂Si-Si interface. Such information is important in understanding the formation of Schottky barriers at the metal-semiconductor interface. Because such interfaces are very important in integrated circuits, the chemical nature of the surface compounds and the abruptness of the interface can affect the performance and reliability of the circuits.

The Auger signal can be relatively strong when generated by an electron beam. This high signal level, together with the wide availability of low-resolution electron spectrometers (resolving, say, $\frac{1}{2}$ - or 1-eV differences in electron energies) has made Auger spectroscopy the earliest and still most widely used spectroscopic technique for surface science. Using electron beams to create the holes in core states has a further advantage: The beam can be focused and scanned across the sample, providing information on the local composition of the surface. Typically, one can use a beam focused to about a 100-micron spot; the intensity of Auger electrons at various energies can then be displayed on a screen—essentially an element-specific Auger micrograph.

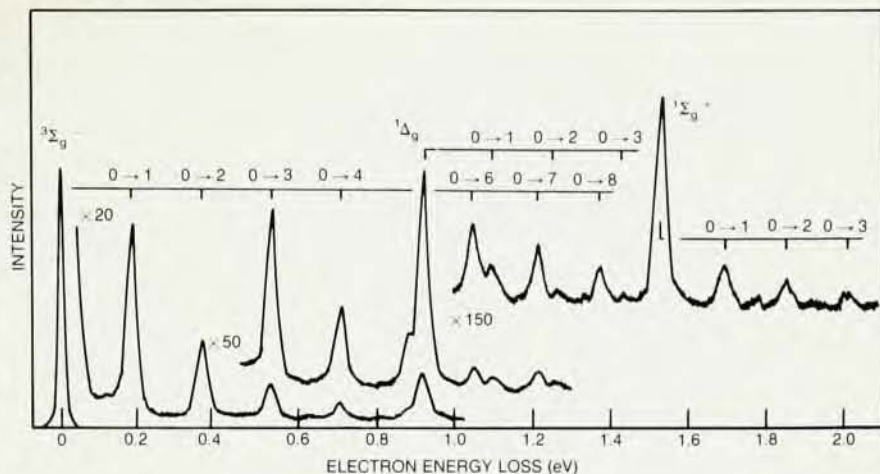
Electron energy-loss spectroscopy

Unlike the ionization-based spectroscopies we have discussed so far, electron energy-loss spectroscopy is an excitation spectroscopy, similar in many respects to optical spectroscopy. One illuminates the sample with a monochromatic beam of electrons and measures the energy distribution of inelastically scattered electrons. (The closest optical analog is thus perhaps Raman spectroscopy.) Because the inelastic scattering processes can involve the excitation of core or valence electrons to unoccupied states, energy-loss spectroscopy provides information on both occupied and unoccupied levels of atoms near the surface. The quantitative interpretation of the energy-loss spectra is made difficult by the fact that both occupied and unoccupied levels are involved; however, if one has detailed information (from photoemission spectroscopy, say) about the occupied states, then energy-loss spectra can be analyzed for information on the unoccupied states. Like Auger and photoelectron spectroscopies, energy-loss spectroscopy provides information that can be used for chemical analyses.

A unique and important application

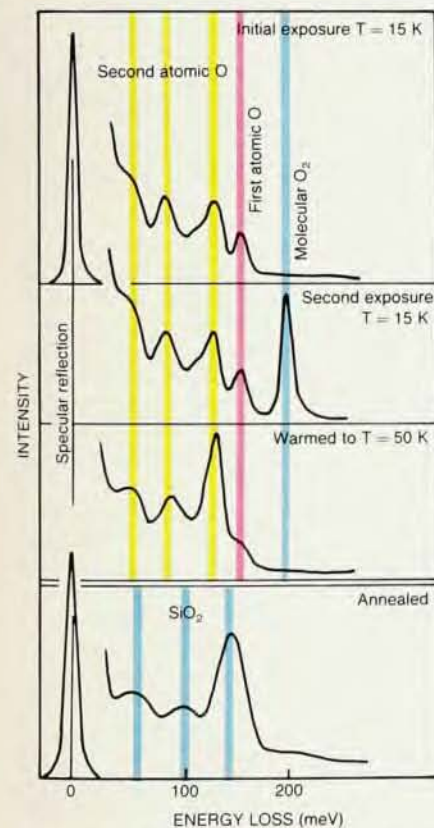
of electron energy-loss spectroscopy, and the one which we focus on here, is to the study of vibrational excitations—particularly those of adsorbates. The ionization spectroscopies are in general not suited for such studies because rapid neutralization of the hole states by valence electrons results in severe lifetime broadening of the observable spectral lines; the resulting linewidths (about $\frac{1}{2}$ eV) are too broad to show vibrational structures. The surface vibrational states themselves are of course broadened by coupling to excitations in the substrate, this broadening is sufficiently small—about 0.001 eV—that it does not prevent one from resolving vibrations.

It has long been recognized, particularly by chemists and materials scientists, that the vibrational spectrum provides a fingerprint of a molecular structure. The vibrational frequencies are a measure of the strength of the bond between atoms and groups of atoms and provide sensitive probes of



Molecular vibrations. Electron energy-loss spectra for a 6-eV incident beam of electrons scattered from the (111) surface of a silver crystal covered with a monolayer of molecular oxygen at a temperature of 20 K. Under these conditions the excitation mechanism involves the formation of a temporary negative ion which in turn decays to give an electrically or vibrationally excited state. The spectrum shows vibrational excitations from $\nu=0 \rightarrow \nu=1$ up to $\nu=0 \rightarrow \nu=8$ for the electronic ground state $^3\Sigma_g^-$ as well as showing several vibrational overtones for two electronic excited states, $^1\Delta_g$ and $^1\Sigma_g^+$. The electronic transitions are optically strongly forbidden.

Figure 7



Electron energy losses suffered by a 15-eV beam of electrons on a Si(111) surface exposed to oxygen. The initial exposure of the clean Si(111) 7×7 surface at $T = 15$ K produced a covering of roughly 0.2 monolayer of atomic oxygen; the spectrum shows vibrational characteristics of two different atomic phases. Adding more oxygen, to produce a coverage of about 0.8 monolayer, results in the appearance of molecular oxygen on the surface. Warming to 50 K dissociates the O_2 . Finally, laser annealing allows all the oxygen to react with the silicon to form SiO_2 . Figure 6

changes in valence electron density distributions. It is just this sensitivity that makes infrared spectroscopy—which also involves the vibrational states—such a powerful tool for analytic chemistry. The inherent surface sensitivity of electron beams allows us to use the unique features of vibrational spectroscopy in the study of surfaces and adsorbates.

To study vibrations, one directs a low-energy collimated electron beam with a narrow energy spread towards the surface; the reflected or back-scattered electrons are analyzed to measure their energy loss. Typically the incident beam has an energy of 1–10 eV, with a spread of 5–10 meV; the energy lost to vibrations is generally of the order of 0.1 eV. Both long-range and short-range interactions are involved in the scattering, and they determine what excitations can be detected. The long-range interaction involves the scattering of the incident electrons by the fluctuating dipole field of the oscillating nuclei. In that case, the inelastically scattered electrons are found in a relatively narrow lobe near the specular direction, the momentum transfer involved is small, and dipole matrix elements and optical selection rules apply. (The angular spread of the scattered electrons is on the order of the ratio of the vibrational energy to the energy of the incident beam.) When the scattering is via short-range interactions, large momentum transfers are involved, and the inelastically scattered electrons can be found at large, off-specular, angles. The short-range impact scattering involves essentially all possible surface excitations, not just those which are allowed by

dipole transitions. In certain cases, the incident electron may be captured by the target to form a temporary negative-ion state, which decays (via electron emission) to give an excited state of the neutral target.

The main difficulty in performing vibrational spectroscopy via electron energy loss is the requirement for high-resolution electron beams and detectors. Although one can achieve sufficiently high resolution for a variety of vibrational studies, some optical methods can provide an order-of-magnitude higher resolution⁸ when applied to surfaces. The main advantage of using electrons for vibrational spectroscopy is the overall flexibility in examining wide spectral ranges or in varying the excitation energy. Here, changing incident energies or scanning wide spectral ranges requires only changing the voltages on the electron optics of the spectrometer.

As an example of the use of electron energy-loss spectroscopy to examine the vibrational states of an adsorbate on a surface, we show in figure 6 a sequence of spectra for oxygen adsorbed on the (111) surface of a silicon crystal.⁹ Here we perform our studies at low temperature (about 15 kelvin) to enable us to follow the individual steps of the adsorption and reaction processes. The spectra reveal that the oxygen exhibits several different phases, depending on the coverage and temperature of the surface. After the initial, lowest exposures, the spectrum shows no evidence of molecular oxygen, as detected by a molecular vibration with $\hbar\omega$ near 200 meV. Instead, we observe four other peaks apparently associated with atomic oxygen on sili-

con. Exposing the surface to more oxygen—covering it to still less than a monolayer—produces molecular oxygen. The molecular oxygen vibration at 200 meV shows up clearly in addition to the atomic oxygen peaks seen in the initial spectrum. When the sample is warmed to 50 K, the O-O peak disappears from the spectrum, indicating that the molecular O_2 decomposes, and three of the original four peaks intensify. At even higher temperatures SiO_2 forms, producing a different set of peaks in the spectrum.

From such coverage-dependent measurements, one concludes that the initially adsorbed atomic oxygen has two states that differ in their coordination and binding sites with silicon. The number of vibrational peaks for these different atomic oxygen states has structural implications that can be derived with the help of dipole selection rules. One of the states has three dipole-active vibrational modes; the oxygen atom is apparently bound with sufficiently low symmetry that the rocking mode and symmetric and asymmetric stretching modes of a bridge-bonded oxygen species are observed.¹⁰ The other state shows only one band, which implies binding at a high-symmetry adsorption site—likely on top a silicon atom. Such investigations of the chemical forms of atomic and molecular oxygen on silicon surfaces, and their transformation to bulk oxide have very practical implications because SiO_2 is widely used in electronic devices as a uniform insulating barrier. In fact, it is just this ability of silicon to form the oxide that has made it the primary material for electronic devices.

One important advantage of using electrons rather than photons is that one can excite optically forbidden transitions or enhance the scattering cross sections by tuning the electron beam to energies at which resonance electron scattering can occur. Figure 7, for example, shows loss spectra for resonance electron scattering off a monolayer of molecular oxygen on the (111) surface of silver. The spectrum shows not only the absorption of vibrational quanta $\hbar\omega$ from the electron beam but also excitation to higher vibrational states (overtones). In addition to the vibrational excitation, the electron beam also produces electronic excitations together with their vibrational progressions. From an analysis of these spectra one can derive detailed information regarding the effect of the surface on the intramolecular potential-energy curve of the adsorbed molecule.¹¹ Such information is vital to understanding how adsorbate bonds break at surfaces—an important aspect of all chemical reactions on surfaces.

In the case of O_2 on Ag (111) at 20 K, the nearly even spacing of the vibrational lines indicates that the O-O potential is quite harmonic and not too different from the potential of free O_2 . The molecule is reversibly and weakly adsorbed. In contrast, molecular oxygen on Si (111) shows changes in the energies of the overtones that indicate a strongly reduced barrier for dissociation—a reduction consistent with the observation of dissociation at a temperature of 50 K seen in the experiment of figure 6.

Future prospects

The many advances over the last 15 years in surface spectroscopy have created a golden era of surface science. More detailed information regarding the three major surface spectroscopies we describe, as well as general information on surface science, is provided in references 1 and 2. Here we have considered only some basic principles of these spectroscopies, and we have noted some of the physical processes that complicate their utilization. Many of these same processes also offer unique opportunities to gain additional information. For example, electron emission from localized states at a periodic surface gives rise to interference features that show up in angular distributions and can provide structural information.¹² Similarly, electron or optical adsorption at an energy near a core-level edge sets up a standing wave that modulates the energy dependence of the adsorption cross section; these modulations also can provide structural information.¹³⁻¹⁵ Such interference phenomena, when quantitatively understood and applied, provide detailed structural probes. In addition, several groups are developing¹⁶ a technique called inverse photoemission. Here they bombard the surface with electrons, some of which drop into unoccupied states and emit photons; these are then energy analyzed to provide information regarding the unoccupied states.

In the future, we expect increasingly sophisticated uses of surface spectroscopies to obtain novel or more detailed information. Already we find many surface scientists combining several spectroscopic methods to exploit advantages of each and to compensate for their disadvantages. In this way they can not only address specific problems about surfaces but they can also better understand the subtleties of any one method. We can expect the future development of optical methods to probe surfaces in nonvacuum environments. This includes reflection infrared spectroscopy,¹¹ high-sensitivity Raman spectroscopy,¹⁷ and possible nonlinear optical spectroscopy at sur-

faces.¹⁸ Already, the availability of intense, widely tunable radiation from synchrotrons has extended the energy range and types of surface spectroscopies possible. The applications of existing surface spectroscopies and the development of new methods will continue to make surface science an active and exciting field.

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