Photoelectron spectroscopy

With its power enhanced by synchrotron radiation, this technique for studying bulk and surface electronic structures goes to the heart of many problems in atomic, molecular and condensed-matter physics.

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The electronic structure of materials not only is fascinating from a theoretical point of view, but also has tremendous implications for technology. Electronic-structure studies, in fact, account for the majority of uses of uv radiation from synchrotron sources. Most of these studies involve photoelectron spectroscopy, a measurement technique that goes to the heart of many problems in atomic, molecular and condensed-matter physics. For example, photoelectron spectroscopy permits direct measurement of all quantum numbers of the electronic states in a material, and in particular determination of its band structure—that is, the relationship between energy and momentum of electrons in the material.

In this article we illustrate the capabilities of photoelectron spectroscopy in the study of condensed matter (solids and surfaces) with emphasis on how these have been extended—and will be extended further—by the use of synchrotron radiation.

A powerful technique

Photoelectron spectroscopy has been used to test several essential concepts in condensed-matter physics, such as the itinerant ferromagnetism of the common ferromagnets (iron, cobalt and nickel) and the localization of electrons near a surface in well-defined surface states. The technique has revealed unusual types of bonding at surfaces and interfaces—for example, intermediate oxidation states at the Si/SiO_2 interface that are unstable in the bulk, π bonds at a silicon surface and partially reacted molecules at a metal surface.

Synchrotron radiation, with its tunability, polarization and high intensity, adds several essential features to this technique. One can boost the sensitivity to surface states by using monochromatic radiation tuned to produce photoelectrons with energies of about 50 eV. At this energy their mean free path is a minimum. One can also tune the radiation to scan the component of the electron momentum perpendicular to the surface, thereby permitting measurements of the complete bulk energy-band dispersions. The polarization dependence of photoelectron emission can be used to determine the orientation of molecules adsorbed on a surface and the direction of chemical bonds.

The rapidly growing interest in surfaces and interfaces is due to not only the scientific appeal of working in two dimensions, but also the needs of the microelectronics and chemical industries. The ever-smaller electronic devices have ever-larger surface-to-volume ratios. Interface phenomena begin to dominate their perfomance when the dimensions of the devices become comparable with electronic characteristic lengths, such as the Debye screening length, the diffusion length and the de Broglie wavelength. With dimensions larger than a micron, today's devices still are comfortably larger than the critical sizes, but in the submicron regime such size effects will become dominant. In chemistry, directed progress in heterogeneous catalysis will require a step-by-step understanding of surface chemical reactions. Similarly, we need to understand the reactions that take place during the fabrication of microstructures to turn that art into a science.

The background

If we are to catapult our thoughts into the future of photoelectron spectroscopy, we should first stretch our memories back to its beginnings two decades ago. Two experimental technologies—vacuum-ultraviolet spectroscopy and routine production of ultrahigh vacuum—simultaneously matured in the early 1960s. With the benefit of hindsight, we can see that these made possible studies of valence-electron band structures using uv-stimulated photoemission. There are two reasons for this. First, with a few exceptions, such as the alkali metals, the work function of typical materials is in the range 4–6 eV, so that monochromatic radiation in the vacuum uv ($\hbar\omega$ above 6 eV) is essential for such studies. Second, because photoelectrons have a very short mean free path, the sampling depth of these experiments is small (sometimes as little as 5 Å); one therefore needs an ultrahigh vacuum to prepare and maintain atomically tailored surfaces. In a similar way, the study of core-electron structures began in the 1950s with the simultaneous development of two technologies: intense, monochromatic x-ray sources and electron-energy analyzers with extremely high resolution—achievements for which Kai Siegbahn received[1] the Nobel Prize (PHYSICS TODAY, December 1981, page 17).

Another of these happy convergences took place in the 1970s, which witnessed two important advances in experimental technique. The first was the development of angle-resolved photoelectron spectroscopy—that is, of

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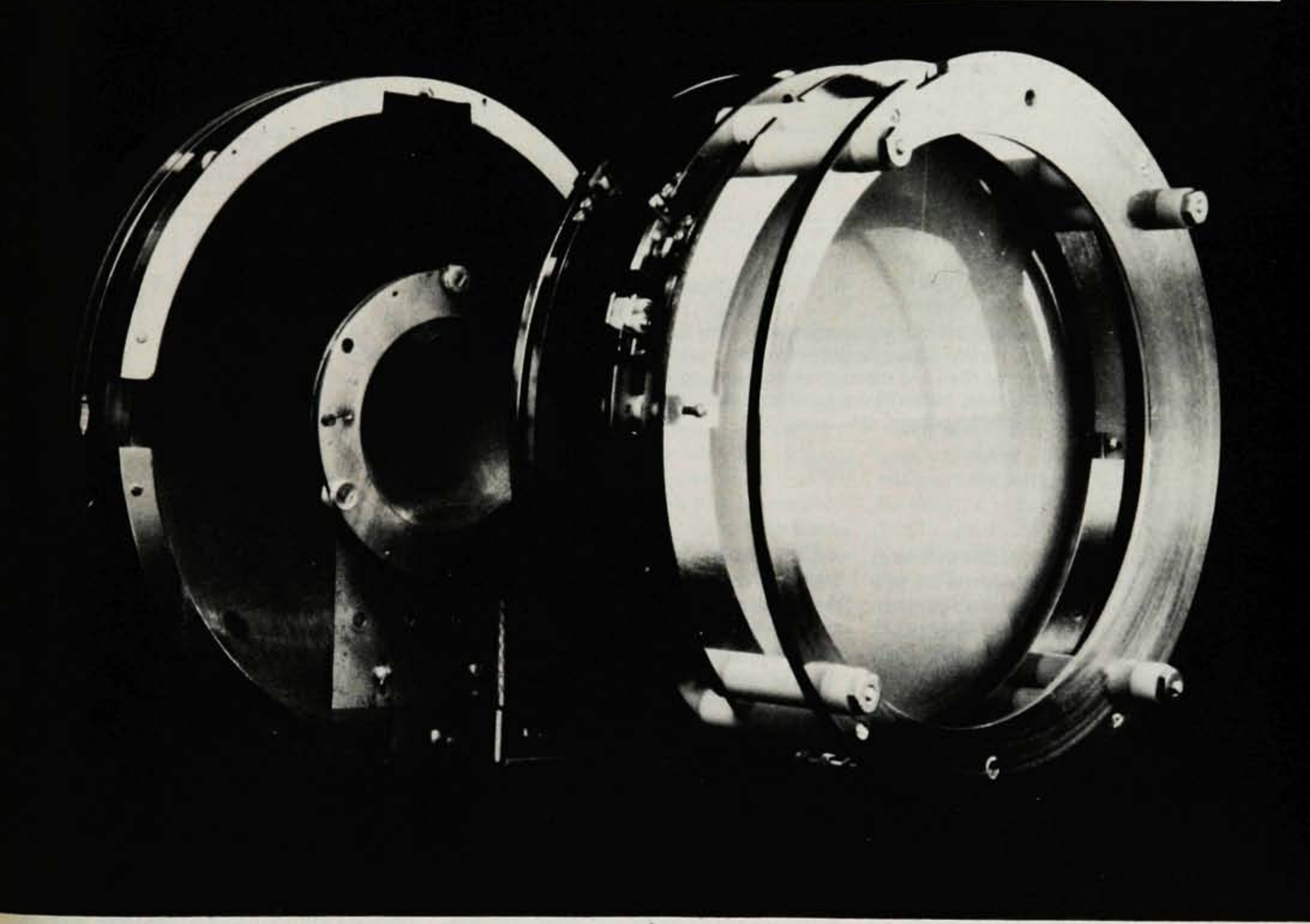


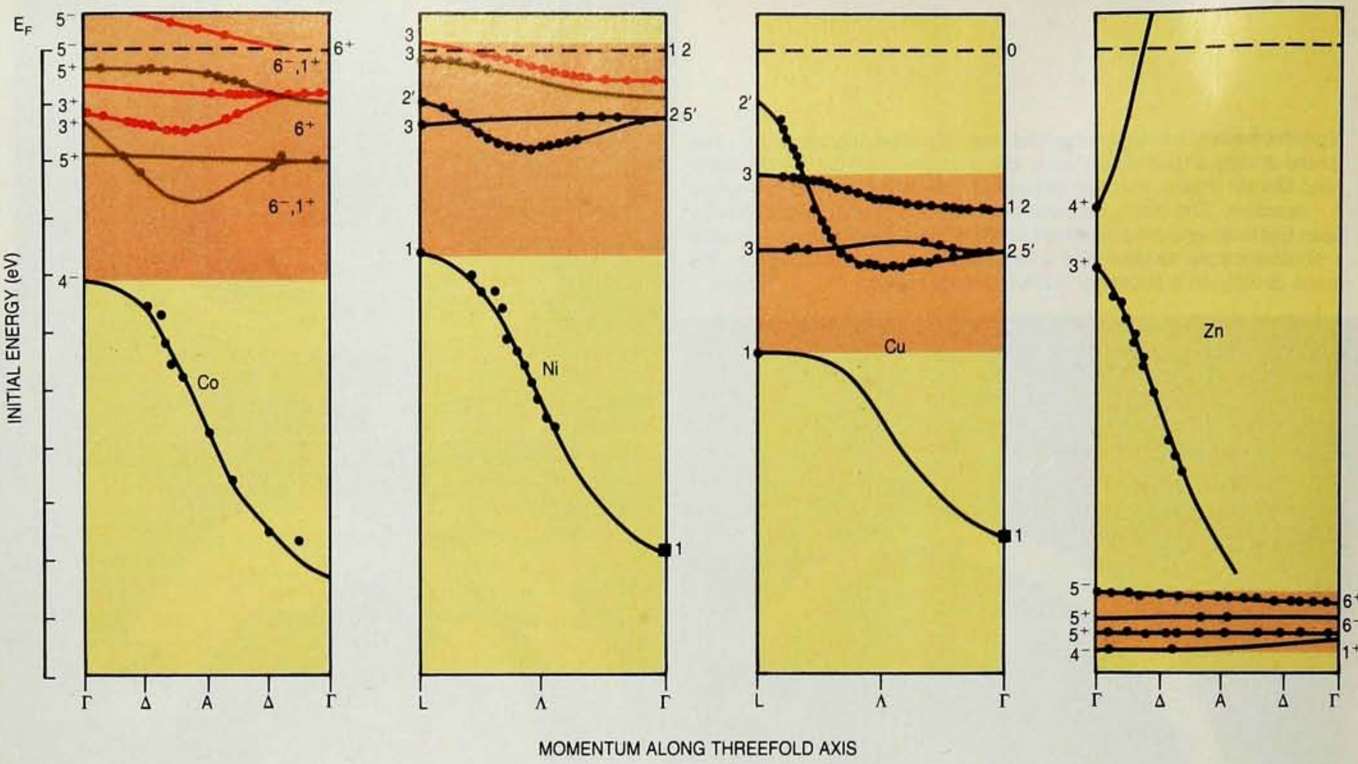
Spectrometers for angle-resolved photoelectron spectroscopy. The photo at right shows a very early spectrometer, built by Neville Smith and Morton Traum, that can detect only electrons emitted in a single direction. The photo below shows a device built more recently by Dean Eastman and his coworkers at IBM; it can detect simultaneously photoelectrons emitted over a large angular field and it displays the results directly on a phosphor screen (on the right). Figure 1

techniques to measure both the energy and momentum of the photoelectrons (see figure 1). The second was the exploitation of synchrotron radiation. At the middle of the decade these developments converged, giving rise to the versatile version of photoelectron spectroscopy that we know today: It provides information not just on electron energy E but also on other fundamental quantum numbers such as the three components of electron momentum $\mathbf{k}$ and the symmetry of the wavefunction. The addition of Mott-scattering technology permits measurement of the electron spin.

We fully expect this process to continue as advances in experimental technology reveal new physics to be explored. Thus we can expect that the higher brightness of the beams available from insertion devices (wigglers and undulators) in existing and proposed synchrotrons and storage rings will again expand the experimental horizons.

Band-structure mapping

The band structure, or energy–momentum dispersion relation $E(\mathbf{k})$, for electrons in crystalline solids is one of the most fundamental concepts in solid-state physics. Given $E(\mathbf{k})$, one can in principle derive most other electronic properties of a solid or surface, such as its optical properties, magnetism and electronic transport properties. Band dispersions have been calculated theoretically for decades but could not be measured directly until the advent of angle-resolved photoemission spectroscopy (ARPES). Because ARPES determines E and $\mathbf{k}$ of the emitted photoelectron, and because one knows $\hbar\omega$ and $\mathbf{q}$ of the incident photon, simple conservation laws allow one to determine the energy and momentum the electrons had before they were ejected. (Al-



Energy bands of elements in the first row of transition and noble metals, measured with photoemission spectroscopy. As the atomic number increases, the relatively flat 3d bands (on orange background) become filled and move down in energy relative to the more strongly energy-dispersed 4s and 4p bands. In the ferromagnetic elements Co and Ni, the bands are split into majority (red) and minority (orange) spin bands. Figure 2

though the component of momentum along the surface is conserved in the photoemission, the component perpendicular to the surface is not. This poses something of a problem. Suffice it to say that one can reach all values of $k_\perp$ only with a tunable photon energy. Synchrotron radiation has therefore been indispensable for the complete determination of band structures.[2,3])

By and large, the maps of $E(\mathbf{k})$ resulting from ARPES studies, such as those shown in figure 2 and those for other metals and semiconductors, are in agreement with expectations based on first-principles one-electron band calculations. Such measurements therefore serve to refine band structures already known with some confidence and to resolve uncertainties in cases where the band structure is not well established. Indeed this approach has been so successful that a considerable amount of attention is now directed toward those cases which are not in agreement with the expectations of one-electron band theory.

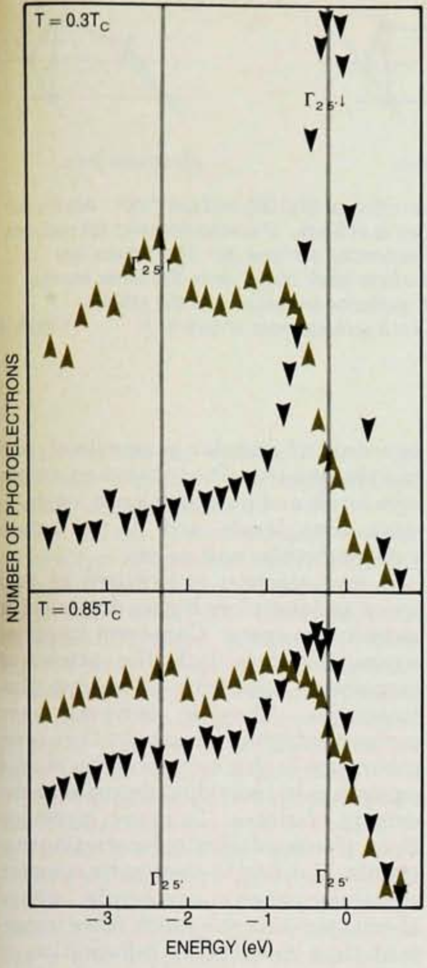
A notable case is that of nickel. The width of the d-electron band and the magnetic-exchange splitting observed in ARPES are significantly smaller than predicted by one-electron band theory. These discrepancies are attributable[4] to self-energy corrections associated with strong hole–hole correlations within the Ni d band; a related effect is the appearance of a two-d-hole or "excitonic" satellite peak below the d band at an apparent binding energy of 6 eV. A few years ago the photoemission group at Orsay reported[5] an enhancement or resonance of the 6-eV satellite on tuning the photon frequency $\hbar\omega$ through the threshold for excitation of the 3p Ni core level (about 67 eV). This observation (not possible without the synchrotron radiation continuum) generated considerable excitement and has spawned a subdiscipline known as resonant photoemission, in which resonant enhancement of a subset of states allows one to separate them out from the other states. This technique is used routinely to distinguish f-like from d-like states in rare earths and helps in understanding the formation of "heavy fermions" (PHYSICS TODAY, December 1983, page 20).

Ferromagnetism

In ferromagnetic materials, such as nickel, there are in fact two band structures, one for the majority-spin electrons and another for the minority-spin electrons. These can be resolved from each other in the vicinity of the Fermi level. For an unambiguous identification it would be desirable to differentiate the spins experimentally. Mott-scattering analysis—essentially spin-polarized ARPES—allows one to do so. Erhard Kisker and his coworkers at Jülich have already done[6] a number of such experiments using synchrotron radiation.

Spin-polarized spectra for photoelectrons emitted normal to the (100) surface of iron are shown in figure 3. The spectra do indeed differ dramatically for the two spin systems, and the difference diminishes as the temperature approaches the Curie temperature T_C. Note that while the spectra smear out and approach each other in intensity, the energy separation between the peaks labeled $\Gamma_{25'}{}^{\uparrow}$ and $\Gamma_{25'}{}^{\downarrow}$ (that is, the magnetic-exchange splitting) does not diminish appreciably. A simple model of ferromagnetism, the Stoner model, postulates that the exchange interaction splits the energy bands of electrons much as an external field would in a paramagnetic material. The experimental result indicates that any such model requiring a decreasing exchange splitting is inapplicable; it favors theories that require the existence of locally magnetized regions above T_C, for example, the local-band-structure theory or the disordered-local-moment picture.

Further studies of this kind are



Spin-polarized-photoelectron spectra from the (100) surface of ferromagnetic iron. The spectra for the majority carriers are shown in black; those for the minority carrier in color. The effect of the magnetic-exchange splitting is seen as the difference in the positions of the "$\Gamma_{25'}$" peaks for the two spin directions. The upper graph shows data for a temperature of $0.3T_C$; the lower graph shows data for $0.85T_C$. Although the difference between the spin-up and spin-down curves is less dramatic at the higher temperature, the exchange splitting is not appreciably diminished. Figure 3

clearly desirable if we are to gain a better understanding of ferromagnetism. High-brilliance sources, such as undulators and wigglers, will have an important effect on these studies, because the use of Mott scattering for spin discrimination reduces the signal by a factor of about 10^{-4}. Experiments with spin-polarized ARPES can clearly profit from brighter sources.

Because the Fermi level intersects the d bands in the elemental ferromagnets (Fe, Co, Ni), a study of the unoccupied states in these bands would be a desirable complement to ARPES studies of the occupied states. Such studies may become possible with the newly developed technique of inverse photoemission, which we discuss briefly below.

Surface states

As we have mentioned, photoelectrons sample only a small depth of material; by tuning their energy, one can make the sampling depth as small as 5 Å and reach monolayer sensitivity. Surface electronic structures are therefore just as amenable to ARPES studies as are bulk band structures. Because the surface is two dimensional, the normal component of the momentum, $k_\perp$, is no longer a meaningful parameter and the problems of determining it mentioned earlier are not relevant: The relation $E(\mathbf{k}_\parallel)$ is a complete description of a surface-state or adsorbate-induced band structure. Recent work by Steve Kevan and Ned Stoffel at Bell Labs on the Ge(100) surface shows[7] the sort of information one can obtain about surfaces as well as illustrating some present and future trends.

The Ge(100) surface, like the Si(100) surface, undergoes a reconstruction involving the creation of a superlattice. Atoms in the surface plane are believed to relax through the formation of asymmetric dimers (see figure 4): One atom moves away from the surface while the other moves toward the surface. The asymmetry has two senses, depending on whether the "up" atom is on the right or left. The process can be described by the Ising model, with the sense of the dimer playing the role of electron spin. Jisoon Ihm and his coworkers at MIT have recognized this similarity and have used[8] renormalization-group methods to deduce the phase diagram. They conclude that the ground-state configuration is not the simple 2×1 superlattice but more likely a centered 4×2 superlattice; these results are consistent with low-energy electron diffraction data obtained at low temperatures. They conclude in particular that this "antiferromagnetic" c(4×2) superstructure will undergo an order–disorder transition near room temperature.

These ideas are borne out by the high-resolution ARPES data of Kevan and Stoffel. Figure 5 shows some of the spectra they have obtained for photoemission perpendicular to the surface. Note the small peak within about 0.1 eV of the Fermi level in the ARPES data. The natural width of the peak is less than 100 meV, and it exists over a very narrow range of angles—on the order of 1½°. The occurrence of this "metallic" peak is associated with disordering of the c(4×2) superlattice reconstruction. One can deduce the c(4×2) reconstruction from the intensities of the quarter-order diffraction spots seen in the LEED data shown at the right in figure 5; these spots disappear as disorder sets in at higher temperatures.

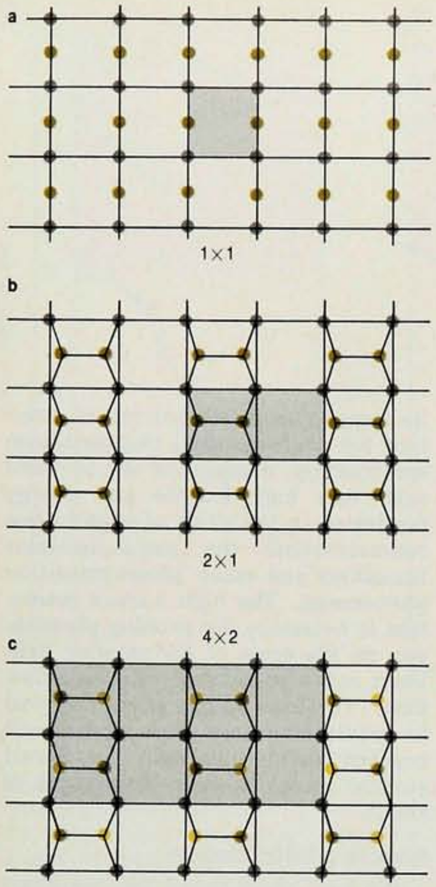
Aside from their results, these studies suggest an important future direction for angle-resolved photoemission spectroscopy, namely the use of ARPES with very high k-space and energy resolution in the study of superlattice reconstruction, the metal–insulator transition and other phase-transition phenomena. The high k-space resolution is necessary for probing phenomena on the scale of the smaller Brillouin zones associated with superlattices. The high energy resolution will be required because these studies will concern instabilities near the Fermi surface where lifetime broadening is small.

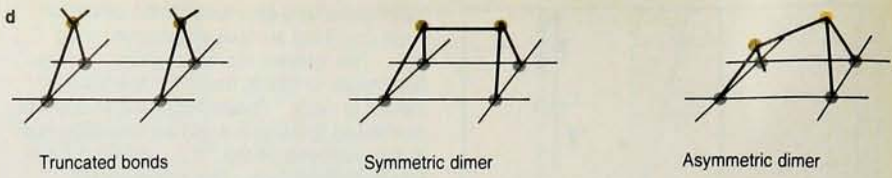
Inverse photoemission

We have emphasized the completeness of ARPES information obtained with synchrotron radiation. There is, however, a range of energies—from the Fermi level to the vacuum level—inaccessible to ARPES because there are normally no electrons in these states. A new technique, k-resolved ultraviolet inverse photoemission, promises to fill this gap. As the name implies, the technique consists of bombarding a sample with an electron beam of variable energy and well-defined direction and energy analyzing the emitted photons.

Signal levels in inverse photoemission are quite low compared with those in ordinary photoemission (by a factor of around 10^{-4} or 10^{-5}); this presumably accounts for its slow start. Indeed, it was only in the late 1970s that the first surface-sensitive studies were performed[9] in the uv, by Volker Dose's group at Würzburg. Since then the pace has quickened, and recent years have seen[10] the introduction of angle-resolved work, spin-polarized studies, observations of surface states, investigations of adsorbate features and exploitation of the photon-energy continuum—events that were spread over two decades in the case of ordinary photoemission.

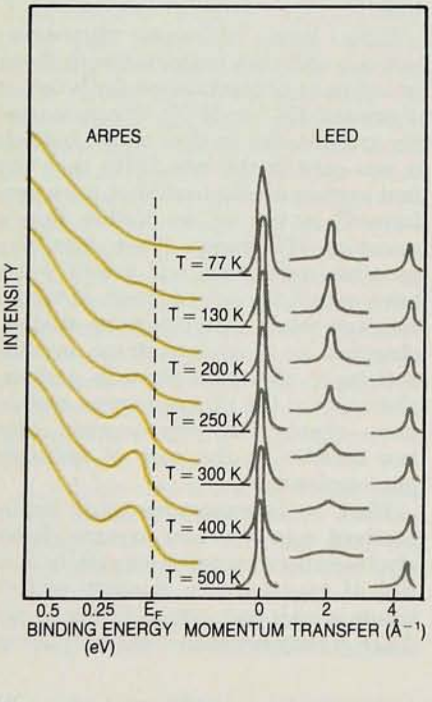
Work on ferromagnets using angle-resolved spin-polarized inverse photoelectron spectroscopy is especially worthy of mention. In current experiments of this sort, signal levels do not differ grossly between ordinary photoe-





Asymmetric-dimer model of the surface reconstruction of Si (100) and Ge (100). Atoms on the surface are shown in color; the next layer down is in black. Pairwise bonding (**b**) reduces the large number of dangling bonds in the unreconstructed surface (**a**). The dimers are asymmetric in that one atom moves toward the surface (dark color) while the other moves away (bright color). Experimental and theoretical evidence indicates that the stable configuration is the antiferromagnetic, centered, 4×2 arrangement shown in **c**. Figure 4

Metal–insulator transition on the Ge (100) surface. The small peak just below the Fermi level in the ARPES data taken at room temperature indicates the presence of a "metallic" surface state. This state disappears at low temperatures, where there is an ordered c(4×2) arrangement of the surface dimers. The low-energy electron diffraction data at right also show the transition, as the peak corresponding to diffraction from the larger, 4×2 unit cell disappears at high temperatures. Figure 5



mission and inverse photoemission. The signal level in inverse photoemission is inherently low, but is not limited by the nature of the electron source; one can produce the requisite incident electron current whether or not the electrons are spin polarized. Jürgen Kirschner at Jülich and his coworkers at Würzburg have recently used[11] spin-polarized inverse photoemission to investigate the Fe (100) surface. Their results are relevant to our discussion of the magnetic-exchange splitting in iron, as they indicate that the exchange splitting—whether or not it disappears at T_C—may be k dependent. The intimate connection between magnetic properties and unoccupied bands can be seen from the fact that for the rather common "strong" ferromagnets the number of Bohr magnetons is the same as the number of unoccupied minority-spin states. The transition to a "weak" ferromagnet (in which some of the majority-spin states are also unoccupied) can be followed directly by use of spin-polarized inverse photoemission.

Core levels

One can probe deeply bound, or core, electrons with two types of spectroscopies: absorption-edge spectroscopy, in which the photon energy is scanned while the electron energy remains fixed, and photoelectron spectroscopy, in which the energy distribution of emitted electrons is measured at fixed photon energy. The first method measures unoccupied valence states; the second determines the binding energy of the core levels themselves. These two experimental techniques provide complementary information about the band structure of a material.

One can probe the unoccupied valence states by measuring inverse photoemission, or one can monitor the photon absorption as $\hbar\omega$ is scanned across a core-level threshold. Features of the spectrum near absorption edges correspond to optical transitions between a core level and unoccupied valence states; the details of the spectra provide information about the density of states for the unoccupied levels. Because the absorbed photon carries one unit of angular momentum, one can observe transitions between s-state core levels and p-state valence levels, p-state core levels and s- or d-state valence levels, and so on.

A core electron is localized in real space and therefore highly dispersed in momentum space. Core-level spectroscopies therefore lack the attractive momentum specificity of inverse photoemission. They do, however, have compensating advantages. Core-level absorption is able to resolve the atomic parentage of individual features in the density of states. In many investigations of technologically interesting materials, one has to deal with complex multicomponent materials where atomic parentage is much more important than momentum information.

There is considerable enthusiasm about working in the energy range at and above the threshold given by the K edge in the carbon spectrum. Organic chemistry—and maybe biochemistry in the future—can benefit from the analysis of the 1s level, the only core level of carbon, nitrogen and oxygen. Polymers are being introduced into the electronics industry for inexpensive packaging, and engineers are beginning to study their surfaces and interfaces with the aim of tailoring their adhesive and electrical properties to particular uses. The new photoemission subdiscipline associated with the electronic properties of small organic molecules on surfaces is destined to grow, as many processes important in oil refining take place on the surfaces of transition-metal catalysts.

The binding energy of the 1s core level (K edge) of carbon is near 284 eV, in the soft-x-ray region; experimentally, this is a difficult region, in which grazing-incidence mirror optics and gratings are essential. But there is an additional difficulty associated with optical absorption of carbon itself. Carbon is a universal contaminant on surfaces, even in ultrahigh vacuum. Experimenters therefore run up against one of the frequent perversities of nature: The observation of an effect, in this case carbon K-edge absorption, is impeded by the effect itself elsewhere in the measuring system. One must take care to protect reflecting surfaces against carbon deposits.

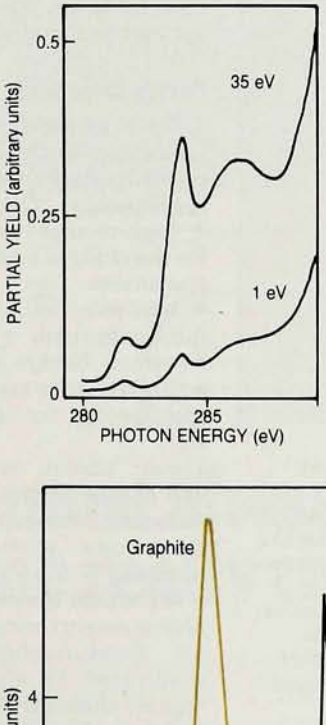
The K-edge photoemission spectra for the two crystalline forms of carbon (graphite and diamond) show strong differences, which are readily associated with differences in chemical bonding. These spectra, recently obtained[12] by John Morar and his coworkers at IBM, Yorktown Heights, are shown in figure 6. Whereas in a diamond lattice each carbon atom is bound to four others via single, or σ, bonds, graphite has a considerable degree of double, or π, bonding associated with its well-defined six-member ring structure. Because π bonds are weaker than σ bonds, the energy splitting between the bonding π and antibonding π^* orbitals is smaller than between the σ and σ^* orbitals. Hence in graphite we find that the carbon K edge is dominated by a prominent π^* peak lying well below the σ^* structures.

The core-level absorption in these experiments was not measured directly (by, for example, monitoring the transmission through a thin sample), but was measured indirectly by collection of secondary and Auger electrons generated by the creation and decay of the core hole. Using this technique, one can make the measurement sensitive to the bulk or the surface by judicious choice of the kinetic-energy window of the collected electrons. For a collection energy of 1 eV the electron mean free path is relatively long, and one probes bulk properties. At 35 eV, on the other hand, the mean free path is short, and one probes the surface atomic layers. Figure 6 shows that at 35 eV there exist π^* orbitals, which indicates the presence of π bonding on the surface of diamond.

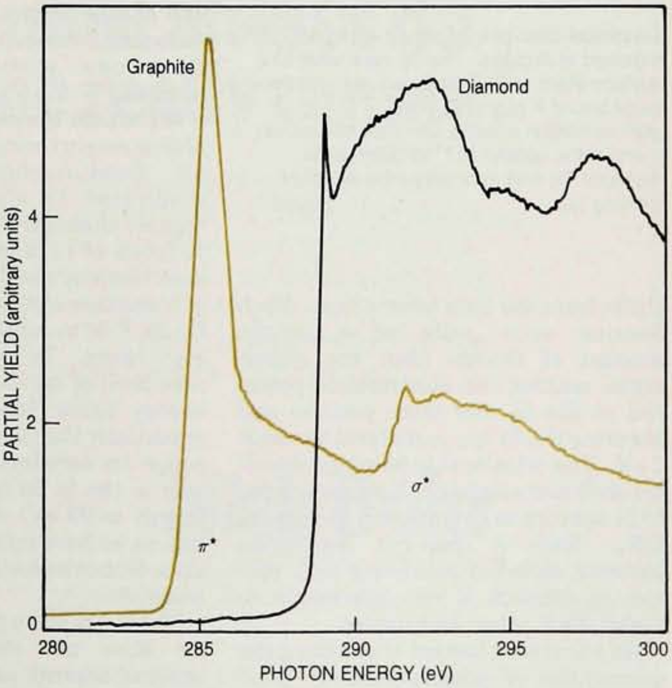
Silicon surface processing

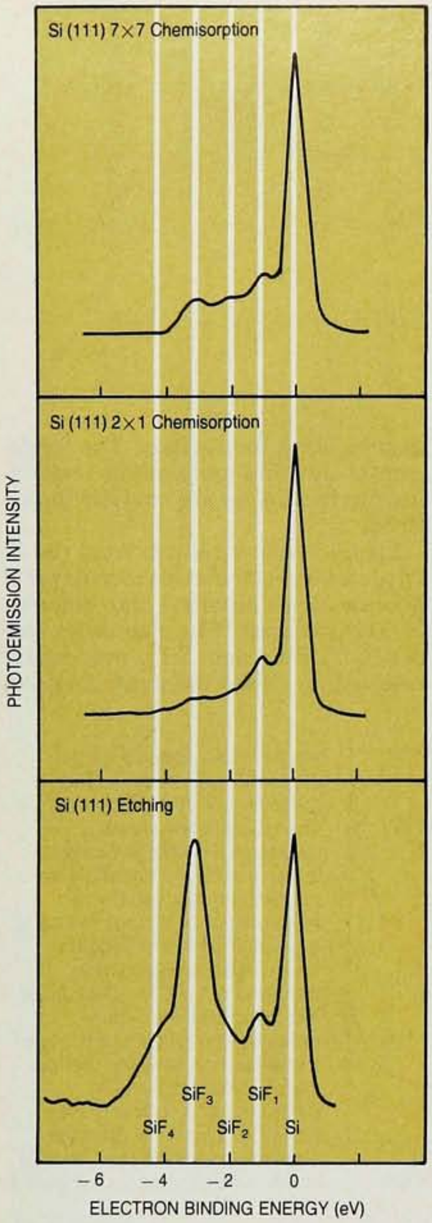
The photoelectron energy spectrum is the best means of studying the energies of core levels and their chemical shifts; it is therefore used in many technologically important studies. We discuss now an investigation directed toward the better understanding of silicon etching by fluorine, an important process in the microelectronics industry. To produce fast integrated circuits it is necessary to etch micron-scale anisotropic features into silicon. In plasma processing, currently the method of choice, silicon wafers are exposed to a fluorocarbon plasma that produces fluorine atoms, which in turn react with silicon; the resulting volatile silicon fluorides carry off silicon atoms as they leave the surface. The fundamental chemical mechanisms underlying this technology are not fully understood.

Figure 7 shows spectra from the Si $2p_{3/2}$ core level for about a monolayer of fluorine atoms adsorbed onto different Si (111) surfaces. The fluorosilyl species, SiF, SiF_2 and SiF_3, are clearly resolved by their different chemical



Partial-yield spectra for the carbon K edge obtained for graphite (color) and diamond. The graph below shows results as the photon energy is swept across the threshold for excitation of the carbon 1s electrons; only photoelectrons of a given energy are detected. The spectra represent the transition of core-level electrons into unoccupied π^* and σ^* orbitals. The graph at left shows the difference between the bulk states (detected by 1-eV electrons) and surface states (35-eV electrons) of diamond. Note the presence of π^* orbitals in the surface states. Figure 6





Chemical changes of silicon surfaces exposed to fluorine. The 2p core level of a surface atom of Si exhibits a 1-eV shift for each bound F atom (**a**). The photoemission spectra can thus be used to monitor the uptake of F on different Si surfaces (**b**) and to observe the effect of etching (**c**). Figure 7

shifts from the bulk silicon line. Each fluorine atom pulls off a certain amount of charge from the silicon atom, making the electrostatic potential at the Si core more positive and lowering the Si $2p_{3/2}$ core level by about 1 eV. The relationship between chemical shift and number of F atoms bonded to Si appears to be linear all the way to SiF_4. Such a clear-cut distinction between different coexisting SiF_x species is difficult if not impossible to make with other techniques.

As a first step toward elucidating the mechanism of plasma etching, Read McFeely and his coworkers at IBM, Yorktown Heights, have studied[13] the chemisorption of fluorine atoms on some model silicon surfaces. Figure 7 shows some results. On the Si (111) 2×1 surface (reconstruction after cleaning) one sees a single chemically shifted Si $2p_{3/2}$ core level, indicating a surface monofluoride, while on the Si (111) 7×7 surface (reconstruction after annealing), one sees peaks characteristic of mono-, di- and trifluoride species. The monofluoride is characteristic of a truncated bulk structure in which F atoms terminate the single broken bond on each surface atom. Higher fluorides can be formed only by breaking back bonds, so their presence indicates a more open structure for Si (111) 7×7 in which F atoms can penetrate through the surface and attack back bonds. At much higher fluorine exposures, SiF_3 begins to dominate and the surface begins to etch away. Apparently the removal of SiF_3 represents a bottleneck in the etching reaction. Core-level spectroscopy thus allows one to watch the entire transition from an idealized well-ordered surface to a complex etched surface.

Future directions

We have already mentioned several important future directions for synchrotron-radiation-based photoelectron spectroscopy. These include:

- ▶ high-momentum-resolution ARPES for the study of superlattices and phase transitions
- ▶ spin-polarized ARPES for the study of ferromagnetism
- ▶ carbon K-edge studies
- ▶ high-energy-resolution core-level spectroscopy for chemical-shift analysis.

These "photon hungry" experiments will surely advance rapidly given the enhanced intensity and brightness from new synchrotron-radiation sources.

We attach special importance to the photon-energy range from 200 to 1000 eV. Good resolution in this region would open up a new field of surface organic chemistry, one using the sharp 1s levels of C, N and O. The sharpest core levels of the first and second rows of transition and noble metals (Sc 2p to Cu 2p, Y 3d to Ag 3d) also fall in this energy range. In general the sharpest core level of an element has a binding energy below 1000 eV, making this potentially the most important spectral range for core-level spectroscopy. Access to the Si 2p level (whose binding energy is 99 eV) with good resolution has, as we have indicated above, opened up a technologically important line of research.

There are some promising directions we have not mentioned. If light sources several orders of magnitude more brilliant than current sources become available, one can contemplate photoelectron spectroscopies with spatial or temporal resolution. The implementation of spatially resolving photoemission microscopes will be driven in large part by the future needs of the microelectronics industry.[14] The relevant comparison here is with scanning Auger spectroscopy, which constitutes a microscope for elemental analysis. A photoemission microscope would supplement elemental investigations with detailed information on chemical bonds.

Time-domain photoemission spectroscopies are an exciting prospect. Some investigators are already using[15] picosecond laser pulses for ARPES studies. We envisage double-photon experiments in which a system excited by a synchronized laser pulse is subsequently probed with a synchrotron-radiation pulse. Alternatively, both pulses could be derived from the same synchrotron-radiation source. We can also foresee experiments in which ions or neutral atoms are detected in coincidence with photoelectrons, enabling us to elucidate the photochemical reaction. And we can dream of monitoring surface chemical reactions in real time.

At present, however, we are limited by the brightness and pulse duration of the available synchrotron-radiation sources.

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