

# Working Group on New Directions in Surface and Interface Science

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## 1. Research Frontiers and Relationship to the Advanced Light Source

Surface and interface science is an all-pervasive component of contemporary materials science, physics, and chemistry. Interfaces in the atmosphere and in aqueous solution are also ubiquitous in the environmental and life sciences. By one estimate, nearly 80% of all chemical reactions in nature and in human technology take place at boundaries between phases, i.e., at surfaces or interfaces. During the last 15 to 20 years, several key technologies based on surface and interface properties have become the basis of major industries. These include microelectronic devices, the discs and read-write heads for magnetic information storage, industrial and environmental catalysis, copying via Xerography, optical fibers, chemical sensors, biocompatible implants, and selective surfaces for gas

separation and air and water purification. These technologies are becoming ever more sophisticated and are in turn driven by advances in surface and interface science. Atomic- and molecular-scale studies at the interfaces between solid and vacuum, solid and high-pressure gas, solid and liquid, as well as solid and solid are needed to advance the state of the art. These will require studies at higher pressures, higher spatial resolutions and shorter time scales. One of the challenges of modern surface science is thus to expand its range of investigations to all these types of interfaces and to develop a thorough understanding of the relationships between molecular-scale surface properties and parameters relevant to potential applications and devices.

The current research frontiers focus on atomic- and molecular-level studies of the structure (atomic and electronic), bonding, reactivity, dynamics, restructuring, and magnetism at the surfaces and interfaces of metals, oxides, semiconductors, polymers, biological molecules, and liquids. Such studies are becoming steadily more important in view of the increasing emphasis on nanometer-scale structures in almost every technological application, from heterogeneous catalysis to microcircuit fabrication to magnetic data storage. As the scale of devices continues to be reduced, the distinction between bulk and surface properties becomes blurred, and all of the properties of materials tend to become interfacial. *In fact, it is difficult to find any modern materials technology that does not involve reduced-dimension structures and thus also a crucial importance of surfaces, interfaces, and/or thin films.* In all of these applications, we thus desire to understand and control the fabrication of materials at the nanoscale, including small particles, thin films, multilayer structures, and microporous systems. Some of the structures that are important in contemporary surface and interface science are shown in Figure 1(a).

Beyond these technological drivers, however, is a rich range of novel and fundamental physical and chemical properties at surfaces and interfaces and in various types of nanoscale structures whose study represents the intellectual frontier. These include new electronic, magnetic, and bonding properties; structural, electronic, or magnetic phase transitions, as well as chemical reactivity, that are markedly different from those in the bulk material; and other properties that result from the confinement of quantum-mechanical states in such short length scales. For example, it has recently been found that the surface of water has an atomic structure quite different from the bulk, a finding with important implications for a range of phenomena. As an illustration of an even more complex water structure, Figure 2 shows atomic force microscope (AFM) images of ice islands of about 1- $\mu\text{m}$  diameter but only 15- $\text{\AA}$  thickness for which the internal atomic and electronic structure may be quite different from that of liquid water. Surface reaction kinetics can also exhibit oscillatory and soliton-like behavior. Surfaces also can exhibit different melting points and magnetic transition temperatures, as well as unique surface states and two-dimensional charge-density waves. Quantum confinement of electrons in nanostructures has led to the quantum Hall effect and, in metal multilayers, to the giant-magnetoresistance (GMR) effect that has recently passed from basic surface-physics research to technological application in read heads. The study of surfaces has thus created a fundamental paradigm shift in our understanding of condensed matter from an approach that focused on ordered solids with long-range order to a picture with broken translation symmetry that required a host of new experimental and theoretical techniques to deal with aperiodic materials and structures. Such aperiodic structures often have only local atomic order rather than long-range order, and their study will become even more important in the future.

From this discussion, it is also clear that surface and interface studies overlap with the interests of most of the other working groups at this workshop. In addition, the emphasis on atomic- and molecular-level understanding strongly links surface/interface science to atomic, molecular, and optical physics. This synergism will be evident in repeated themes over several sections of this report.

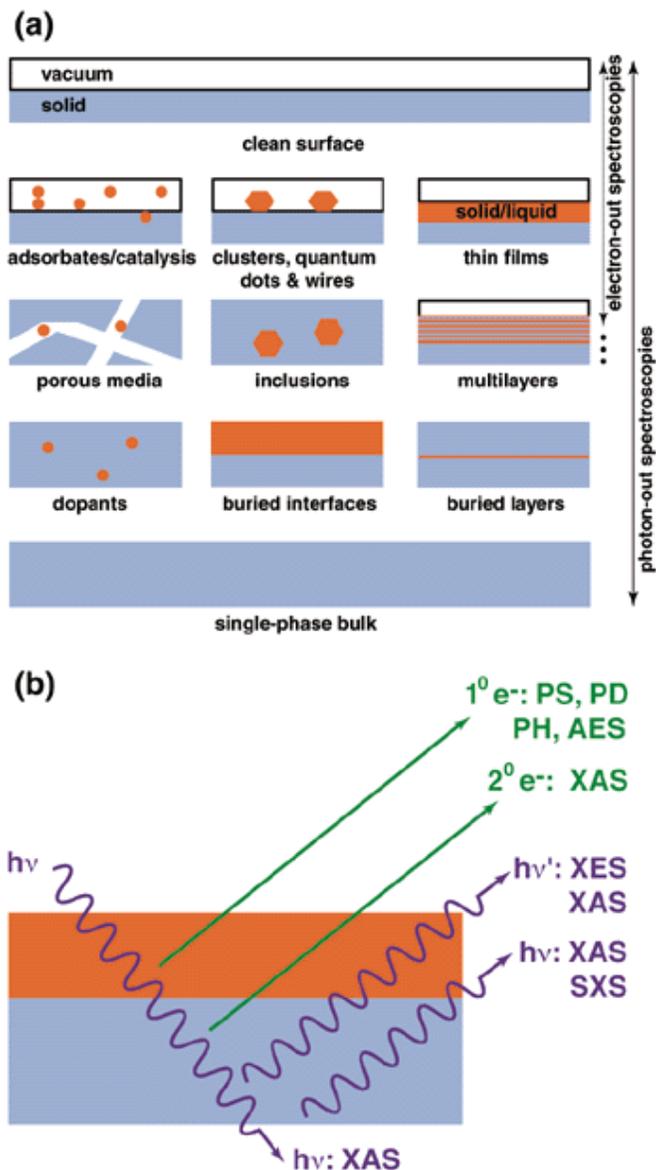


Figure 1. (a) Various surface and interface morphologies of current interest, with the approximate ranges of vertical sensitivity using electron detection or photon detection indicated. (b) Schematic illustration of some of the most important VUV/soft x-ray techniques and their approximate ranges of vertical sensitivity. Here, the detected species are primary electrons (photo- and Auger electrons =  $1^\circ e^-$ ), secondary electrons (inelastic secondaries =  $2^\circ e^-$ ), primary scattered, reflected, or transmitted x-rays at  $h\nu$ , or secondary fluorescent x-rays at  $h\nu' < h\nu$ . The resulting techniques are photoemission (PS), photoelectron diffraction (PD), photoelectron holography (PH), Auger electron spectroscopy (AES), x-ray absorption spectroscopy (XAS) which includes near-edge absorption fine structure (NEXAFS, also known as XANES) and extended x-ray absorption fine structure (EXAFS, XAFS), x-ray emission spectroscopy (XES), and surfacel/interface x-ray scattering (SXS), including reflection and transmission experiments.

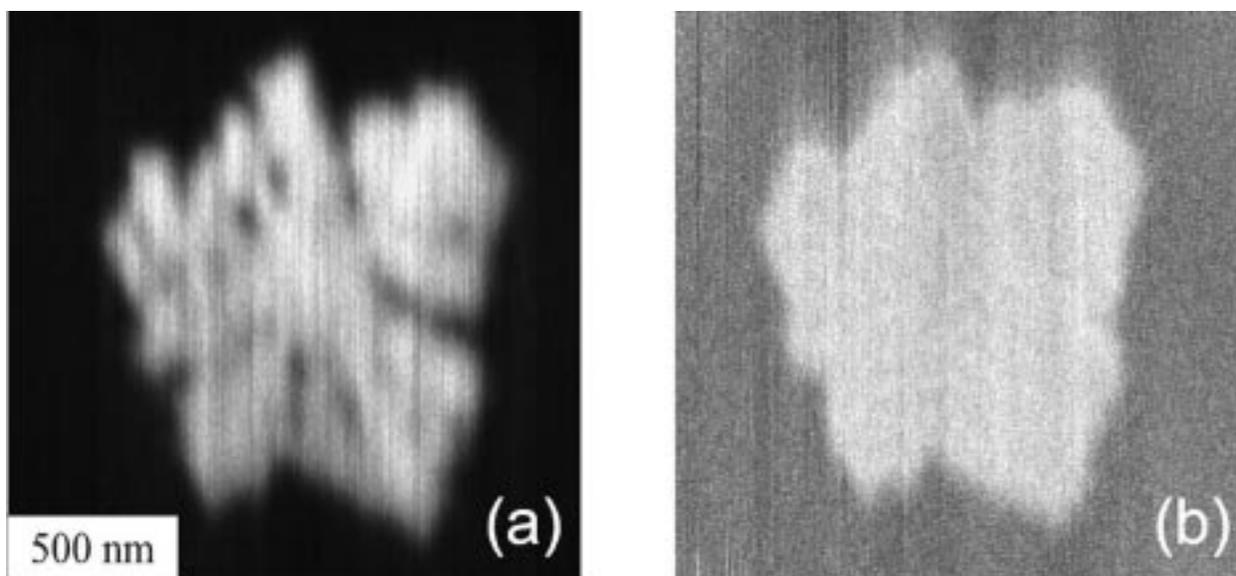


Figure 2. Images of ice crystals obtained with scanning atomic force microscopy. The ice crystals have approximately  $1000\text{ nm} = 1\text{ }\mu\text{m}$  diameter and  $1.5\text{ nm} = 15\text{ }\text{Å}$  thickness (about two lattice constants) as grown on a cooled mica (0001) single-crystal substrate. The temperature is  $-25^\circ\text{C}$ , and the water vapor pressure is  $0.43\text{ torr}$ . The left panel (a) shows a contact force image, and the right (b) a lateral force image. [Figure taken from H. Bluhm, S. H. Pan, L. Xu, T. Inoue, D. F. Ogletree, and M. Salmeron, *Rev. Sci. Instrum.* **69** (1998) 1781.]

Much has been learned about the fundamental physics and chemistry of surfaces (especially concerning the gas-solid interaction) over the past 30 years or so, but many questions remain unanswered and more complex systems need to be studied. Some of the key frontiers in surface and interface science are:

- Gas-solid interactions at higher pressures; liquid-solid and solid-solid interfaces.
- Systems less investigated to date; for example, oxides, minerals, polymers, and biopolymer interfaces.
- Understanding and controlling thin-film and nanostructure growth and self-assembly at the atomic level.
- Selective growth of nanoscale and atomic-scale structures via improved methods of molecular-beam epitaxy (MBE), vapor deposition, lithography, photo-induced surface chemistry, self-assembly, probe-tip manipulation, and other methods.
- Dynamic processes at a range of times from seconds (atomic diffusion, macroscopic-reaction kinetics) down to  $10^{-18}\text{ sec}$  (electronic transitions).
- Novel electronic and magnetic structures, including quantum-well states, charge-density waves, and spin and magnetism at surfaces, interfaces, and in nanostructures.
- Use of novel properties and nanostructure configurations for various technological applications.
- Continued development of new experimental techniques for carrying out the above, with special emphasis on studying interfaces in complex environments (even as they undergo chemical reaction or overlayer growth) and on achieving shorter time scales and better lateral, vertical, and atomic-scale resolutions of structures.
- Parallel theoretical advances to understand and make use of all of the above.

Although synchrotron radiation certainly cannot contribute to all of these frontier areas, we will point out in the following which aspects can be significantly advanced via a third-generation source such as the Advanced Light Source (ALS) whose primary unique feature is high brightness in the vacuum ultraviolet (VUV)/soft x-ray regime from approximately 20 eV to a few keV.

Historically, surface science has focused on the solid-vacuum interface, and it has over the past few decades produced a wealth of information, in particular on metal and semiconductor surfaces and various interactions occurring on them. A wide variety of experimental and theoretical techniques have been developed, and their successes have spawned research in other fields and led to characterization tools that are ubiquitous in industry. These techniques include low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), electron-energy-loss spectroscopy (EELS), and various kinds of ion-scattering and secondary-ion measurements, such as ion-scattering spectroscopy (ISS), Rutherford back scattering (RBS), secondary-ion mass spectroscopy (SIMS), etc. Synchrotron-radiation-based methods include photoemission spectroscopy (PS), photoelectron diffraction (PD), photoelectron holography (PH), x-ray absorption spectroscopy (XAS) in either the near-edge x-ray absorption fine structure (NEXAFS, also known as XANES) mode or the extended x-ray absorption fine structure (EXAFS or XAFS) mode, x-ray emission or fluorescence spectroscopy (XES or XFS), and surface x-ray scattering (SXS), including reflectivity measurements from surfaces, buried interfaces, and multilayers. The synchrotron-radiation-based techniques are illustrated in Figure 1(b). Significant recent entries to the scene are the scanning-probe microscopies and atomic-manipulation methods, such as scanning tunneling microscopy (STM), AFM, etc. Pumping and probing surfaces with laser pulses on the femtosecond time scale and/or making use of non-linear optical phenomena at surfaces, such as sum-frequency generation (SFG) or second-harmonic generation (SHG), are also now being carried out in several laboratories. Both the need for atomic-level control of surfaces and the electron- and ion-based techniques used to study them have led to the necessity of working in whole or in part in an ultrahigh-vacuum (UHV) environment in most studies to date. One of the challenges for the next generation is to expand research in the direction of molecular studies at interfaces involving solids and high-pressure gases, solids and liquids, and solids and solids. Such work will involve both new experimental techniques (e.g., photon-in/photon-out experiments to complement photon-in/electron-out) and special sample-handling facilities (e.g., differentially-pumped cells). However, it is also clear that we will continue to need to study well-defined and in some sense model systems (even if they are more complex than the often low-index single-crystal surfaces in prior work) that are initially prepared in UHV in order to develop a microscopic understanding of the new interface processes and structures involved.

The ALS has already been utilized with considerable success in surface studies from UHV to low pressures ( $\leq 10^{-5}$  torr) in studies of atomic and electronic surface structure using mostly photon-in/electron-out techniques (e.g., photoelectron spectroscopy, diffraction, holography and spectro-microscopy). Photon-in/photon-out studies of the x-ray emission or fluorescence spectroscopy type have also been significantly advanced there. The facilities that have been constructed already for these studies form an excellent basis for next-generation work in surface and interface science, but we discuss below several new directions as part of our future roadmap.

Solid surfaces are known to restructure in the presence of adsorbates or overlayers, and this restructuring is known to depend on the adsorbate or overlayer, its coverage or thickness, and for gases also the ambient pressure (or more correctly the chemical potential). Therefore, *in-situ* studies at conditions approaching various “real world” environments are needed to determine interface properties (structure, composition, reactivity, oxidation state, magnetism, etc.). Photon-in/electron-out tech-

niques will continue to be essential components of such studies and should be extended so as to reach both higher pressures and buried interfaces to the maximum degree possible. However, photon-in/photon-out techniques present advantages of greater penetration depths in all phases and should be exploited across the electromagnetic spectrum available from the ALS—from x rays to infrared. Studies on buried liquid-solid or solid-solid interfaces will in particular benefit several applications of surface and interface science, including heterogeneous metal and acid catalysis (using microporous systems), electrochemistry (fuel-cell electrode reactions), biopolymer surface chemistry (biocompatibility), environmental chemistry (earth science, tropospheric chemistry of acidified water droplets), microelectronic-circuit fabrication (semiconductor/conductor/polymer interfaces), magnetism (magnetic storage), and tribology (friction, lubrication, and wear).

Oxide and other compound surfaces and interfaces play an especially important role in technology and environmental science, and their study should be emphasized. The interfaces between aqueous solution and oxides and minerals are of particular importance in the environmental context. Metal oxides are also ubiquitous among the complex materials [e.g., oxides with high critical temperatures ( $T_c$ ) and colossal magnetoresistance] and so understanding their surface and interface properties is important to any of their potential applications.

The complexity of the next generation of surfaces and interfaces will involve heterogeneity in all three dimensions (e.g., vertically in multilayer structures, and vertically and laterally in magnetic wires and quantum dots or more complex environmentally relevant minerals). This heterogeneity requires the development of new techniques that can resolve features in all these dimensions, such as laterally resolving laboratory-based low-energy electron microscopy (LEEM) and the synchrotron-radiation-based spectromicroscopies or microspectroscopies that are a key element of the ALS scientific program. Making use of the internal reflection of x-rays at buried interfaces provides a further handle on the vertical dimension that is just beginning to be explored in the soft x-ray regime. Furthermore, the dynamics of most surface properties should be studied on ever-shorter time scales. Continuously improving spatial and time definition in various experimental techniques should thus be a constant thrust of the ALS program in the surface-science domain.

This complexity of surfaces (e.g., oxidation or vapor deposition on semiconductors, catalysis, corrosion, lubrication, and biocompatibility) also requires the use of a combination of techniques in addition to those that might be available at the ALS. Whenever possible, these ancillary techniques should be available *in situ*, with additional tools, such as electron microscopy at the National Center for Electron Microscopy (NCEM) or STM and AFM, also available to users of the ALS at nearby locations. Sample preparation is also often complex and in a UHV environment, and so independent preparation chambers, convenient loadlocks for quick insertion, and vacuum suitcases should also be provided.

New experimental capabilities always challenge theory for their interpretation and use, and conversely, theoretical developments challenge experiment and generally enable more quantitative investigations and conclusions. Thus, theories of surface and interface phenomena, ranging from the quantitative description of the emission of electrons and x rays to charge distributions and atomic structures at the gas-solid and solid-liquid interface to molecular motion of bilayers under pressure at the solid/solid interface, should be an integral part of all surface studies at the ALS. Moreover, it is desirable to develop efficient and physically intuitive theoretical tools to aid in experimental analysis.

We thus recommend a balanced portfolio of studies that takes advantage of the unique capabilities of the ALS, particularly in the VUV/soft x-ray regime, and that emphasizes both the fundamental

physics and chemistry of surface and interface behavior on the molecular scale and investigations of more complex surface systems that are or could be utilized in surface technologies (e.g., catalysis, semiconductors, magnetic storage) or that could impact the environment (air, water, and soil purity). Pursuing such a portfolio would make the ALS the leading synchrotron-radiation center in this field and would build on strengths that it is already developing.

## 2. Scientific Frontiers and Challenges

In the following sections, we elaborate on the above points and highlight several areas that are important for future emphasis. Each section is organized roughly with scientific frontiers and challenges first, contributions the ALS may already be making or anticipating in this area second, and recommendations for new tools or actions in order to optimally address the challenges at the end. We also note that other sections of this report (e.g., Working Groups on Magnetism and Magnetic Materials, Complex Materials, Nanostructures and Special Opportunities in Semiconductors, and Environmental and Earth Sciences) will deal with other aspects of surface and interface science that our roadmap will benefit both directly and indirectly.

### 2.1 Surface Reactions and High-Pressure Studies/Catalysis

Solid catalysts accelerate chemical reactions on their surfaces. The surfaces of industrial catalysts are almost all structurally and compositionally complex. A great deal of understanding has emerged from the investigation of simple systems (e.g., single crystals) under simple, usually UHV, conditions. Beyond this, the ALS offers excellent opportunities and challenges for extending the understanding of catalyst surfaces. We envision fundamental investigations that are simultaneously of practical value for materials ranging in complexity from single crystals to multicomponent nanostructured materials, such as clusters and particles of metals, metal oxides, and metal sulfides on the surfaces of microporous and mesoporous supports (including zeolites and metal oxides).

Much is now known about the structures of simple surfaces in a UHV environment, but these structures can change significantly in the presence of surrounding atmospheres. It is thus important to understand the surfaces of these materials in the presence of reacting gases. We envision experiments characterizing these surfaces in the presence of components ranging from simple adsorbates to multicomponent mixtures, even while they undergo chemical reactions; that is, we wish to study real catalyst surfaces under practical reaction conditions. Realistic near-term goals are to apply the available experimental methods to complex catalysts at pressures up to a few torr and then up to 20 torr to 25 torr in the longer term. We would eventually like to apply the electron-out techniques at pressures up to 1 atm.

Furthermore, these experiments can be done under transient conditions, even with flowing reactants in contact with the sample. The time scales in prospect should range from femtoseconds to days (or longer, with the samples being on line but away from the beam for extended periods). It is important to correlate the reactivity of surfaces and different species with a molecular-scale understanding of bonding to understand the relationships between adsorption site, electronic structure, and bond strength. This holds both for the static adsorbates on surfaces and for intermediates generated under reaction conditions.

For the more complex materials, it is essential to obtain length-scale information, for instance, to establish the different species adsorbed on support materials, metal particles, and the interfaces between them. The length scales of interest should range from 5 Å to 1 μm.

It is also important to synthesize and characterize catalytic sites (such as titanium cations in a zeolite framework) and to analyze them structurally in terms of geometric and chemical state, the manner in which bonding to the reactants occurs, and the way in which these properties change depending on the adsorbate.

A further crucial aspect is the understanding of catalyst supports, such as microporous or mesoporous materials, and their interaction with catalytic sites. Examples include: (1) zeolite supports with metal clusters or complexes in the pores or (2) single crystals of metals coated with ultra-thin layers of oxide and then with size-selected metal or metal-oxide clusters dispersed on the surfaces.

Studies over a wide range of pressures with improved spectroscopic and spatial resolution promise to provide unprecedented information regarding catalytic materials and catalytic processes. Special emphasis should be placed on providing a user-friendly environment for beamline experiments and materials preparation.

The ALS has the following unique characteristics for such studies:

- The high brightness and intensity available will play an important role in improving the time resolution of kinetic experiments so important for characterizing the reaction mechanisms of a broad range of surface reactions. Time scales for monolayer experiments on the submicrosecond time scale will advance our ability to assess the stability of reaction mechanisms in complex reaction systems.
- The high energy resolution available enables detailed determination of oxidation states and chemical structures for low concentrations of species and for the isolated surface species. Because of the high brightness and high energy resolution possible at the ALS, microscopic examinations of catalytic materials can be done at unprecedented spatial resolutions that will approach 100 Å. This advance in accessible resolution will play an important role in complex optimized catalysts with multiple components and promoter packages. Proximity to the National Center for Electron Microscopy will facilitate concerted multi-technique approaches to characterizing these complex materials.
- The soft x-ray probes at the ALS provide element-specific spectroscopy and microscopy capabilities. The multiple methods available for characterizing complex materials under reaction conditions will greatly facilitate the understanding of the relationships between geometric structure, electronic structure, chemical reactivity, and catalytic activity.

The special tools needed in order to realize such a program are as follows:

- A specialized end station on an undulator beamline is needed to enable the study of materials ranging from single crystals to high-surface-area supported catalysts at a wide range of pressures. This should be a multi-technique system with a pressure range from UHV to 1 atm. The key soft x-ray techniques will be XES and XAS (carried out in photon-in/photon-out mode) and XPS and XPD (photon-in/electron-out). XPS with a wide pressure range will require a differentially pumped gas cell and special electron optics to isolate the sample region from the spectrometer so as to reach pressures in the multi-torr range. The soft x-ray measurements will require two types of instruments: (1) a high-resolution grazing-incidence spectrometer for measuring the soft x-ray emission spectra (XES) with high resolution so as to study chemical bonding and (2) a high-sensitivity, large-solid-angle, wavelength-selective detector for soft x-ray absorption spectroscopy (NEXAFS). This detector will be optimized for carbon, nitrogen and oxygen K- $\alpha$  fluorescence. It is also anticipated that interchangeable gratings will be needed in the monochromator on this undulator beamline to allow optimization for either high resolution (XPS, XES) or high flux (NEXAFS).

- A second need is a beamline optimized for x-ray absorption spectroscopy in the 1-keV to 4-keV energy range, using both secondary-electron and fluorescence yields. Key requirements are: (1) an improved monochromator in this energy range allowing for high flux and moderate resolution or lower flux and high resolution and (2) a simple materials end station to allow the study of complex materials at high pressures (up to 1 atm), including facilities for rapid sample transfer.
- A third need is general facility support for the efficient study of catalytic materials. This includes: dry box and load-lock sample transfer, calcination/pretreatment capabilities, the ability to handle toxic gases safely, and on-line product analysis using, for example, gas chromatography or mass spectrometry.

## 2.2 Solid-Solid Buried Interfaces

Solid-solid buried interfaces represent systems that are ubiquitous in technological applications, including for example the ever-thinner oxide gate layers in semiconductor devices, the metal-metal interfaces in magnetoresistive elements, and the metal-semiconductor interfaces in Schottky barriers. Many other multilayer devices or structures consist of such buried interfaces. Understanding the structure and properties of such interfaces is thus a key challenge for the future. Some questions that need addressing are: What is the atomic structure at the interface? How are species intermixed or perhaps segregated at the interface? What are the electronic and magnetic structures?

Experiments at the ALS based on soft x rays should assist in answering these questions via several sorts of measurements. High-resolution XPS and XPD will, via chemical shifts in core levels and spin resolution, provide information on the oxidation state, magnetic state, and atomic structure for shallow interfaces at a depth of perhaps 10 Å to 100 Å. X-ray diffuse reflectivity or x-ray fluorescence in a total-reflection geometry accentuated by tuning to a core absorption edge, should permit selectively studying the compositional and magnetic roughness or the electronic structure, respectively, as recently demonstrated for the first time. An example of this kind of experiment using diffuse reflectivity from a metal-metal Cu/CoFe interface is shown in Figure 3. The photon energy was tuned to the  $L_3 = 2p_{3/2}$  edge of cobalt, thus permitting the study of the compositional (or chemical) roughness of the first Cu/CoFe interface. Using circular polarization and taking difference signals also permitted simultaneously studying the magnetic roughness of the same interface.

There are related problems in tribology, in which we would like to study the molecular-scale structure of 100-Å lubricant films (monolayer to multilayers) when confined between solid surfaces. The surfaces exert pressure and shear forces (up to micronewtons). Can intermediate-energy x-ray photons that will penetrate solid walls (10 μm to 100 μm thick) be used to probe molecules of 10-Å to 100-Å thickness sandwiched between? Can photon-in/photon-out fluorescence spectroscopy be utilized, perhaps with angular resolution, to study the molecular orientations in the lubricant film? Is it possible to use diffuse scattering in total reflection for such structural studies? It appears the ALS can contribute to answering these questions.

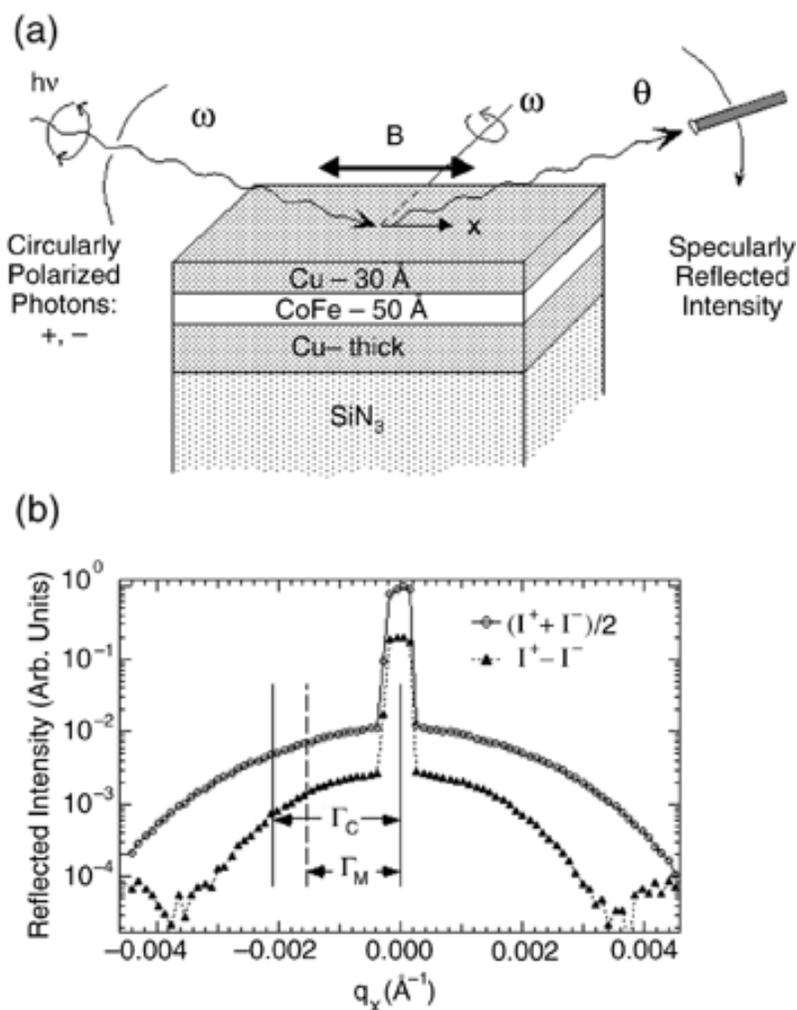


Figure 3. Specular and diffuse soft x-ray reflectivity measurements from a metal-metal interface. Reflected intensities for right and left circularly polarized radiation ( $I^+$  and  $I^-$ , respectively) have been measured from the top Cu/Co<sub>95</sub>Fe<sub>5</sub> interface in a trilayer, with interface sensitivity achieved by working near the  $L_3 = 2p_{3/2}$  absorption edge of cobalt at 778 eV. The interface is schematically shown in (a), and the reflected intensities as a function of scattering wave vector  $q_x$  in the plane of the surface are shown in (b). The chemical roughness, as measured by  $(I^+ + I^-)/2$  and the diffuse width  $\Gamma_C$ , is significantly less than the magnetic roughness, as measured by  $(I^+ - I^-)$  and the width  $\Gamma_M$ . [Figure from Freeland, Chakarian, Bussman, Idzerda, Wende, and Kao, J. Appl. Phys., in press.]

### 2.3 Gas-Liquid and Liquid-Solid Interfaces, Liquid Films

Gas-liquid or liquid-solid interfaces are at least as important as, if not more important than, gas-solid or solid-solid interfaces in modern life. Water-solid interfaces, in particular, play a key role in many disciplines, ranging from physics and chemistry to biology and environmental science. Yet the field has hardly been explored because of the lack of suitable experimental techniques. Electrochemistry, for example, has been a recognized field for more than 100 years, but little is yet known about the structure and dynamics of any electrochemical interface.

For many applications in science and technology, it is important to know the structure of the first monolayer at the interface. The much-discussed electrochemical double-layer is a case in point. In

many instances, the surface-liquid structure is much more ordered than the bulk. It is then also important to know how the surface-induced ordering decays away in transition to the bulk. Although the importance of liquid interfacial structures has been well recognized, few experimental probes are available for their study. Recently, vibrational spectroscopy by sum-frequency generation (SFG) has been successfully employed to obtain structural information about some liquids, but so far it has not been possible to determine the structural depth profile of a liquid at an interface.

Several soft x-ray and intermediate x-ray synchrotron radiation techniques may be applicable to studies of liquid interfaces. X-ray reflection, fluorescence, and diffraction in a total reflection geometry could possibly be used to obtain structural and compositional depth profiles at gas-liquid interfaces. The same techniques with some novel modifications, such as tuning onto specific core-level atomic resonances (see Figure 3), including newly discovered interatomic enhancements of absorption (see Figure 10), could also be applied to studies of liquid-liquid and liquid-solid interfaces. As it stands, the x-ray techniques are probably the only potentially viable techniques for probing the depth profiles of liquid interfaces. We thus urge that the development of such techniques be explored, with photon-in/photon-out techniques permitting the study of deeper interfaces at 100 Å to microns below the surface and photon-in/electron-out being limited to 10 Å to 100 Å, depending on the photon and electron energies utilized (see the more quantitative estimates in Section 3.1.3).

The structure and composition of thin liquid films is an important case to consider. Films of liquids form on solids by condensation from the vapor phase in undersaturation conditions. The thickness of these films can be on the order of nanometers to tenths of micrometers. This is the length scale at which surface forces from the solid support (van der Waals, structural, hydrophobic, double layer, etc.) are important. They modify the film capillary properties, such as contact angle, wetting properties, and spreading properties. They are also influential in surface wetting phenomena. One challenge for the ALS in this area is to be able to probe liquid surface composition with photon-in spectroscopies (XPS, XES, NEXAFS) over extended surfaces and with lateral microscopic resolution (from 1 μm to 100 Å if possible).

Operation at pressures of 1 torr to 25 torr is required in order to maintain the liquid at or near equilibrium with its surrounding; thus windowed cells and/or differential pumping will be needed. A particular reference point is the vapor pressure of water at 25°C, which is 23.8 torr; being able to work at or near this pressure would open up a tremendous range of possibilities. Another challenge is to achieve depth sensitivity to composition below the liquid-gas interface. A possible technique here is the use of photoelectrons of different mean free paths and/or variable angles of emergence.

## 2.4 Electrochemistry

Electrochemistry constitutes a very important special case of the liquid-solid (or gas-solid) interaction with broad applications. Outstanding scientific issues at the electrochemical interface include: (1) the distance of ions from the electrode surface when electron transfer occurs for either the inner-sphere or outer-sphere cases, (2) the structure of water in the double layer, and (3) a method for studying adsorption at electrode surfaces in disordered or weakly ordered systems.

The three *in-situ* spectroscopies currently being used to address these issues are infrared reflection-absorption spectroscopy (IRRAS), surface x-ray scattering (SXS), and x-ray absorption spectroscopy (both NEXAFS and EXAFS), in which the use of photon-in/photon-out measurements permits looking through the liquid film.

However, structure on the electrolyte side of the interface has proven to be difficult to obtain by using any of these methods. SXS is proving to be very powerful for determining the structure on the metal side of the interface in highly ordered systems such as halide ions adsorbed on low-index crystal faces of the noble metals platinum and gold. Even the adsorption of more complicated polyatomic ions and neutral molecules has been successfully studied with SXS. Poorly ordered or disordered systems have been studied with some success by using NEXAFS and EXAFS, although the structural information is generally less satisfying. Adsorption of organic molecules or ions is an extremely important phenomenon in electrochemistry, which one would like to study on a variety of electrode surfaces that may lack long-range order and/or form disordered structures. IRRAS has been successfully used to study many of these systems, but a complementary method is greatly needed.

The ALS soft x-ray beamlines provide a unique opportunity to apply NEXAFS at carbon and oxygen edges to the study of an important class of electrochemical adsorption—organic molecules or ions on a variety of electrode materials. X-ray fluorescence measurements in total reflection could also be an important adjunct measurement.

## **2.5 Metal-Oxide Surfaces and Interfaces**

Metal oxides are now playing a major role in many areas of physics, chemistry, and materials science. In particular, they are prominent in catalysis, strongly correlated materials, environmental and earth sciences, and magnetic materials. However, the surfaces and interfaces of oxides have been much less studied, owing to their difficulty of preparation and the fact that many are insulators, making them more difficult to study with the usual charged-particle probes of surface science. However, synthesis methods have advanced enormously in recent years, and even the neutralization of surface charge during measurement is presently being improved greatly. We divide this discussion into three sections: clean surfaces, molecular adsorption, and solid overlayers on oxides.

### **2.5.1 Clean Oxide Surfaces**

The oxide-vacuum interface has been the subject of increasing experimental interest over the past two decades. However, a great many fundamental surface properties are still not well understood. Photoemission spectroscopy has yielded a great deal of information on the electronic structure of metal oxides, but it has been very difficult to separate the surface and bulk components in those spectra. Higher resolution photoemission and other measurements are needed to determine the role that coordinative unsaturation at the surface plays in electronic structure. Synchrotron techniques can also be very useful in determining the geometric structure of metal-oxide surfaces as well, for example, via photoelectron diffraction and holography. These methods have particular advantages in being element and chemical-state specific, relatively insensitive to surface charge buildup on insulating or partially conducting surfaces (as compared, for example, to LEED), and of being applicable to structures with only short-range atomic order (again as compared to LEED, which as usually employed requires long-range order).

The structures of clean surfaces of well-defined oxides strongly influence their respective reactivities toward small molecules such as water. Key structural questions center on the issues of surface autocompensation and vertical and lateral relaxation. The principle of surface autocompensation states that the energetically most-favored surface is one for which dangling bonds derived from anions (cations) are completely full (empty). But the distribution of charge in surface dangling bonds may be influenced by surface relaxations through rehybridization.

Low-energy photoelectron diffraction in both scanned-angle and scanned-energy modes is a very useful probe of surface structure for oxides. The ALS is the ideal third-generation synchrotron facility in the United States at which to conduct such studies. The high brightness in the VUV and soft x-ray regimes afforded by the ALS makes it possible to conduct experiments with simultaneous high energy resolution (to resolve surface species for example) and high angular resolution (to extract maximum information content). It is also desirable to conduct such experiments with maximum surface sensitivity, which means utilizing electron kinetic energies at about 50 eV to 100 eV, the minimum of the typical inelastic electron-attenuation length. In order to fully open up such avenues into oxide surface structure, there is a need for an effective charge-neutralization scheme for low-energy photoelectrons (a recent advance in technology makes this now feasible), an insertion-device beamline for maximum brightness and thus higher data-acquisition rates, a state-of-the-art high-throughput electron spectrometer, and an accurate specimen goniometer. (For example, Beamlines 7.0.1 and 9.3.2 at the ALS currently possess some, but not all, of these characteristics.)

Many transition-metal oxides have interesting magnetic properties, including metal ions of different spin and magnetic states in the same compound. For example, in those colossal-magnetoresistive oxides with a typical composition of  $\text{La}_x(\text{Ca}, \text{Sr})_{1-x}\text{MnO}_3$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions coexist. Very little is known about the way in which the magnetic order at the surface differs from that of the bulk or what sort of order exists at interfaces between magnetic oxides and other materials. Yet there are proposals for making devices that consist of alternating layers of conducting magnetic and insulating non-magnetic oxides for which surface and interface properties will be crucial elements. Spin-polarized and magnetic-dichroic photoemission and x-ray absorption spectroscopies utilizing circularly polarized radiation can best answer some of these questions.

Several transition-metal oxides (e.g.,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_3$ ) also exhibit metal-insulator transitions. Nothing is known about the possible effect of the surface on the transitions. Since these transitions are potentially useful for sensor applications, it is important to understand how they are manifested at the surface. The above-mentioned spectroscopic and structural probes can also be fruitfully applied to these systems.

Very small metal-oxide particles and structures will play a role in the future of nanostructured materials, as for example, novel ceramics. Very little is known about the geometric or electronic structure of nanometer-size oxides, although there are indications that these materials may have some interesting size-dependent properties. Again, the tools mentioned above should provide very useful information on these problems.

The thermal stability of metal-oxide surfaces is another area in which only a few oxides have been investigated and about which much more information is needed. Fruitful studies of this type should be possible at the ALS.

### 2.5.2 Molecular Adsorption on Oxides

The amount of literature on the catalytic properties of metal oxides is voluminous, and yet the state of our understanding of the position and orientation of adsorbates on oxide surfaces is rudimentary. Experiment is far behind theory in being able to study the adsorption and interaction of molecules with oxide surfaces. Experiments such as photoelectron diffraction on well-characterized oxide surfaces are needed in order to determine adsorbate geometry, initially for the simple systems that theory can calculate and subsequently for the more complex cases.

Surface reactivities of oxides with small molecules, such as water, and the resulting interface structures, determine the outcome of a number of important heterogeneous chemical processes. Examples

include photo- and thermal-catalytic reactions and the sorption of metal ions in aqueous media. The first step in any of these processes is the interaction of the solvent with the surface. For example, water interaction with mineral surfaces, resulting in a hydroxide layer of varying extent, determines in large measure subsequent reactivity with oxy-anions of heavy metals. Thus, detailed knowledge of the surface interaction between the solvent (e.g., water) and the oxide is requisite to understanding the sorption and chemical transformation of more complex species.

The ALS is ideally suited for such investigations for the same reasons as those listed above for clean-surface studies. High brightness in the VUV/soft x-ray range allows photoelectron spectroscopy and diffraction to be carried out with unprecedented energy and angular resolution, particularly near the carbon and oxygen K edges. Possible experiments include real-time kinetic determinations of water sorption and surface hydroxylation, with pioneering adsorption studies of this type already having been performed at ELETTRA (Sincrotrone Trieste in Italy) and the ALS (see Figure 8). However, a UHV-compatible, “high-pressure” water doser is needed to make such experiments truly possible. There are two possible approaches to achieving such pressures: (1) sample retraction and dosing in a high-pressure cell and (2) the use of an *in-situ* water-dosing cell located in the spectrometer chamber and from which photoelectrons can be extracted during dosing. The advantages of the latter are that smaller and more precise doses can be applied, and spectroscopy and diffraction can be performed in real time. Thus, the evolution of, for instance, surface hydroxylation could be traced and related to the clean surface structure, which provides the template on which heterogeneous chemistry occurs. Furthermore, studies of this type can generate mechanistic information that will be valuable in understanding the more complex aqueous-oxide interface, as discussed in more detail in the report of the Working Group on Environmental and Earth Sciences.

Techniques for exploring the diffusion and reaction of atoms and molecules on oxide surfaces are also lacking. With the very high brightness of the ALS beam and the high spatial resolution it provides via various spectromicroscopy approaches, appropriate experimental techniques could be developed, and we recommend this as an area for future study.

### 2.5.3 Solid Overlayers on Oxides

One of the most active current research areas involving metal oxides consists of metal or other oxide overlayers on oxide surfaces. The resulting interfaces are important in a wide range of technological applications, in addition to being of great scientific interest. The interfacial properties can be extremely complicated, and at present we have only a rudimentary understanding of them. In the case of metal overlayers, interdiffusion can lead to the formation of new interfacial compounds.

The intense radiation at the ALS may permit measurements of both interfacial geometric and electronic structure by accessing the interface beneath several nanometers of overlayer. X-ray absorption and emission spectroscopies, perhaps making use of total internal reflection at the interface, have the capability to determine the electronic structure of both the filled and empty electronic states at the interface. Virtually no research in this area has been performed to date, despite its immense technological importance.

Another active area of oxide research is the growth of thin metal-oxide films on other oxides or conducting substrates. Such thin films may permit measurements such as photoelectron spectroscopy to be performed on oxides that would be too insulating in their bulk form. Comparison of the geometric and electronic structure of these thin films with those of the bulk oxides is therefore an important endeavor.

Of equal importance are determinations of the thermal stability of metal-oxide and oxide-oxide interfaces, interdiffusion across the interface, and interfacial segregation. Here also the possibility of interrogating buried interfaces with the intense radiation at the ALS during thermal cycling make such experiments natural ones for this facility.

## 2.6 Semiconductor Surfaces and Interfaces

The future production of electronic devices based on semiconductors will continue to present major scientific and technical challenges. On the one hand, there is the desire to evolve existing technologies to ever smaller dimensions. As a graphic illustration of this evolution, Figure 4 shows cross sections of integrated-circuit elements used in PC microprocessors as a function of size, and thus also time, in technological evolution. On the other hand, new applications, such as sensors, optoelectronics, photonics, and magnetoelectronics, drive the development of novel integrated technologies in which hybrid structures must be fabricated. In addition, when device dimensions shrink to the point that present technologies cannot be scaled further, new scientific input will be needed to develop the next generation of microelectronic devices; single-electron or single-molecule devices are examples here. To reach these goals, we must be able to understand the properties (e.g., electronic and magnetic) and the performance (e.g., transport, thermal stability, adhesion) of advanced materials, as well as of their interfaces to each other and to existing

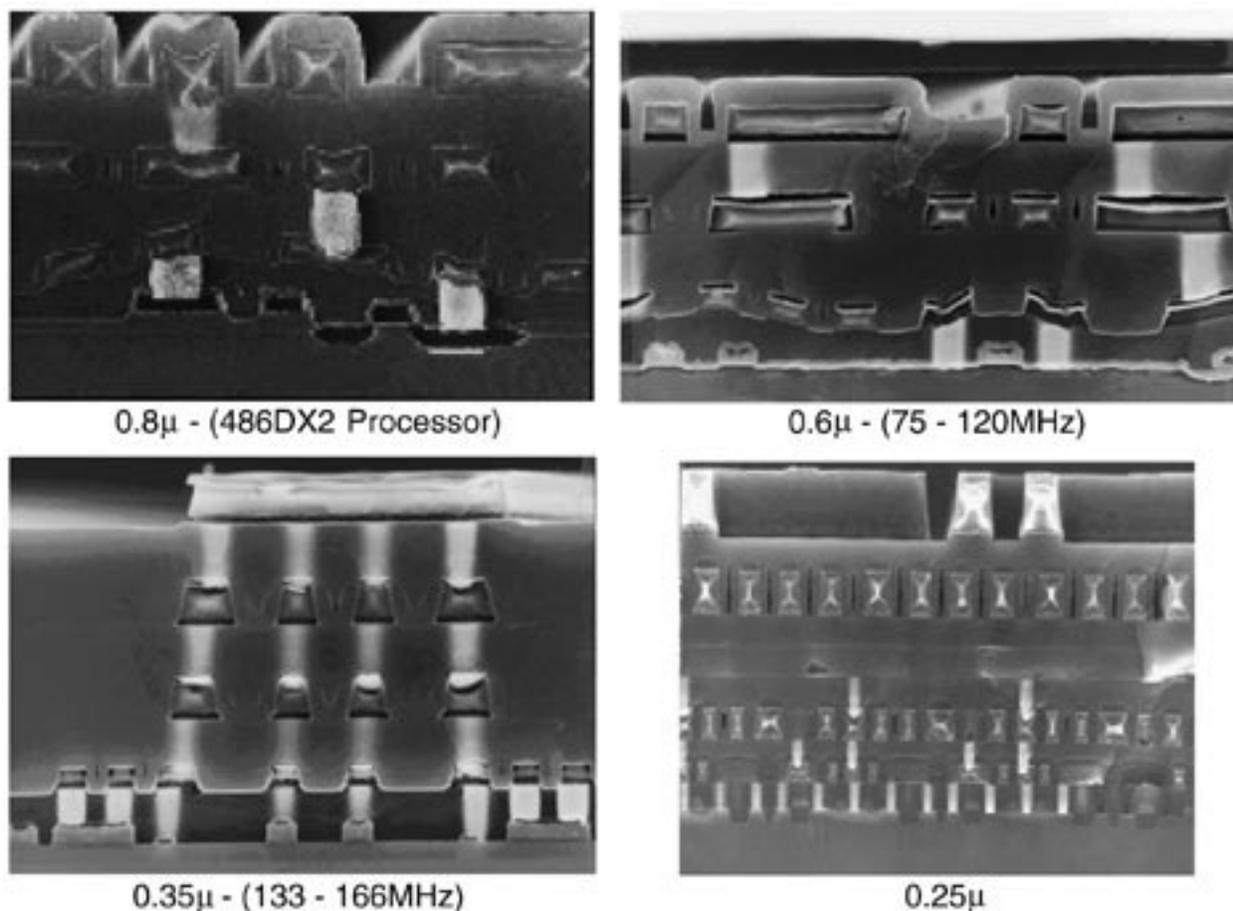


Figure 4. Transmission electron micrographs of cross sections of PC microprocessor integrated circuits representing recent trends in Intel development from 0.8- $\mu\text{m}$  to 0.25- $\mu\text{m}$  feature sizes. [Figure courtesy of B. Triplett, Intel Corporation.]

silicon-based device morphologies. This involves a comprehensive approach that includes both fundamental studies of basic physics and chemistry and applied studies that involve measurements of actual devices or device components under realistic conditions.

Some of the advanced semiconductor materials include SiGe, SiC, GaN, other III-V semiconductors, and II-VI semiconductors. Even more important than the semiconductor core materials themselves are the key associated materials and interfaces that make it possible to (1) miniaturize transistors or devices to sub-micron feature sizes and (2) wire them efficiently into integrated high performance microprocessors or memories. These processors now contain many millions, and soon billions, of individual components. Paramount among these materials are high-k dielectrics with thicknesses below about 15 Å for use as the transistor gate, low-k dielectrics for reduced RC time constants required to electrically connect the individual high-speed components, and copper metallization for reduced electrical resistance and improved stability against electromigration failure. Although the general scientific challenges of analyzing these interfaces have been described elsewhere in this document, it is important to call out in detail the role certain specific materials play in the economically enormously important use of semiconductors. Moreover, the analysis of the surfaces must be done on the scale of the feature size of the devices to be truly representative of the materials science and chemistry that is important. Thus, element-specific microscopy is immediately suggested, as for example, in the recently established micro-XPS facility at the ALS, which is currently at the micron resolution level.

Starting with high-k gate dielectrics, very high quality  $\text{Si}_x\text{N}_y$  and/or silicon oxynitride is being developed to replace  $\text{SiO}_2$  because its higher dielectric constant ( $k=9$  in thick films but decreasing to about 6.5 in thin films) reduces boron diffusion through the gate dielectric and reduces Fowler-Nordheim electrical leakage. However, even this material seems to have a very short useful lifetime, largely because quantum-mechanical inversion effects in the silicon and carrier depletion in the polysilicon gate electrodes add almost 5 Å to 9 Å to the gate-dielectric effective thickness. Therefore, materials with dielectric constants of 20 to 100 that are also stable in very thin film form seem to be required within a very few years to meet the advanced scaling challenges for transistors. This is a non-trivial problem when one considers that, of all the possible binary oxides in the periodic table, only 11 meet the requirement of thermodynamic stability on silicon at 1000 K and fewer still have dielectric constants above 20.

By contrast, low-k dielectrics are urgently needed to reduce the RC parasitic delay of electrical-signal propagation in the interconnect system on advanced microprocessors. Indeed, the metal interconnect system has already failed to meet the challenge of scaling miniaturization, and the industry has currently added six layers of metal to achieve the low-resistance metal interconnections required by today's microprocessors operating at clock speeds of 400 MHz and higher. Unless some other solution is found, even more layers will be required in the near future, at a serious cost in economy. Copper metallization will help slightly, but significant reduction of the interconnect-system capacitance seems to be the best option to provide major benefits. Candidate materials to replace  $\text{SiO}_2$  (with dielectric constant of about 4) in this application are SiOF in the short term (but with only a modest reduction in capacitance) and, in the longer term, polymer materials with much lower dielectric constants extending perhaps down to 2.4. Ultimately, the prospect of structures of cells or foams having some of the structural rigidity of a solid material but with a substantial part of the material consisting of "empty" space may provide the industry an overall  $k = 2.0$  or below. Because of the small size of the mating metal features, the pore size in these "foams" may have to be of order 50 Å to be integrable with the complete process.

With respect to the core semiconductor itself, the material-to-semiconductor interface for all of these materials must also be understood because of its critical use in making the ultrashallow junctions that define the optimal transport of electrons in the transistor. Understanding and achieving ultrathin, epitaxial, high- $k$  dielectric films on semiconductor surfaces are crucial specific steps toward high-density devices. As one measure of this, technologies under development in the next generation cycle will have gate oxides 10 Å thick for which one monolayer corresponds to about one-third of the film. Interfaces to be investigated thus include semiconductor-dielectric/semiconductor, semiconductor-dielectric/metal, metal/semiconductor, metal-silicide/semiconductor, fluorinated-oxide/metal, metal/low- $k$  polymer, metal/porous dielectric, and metal/foam. Major materials issues include: (1) structural evolution during heterointerface formation, including dynamic studies, (2) correlation between electronic properties and defects, (3) correlation between mechanical and adhesive properties, with delamination of layers becoming more problematic with time, (4) surface chemical reactions that are used in device processing, and (5) chemical reactions at interfaces, including those resulting in electronic and structural degradation.

From a fundamental-science approach, we thus seek a detailed understanding of the bulk, surface, and buried-interface chemistry and structure. This includes characterizing surface and interfacial atomic abruptness (flatness, interdiffusion, and roughness) and the physical and chemical processes that operate at these interfaces. To achieve this understanding, we must be able to simultaneously measure both electronic structure and chemical composition of model surfaces and interfaces. But in addition to these studies of simpler model systems, we also need to study materials under realistic conditions. This means conducting experiments on a wide range of length scales (i.e., from the atomic to the micron scale) and on a wide range of time scales (i.e., from picoseconds to seconds). Experiments must be performed at higher pressures, such as those that exist during dry etch with pressures ranging from 5 mtorr to 50 mtorr and during depositions where, depending on the deposition process, the pressures can range from a few mtorr up to atmospheric pressure. One example of a pioneering study of this type is shown in Figure 5. Here the oxidation of silicon and the subsequent thermal decomposition of this oxide have been studied as a function of time by monitoring the relative intensities of oxygen- and silicon-associated valence-band spectral features. Such valence-photoemission measurements have also revealed intensity oscillations with the thickness of epitaxial overlayers like those seen in reflection high-energy electron diffraction, thereby providing another *in-situ* probe of growth mechanisms. In the future, such measurements should be possible at much higher pressures and with 100 to 1000 times faster spectrum-accumulation times, thereby permitting dynamic studies of reaction kinetics. (See also the discussion below of Figure 8, in which *core* photoelectron spectra are used in a similar fashion.) In addition, measurements must be made of buried interfaces, ideally with lateral spatial resolution, and this suggests using photon-in/photon-out techniques to a greater degree, perhaps by means of resonant-enhanced total reflection, as illustrated in Figure 3.

Finally, we note that VUV/soft x-ray photons can be used as one of the “reactants” in semiconductor surface studies, since they can be tuned to various core and valence energy levels, thereby promoting specific reaction pathways, as for example, in oxidation, lithography, and photon-stimulated desorption. Some work of this kind is now going on at second-generation sources (particularly on semiconductor surfaces), but the higher brightness of the ALS should permit studying such processes with greater precision and in entirely different regimes of effectiveness. The ALS should thus permit probing the role of photon-induced surface chemistry, as well as the physical basis of x-ray photolithography (a promising future technology).

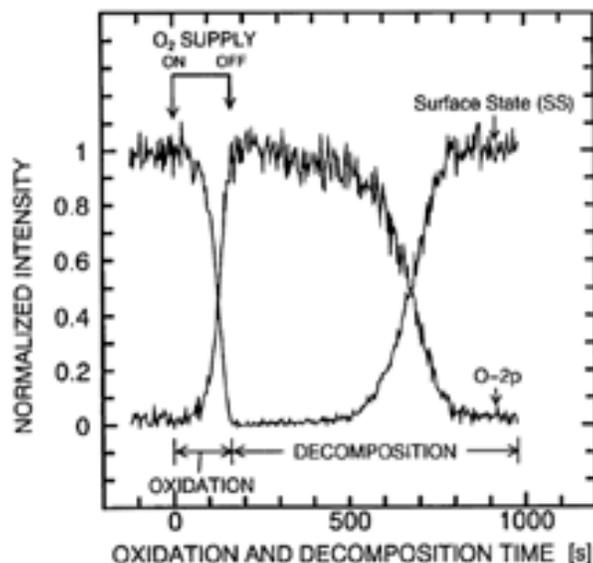


Figure 5. Time-dependent valence-photoemission study of the oxidation of silicon (001). The intensities of oxygen-2p and silicon-surface-state (SS) features have been used to monitor in real time oxide growth and decomposition after the oxygen supply is turned off. For temperatures above 760° C, there is a transition from oxide growth to oxygen etching of the surface, and no oxygen-2p feature builds up. Such time- and temperature-dependent measurements permit quantitatively studying the kinetics of this important reaction, and they will be possible on much shorter time scales with a third-generation source. [Figure taken from Y. Takakuwa et al., Jpn. J. Appl. Phys. **32** (1994) L480 and J. Electron Spectrosc. **88-91** (1998) 747.]

The unique capabilities of the ALS will enable applying such a combined approach to new and advanced materials that are relevant to microelectronics applications. Figure 1 illustrated a variety of system morphologies and the spectroscopies that can study them. Photoelectron spectroscopy is still the best method to simultaneously measure composition (via core intensities), chemical states (via core binding-energy shifts), electronic properties (via both valence-band and core-level measurements) and structure in an element-specific way (via photoelectron diffraction). Photoelectron spectroscopy provides chemical information on surface-reaction products, surface-adsorbate and interface atomic structure, band line-up between insulating overlayers and semiconductor substrates, and critical information on the density of states near the Fermi level of metallic overlayer interfaces (see also discussion in Section 2.7 below on metals). Photoemission also provides a direct measurement of surface and interface states that might affect device performance. The existence of such states may hinder some device applications, but it may also provide new paths for electronic conduction in advanced device applications. The extremely high-spectral resolution available at third-generation light sources will provide the most detailed and accurate spectroscopy of these materials. Applying this related array of photoemission probes to submicron length scales and to moderately buried interfaces (say at depths of greater than 10 Å) requires a soft-x-ray source in the photon-energy range from approximately 20 eV to 2000 eV or 3000 eV with extremely high flux and brightness, yet one that maintains tunability and high resolution of approximately 1 in 10,000. In addition it requires development of photoemission microscopes operating in a variety of modes including direct imaging

(spectromicroscopy) or focused-spot scanning (microspectroscopy). (We comment on these methods in more detail below.) Tremendous progress has been made in these microscopies in past few years, and such instruments can be uniquely exploited at the ALS and other third-generation light sources.

Beyond photoemission, soft x-ray emission spectroscopy (XES) can give electronic (site-selective density of states) and chemical information (orbital symmetry and bond orientation) in dilute and buried systems that are difficult to access with photoemission. This photon-in/photon-out spectroscopy could be used in a high-pressure cell to investigate processing chemistry *in situ*. Fluorescence could also be used to investigate more deeply buried interfaces, such as those in real devices. Combining this method with microscopy would be a difficult yet rewarding challenge, as one could monitor the actual interface at a single component of a real device. This would only be possible at a third-generation light source because of the low fluorescence cross section and the fact that the time to accumulate a fluorescence spectrum is approximately 100 times longer than an equivalent photoemission spectrum.

Thus, a global approach to semiconductor surface and interface science, carried out with the use of a third-generation light source, is a necessary component of our future scientific and technical needs. Such an approach will provide advances in fundamental physics and chemistry that will guide future device development. Such an approach will also provide vital information that will be useful to device manufacturers that are utilizing current technology. This information cannot be obtained without a third-generation light source in the VUV/soft x-ray regime. The ALS fills this need in providing an intense, high-brightness, tunable VUV, soft x-ray, and intermediate-energy x-ray source capable of element- and site-specific spectroscopy, spectromicroscopy, photoelectron diffraction and holography at very high energy and angular resolutions, and x-ray fluorescence emission spectroscopy at high energy resolution.

## 2.7 Metal Surfaces and Interfaces

The investigation of metal surfaces and adsorption thereon has traditionally been one of the strongest areas of surface science. Most of the existing surface-science methodology was in fact developed in the context of the study of metal and semiconductor surfaces. Further progress in methodology and fundamental physics and chemistry will continue to rely on these relatively simple materials as a springboard toward more complex materials. Some of the frontier areas that should be investigated are:

- The nature of the electronic structure and chemical bonding at surfaces, which has potential implications for bonding at buried interfaces as well, and to which both Fermi-surface mapping via angle-resolved photoemission and x-ray emission spectroscopy has added new insights, as shown respectively in Figures 6 and 7 based on recent work at the ALS.
- The dynamics of adsorption and oxidation on surfaces from the slow scale of diffusion and macroscopic reaction kinetics (milliseconds to seconds) to that of the many-body aspects of electron rearrangements after excitation (femtoseconds or less).
- The role of photons in selectively producing chemical reactions via core or valence-level excitations, including the hitherto little-studied effects of radiation damage to samples in general.
- The study of alloy surfaces, for which compositional changes can affect reactivity, magnetism, and other properties, with unique surface alloys now being an active area of investigation.

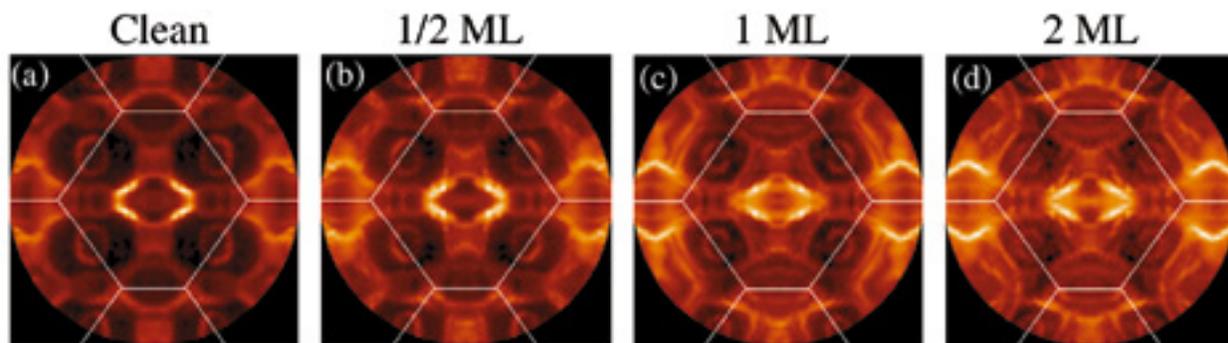


Figure 6. The dependence of the electronic states at the Fermi level of a transition metal (tungsten) on the adsorption of an alkali metal (sodium). Here, the angular distribution of photoelectrons excited from the Fermi energy of tungsten (110) is shown for the clean surface (a) and for the surface with different amounts of sodium (b) 0.5 monolayers (ML), (c) 1.0 monolayers, and (d) 2.0 monolayers. As the sodium atoms are added, various contours shrink or expand in size and relative intensity, illustrating directly how various chemical bonds on the surface attract more electrons to them. Such information is directly relevant to chemical catalysis, where the addition of alkali metals to other metals greatly affects their catalytic activity. [Figure courtesy of E. Rotenberg, ALS, and S. D. Kevan, University of Oregon, to be published.]

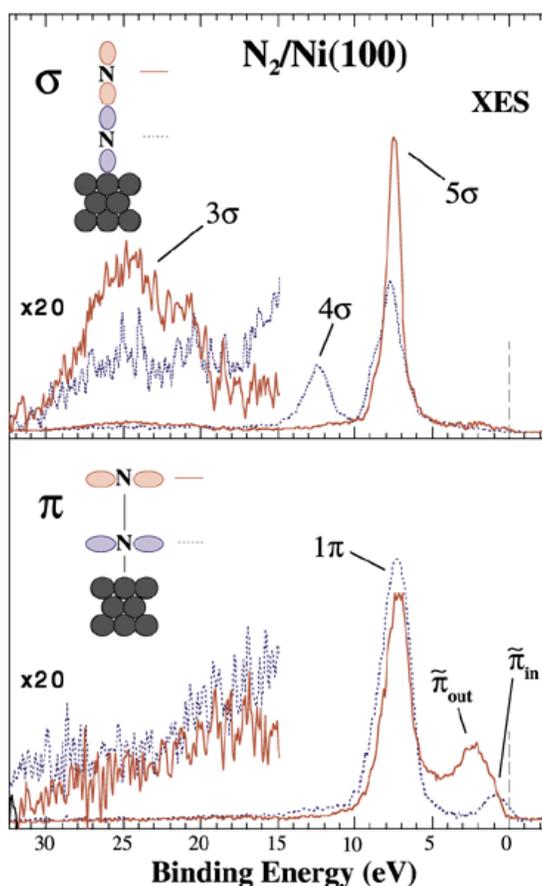


Figure 7. X-ray emission spectra for nitrogen adsorbed on nickel (001). The spectra were obtained at the ALS with the exciting radiation in two different polarization orientations so as to be sensitive to either the 2p-derived  $\sigma$ -bonding character (upper panel) or the 2p-derived  $\pi$ -bonding character (lower panel), as projected onto each nitrogen atom in the molecule (as indicated in red and violet). Such measurements are only possible with a third-generation soft x-ray source. They have permitted better understanding this prototypical adsorbate-substrate bond, and they have called certain aspects of the prior model for this bond into question. [Figure from A. Nilsson et al., Phys. Rev. Lett. **78** (1997) 2847 and P. Bennich et al., Phys. Rev. B **57** (1998) 9275.]

The ALS is particularly suited to contribute in this area because of the high spectral resolution and intensity it affords, and its time-resolution and polarization capabilities. Some recent and ongoing research can be given as examples:

- High-resolution x-ray emission spectra from adsorbates. This is not a viable experiment without third-generation synchrotron radiation, and work at the ALS has forced a rethinking of prior paradigms concerning the surface chemical bond (see Figure 7). Although XES has traditionally been considered a bulk technique, it has been made surface sensitive by exciting adsorbate core electrons and/or by using grazing-incidence excitation. Since the element-specific photons come only from the adsorbate, there is also no interfering signal from the substrate. Angle-resolved XES also permits separating contributions from bonding orbitals with various symmetries. Thus, an atom-by-atom view of the orbitals involved in the formation of the chemical bond can be obtained.
- High spectral resolution in core excitation regions. Vibrationally resolved XPS of adsorbates proves that charge transfer for chemisorbed molecules on metals is fast on the time scale of photoionization.
- Time and state resolved core XPS spectra. Studies at ELETTRA and the ALS permit studying reaction kinetics and atomic structure (by means of photoelectron diffraction) in real time, as illustrated in Figure 8.
- Excitation/decay spectra of adsorbates under Auger resonant-Raman conditions (exciting photon bandwidth below lifetime width). This technique allows the measurement of charge-transfer times for physisorbed and chemisorbed species in the (sub)femtosecond range that is faster than current pump-probe laser systems by means of what has been termed a “core hole clock.”
- Threshold behavior for adsorbates. This shows that the post-collision-interaction effects well-known from free atoms and molecules are totally screened on a metal surface so they do not occur.

Other promising areas for future model studies of a conceptual nature are:

- Use of circularly polarized light for the investigation of chiral adsorbate layers.
- Detection of ionic and neutral fragments of photon-induced surface reactions for the elucidation of their dynamics. Surface reactions induced by VUV and soft x-ray photons can also be followed *in situ* by appropriate spectroscopies. They are the basic processes in surface oxidation, etching and lithographic patterning, the formation of molecules in outer space, and many atmospheric reactions. Incident-beam damage effects, which are of importance to most of the applications mentioned in this report, are associated with the same processes. Improved basic understanding will help in preventing them, as well as in using them to enhance the formation of certain structures or surface species.

Finally we draw attention to the important area of alloy surfaces. The physical and electronic structure of alloys is of both fundamental interest and long-term technological importance. An important technological imperative is to obtain a sufficient understanding of the properties of binary alloys so as to make it possible to optimize the performance of bimetallic catalysts. We are, however, a long way from realizing this objective and must first obtain an understanding of fundamental issues, such as the relationship between the physical and electronic structure of alloys and the relationship between bulk and surface order-disorder transitions. The ALS is well-placed to provide the basic experimental information necessary for progress in both these areas. Its capability for high-resolution photoelectron spectroscopy, coupled with surface microscopy and high photon flux, will make it possible to follow important processes, such as

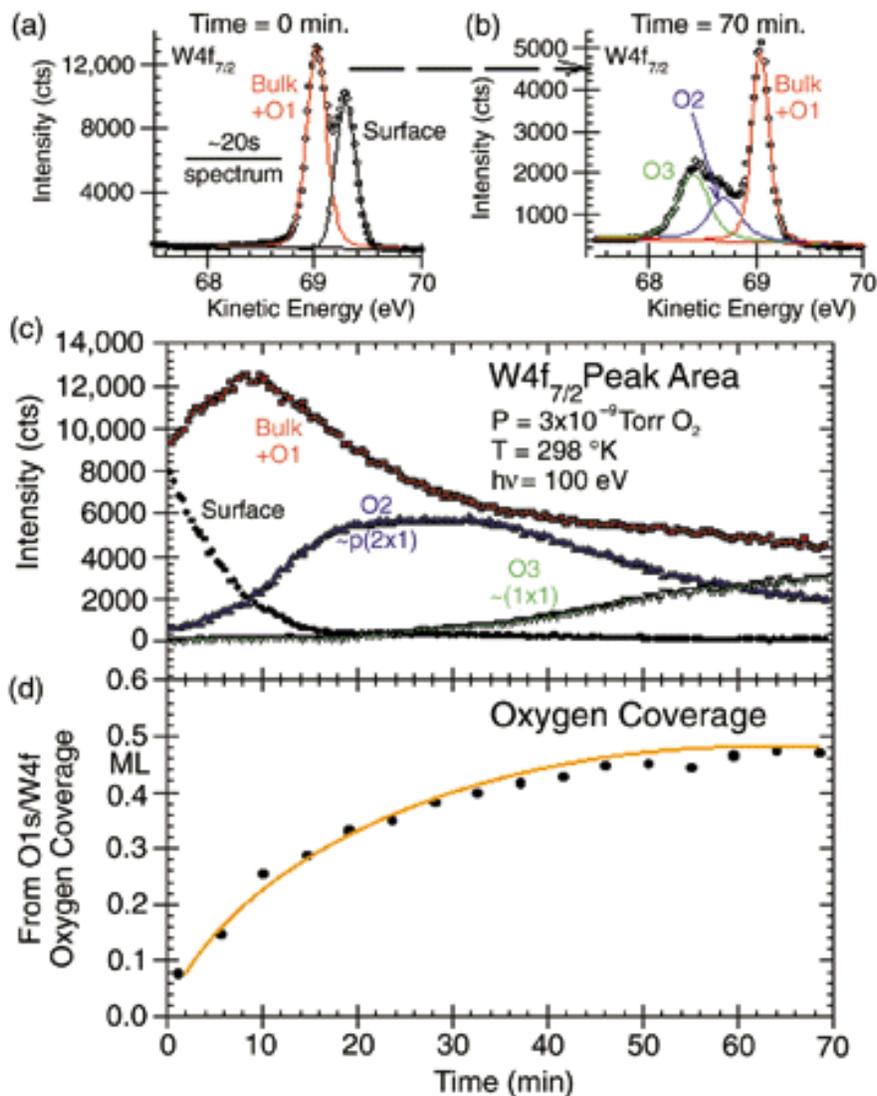


Figure 8. Chemical-state and time-resolved photoelectron spectra obtained during the reaction of oxygen with a tungsten (110) surface. (a) and (b) Four distinct chemical states of tungsten can be resolved in tungsten-4f spectra [atoms at the clean surface (Surface), bulk atoms underneath the surface, which overlap those bound to one oxygen atom at the surface (Bulk + O1), atoms bound to two oxygen atoms (O2), atoms bound to three oxygen atoms (O3)]. Spectra were accumulated at 20-sec intervals over a 70-minute period of the surface reaction. The time dependence of all four of these intensities in (c) and that of oxygen 1s in (d) then permits studying the kinetics of this surface reaction directly, with a highly limited oxygen mobility being indicated. This work was carried out at the ALS, and similar measurements are also ongoing at ELETTRA by Paolucci, Rosei, et al. [Figure taken from R. Ynzunza et al., to be published.]

surface segregation and ordering in real time. This information is essential in classifying the types of behavior exhibited by alloy systems. However, if this information is to be interpreted correctly, a number of important theoretical problems must be resolved. Prominent among these is the resolution of current controversy over the relative importance of initial- and final-state contributions to photoelectron and x-ray emission spectra, with theory playing an important role here.

## 2.8 Surface and Interface Magnetism

This topic will be dealt with also in the report of the Working Group on Magnetism and Magnetic Materials, but we here point out a few aspects that relate more specifically to surface and interface studies.

The electronic states near the Fermi energy play a decisive role in the reactivity of a surface, as noted already in discussing Figure 6. Transition-metal surfaces with a high density of states at the Fermi level are usually rather reactive, whereas noble metals are not. Obviously the unfilled d shell is important, and magnetic effects are in addition expected to play an important role. A detailed understanding of the mechanism of the bonding of specific adsorbates is still evolving, and in particular, the question as to where a localized-orbital picture is sufficient and when more delocalized surface states are important is crucial (e.g., for the understanding of catalyst activity, selectivity, and resistance to poisoning). The Fermi surface is also important in determining other solid and surface properties, including transport, energy transfer, and cohesion. Beyond this, it is clearly important to understand the full electronic structure over all the valence bands, and fundamental questions still exist as to what occurs in these bands as a ferromagnet is taken through its Curie temperature. The ultimate payoff from this knowledge may be our capability to control these properties at will, for example, by surface-alloy formation or by nanostructuring catalyst surfaces.

High-resolution valence photoemission and Fermi-surface mapping offer new opportunities to measure magnetic effects in surface states, interface states, quantum-well states (see Figure 9 in the report of the Working Group on Magnetism and Magnetic Materials), and adsorbate states. Magnetic exchange splittings and magnetic moments for electronic bands that cross the Fermi energy can be measured directly, given the spectral resolution and the flux possible at the ALS. Magnetism can thus be measured just where it arises. An example of this kind of measurement for nickel is shown in Figure 9, where the evolution of the bands near the Fermi level have been studied as a function of temperature. These data were actually obtained with a laboratory UV source, but it should be possible to obtain them much more rapidly and with spin resolution at the ALS. The inclusion of spin detection, perhaps at somewhat relaxed requirements for resolution, furthermore permits identification of the sign of the spin polarization of such states relative to that of the underlying bulk. While this sort of spectroscopy can deliver fundamental answers to many of the pressing questions listed in the magnetism and complex materials sections, it also enables us to study in detail how the bonding of adsorbates relates to the magnetic state of the transition-metal surfaces and to what degree the adsorbate becomes “magnetic” through its bonding to the substrate.

Beyond valence-level photoemission, we note that core-level measurements, which offer a rich array of multiplet and dichroism effects, can also be used to characterize surface and interface magnetic properties. Such effects have been used, for example, to identify surface Curie or Néel temperatures that are different from the bulk values for several materials. And x-ray emission spectroscopy provides a complementary probe that can reach into the bulk and whose applications to magnetism are only beginning to be explored.

The surfaces of magnetic oxides (e.g., the colossal-magnetoresistive oxides) and semiconductors (e.g., the diluted magnetic semiconductors) present highly relevant issues relating to surface magnetism. For example, what are the magnetic moments at the surface and how are magnetic ordering phenomena affected by the lower dimensionality and by the change in magnetic coupling? Magnetism is here more typically a localized kind, and it is also reflected in core levels, which provide element-specific information complementary to that derived from valence studies. Some of the issues here are short-range versus long-range order, surface magnetic-transition temperatures (which can differ from the corresponding bulk transition temperatures), the variation of magnetic properties from the surface

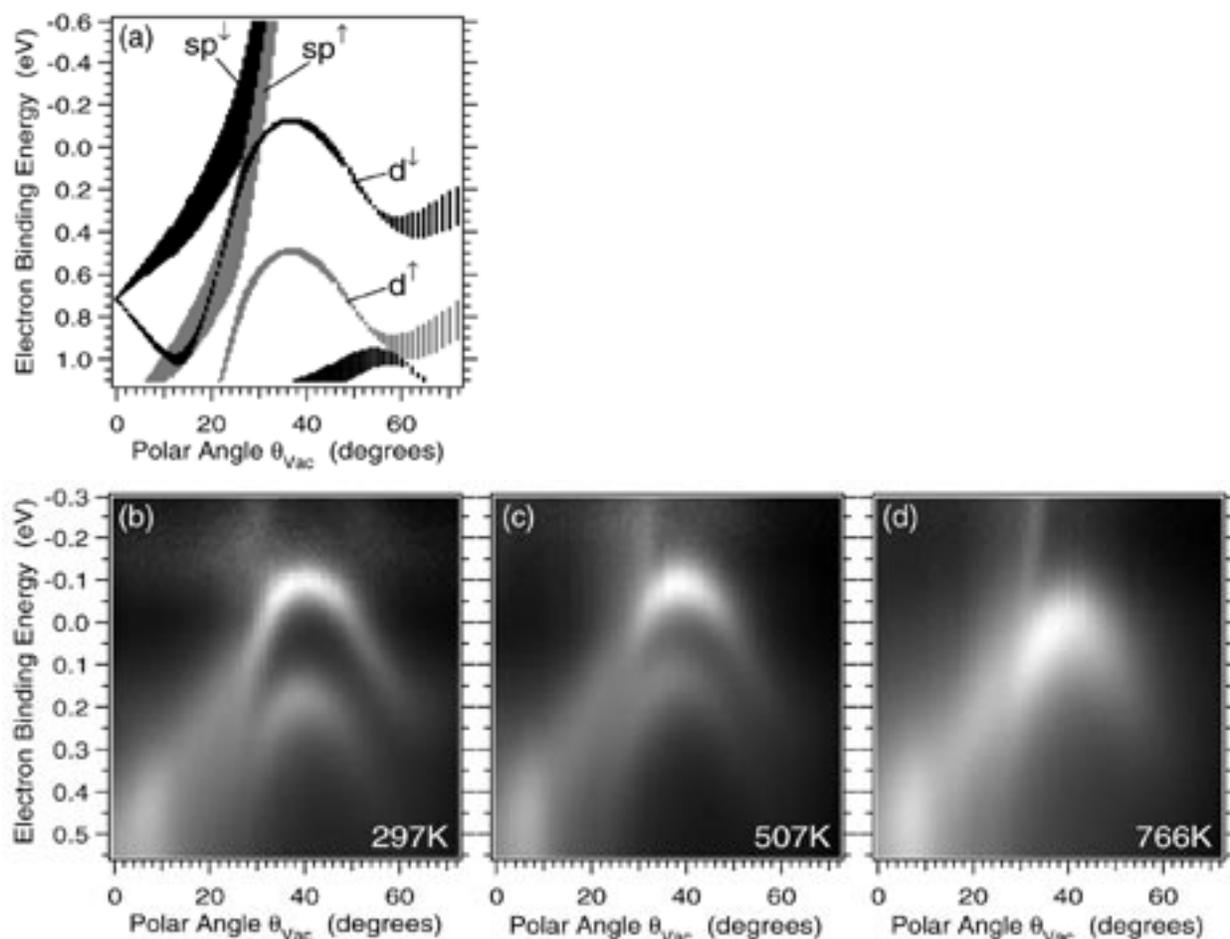


Figure 9. Temperature dependence of the electronic energy bands of a ferromagnet. A section of the electron energy bands near the Fermi energy for ferromagnetic nickel is shown as a function of emitted photoelectron angle relative to the surface normal (or equivalently wave vector parallel to the surface). (a) Bands calculated from theory, indicating band types and spin orientations; (b), (c), and (d) experimentally-observed bands, as seen in angle-resolved photoemission spectra, for temperatures passing from below to above the ferromagnetic-to-paramagnetic transition at a Curie temperature of  $T_C = 631$  K. [Figure taken from T. Greber, T. J. Kreuz, and J. Osterwalder, *Phys. Rev. Lett.* **79** (1997) 4465.]

inward, and the influence of changes in composition, doping levels, magnetic impurities, and overlayers on magnetism. Atoms at steps, on edges, and at defect sites are known to have different reactivities and also may have different magnetic properties, and these may also be resolvable via core shifts, differences in photoelectron-diffraction patterns, or differences in spin polarization or magnetic dichroism.

Being able to study buried metal-metal interfaces via the methods discussed previously [e.g., high-resolution photoemission or x-ray reflectivity (see Figure 3), or photoemission or XES using total internal x-ray reflection at a core resonance] is also of high importance for the future of magnetism studies.

In these studies, the brightness of the ALS is key in permitting studies that achieve sufficiently high energy resolution to be done with variable radiation polarization. Being able to do element- and site-specific or spin-resolved photoelectron diffraction, or to take advantage of the newly discovered effect of interatomic multi-atom resonant photoemission via scanning photon energy, as illustrated in Figure 10, will also add considerably to such magnetism studies, and these methods should be further developed.

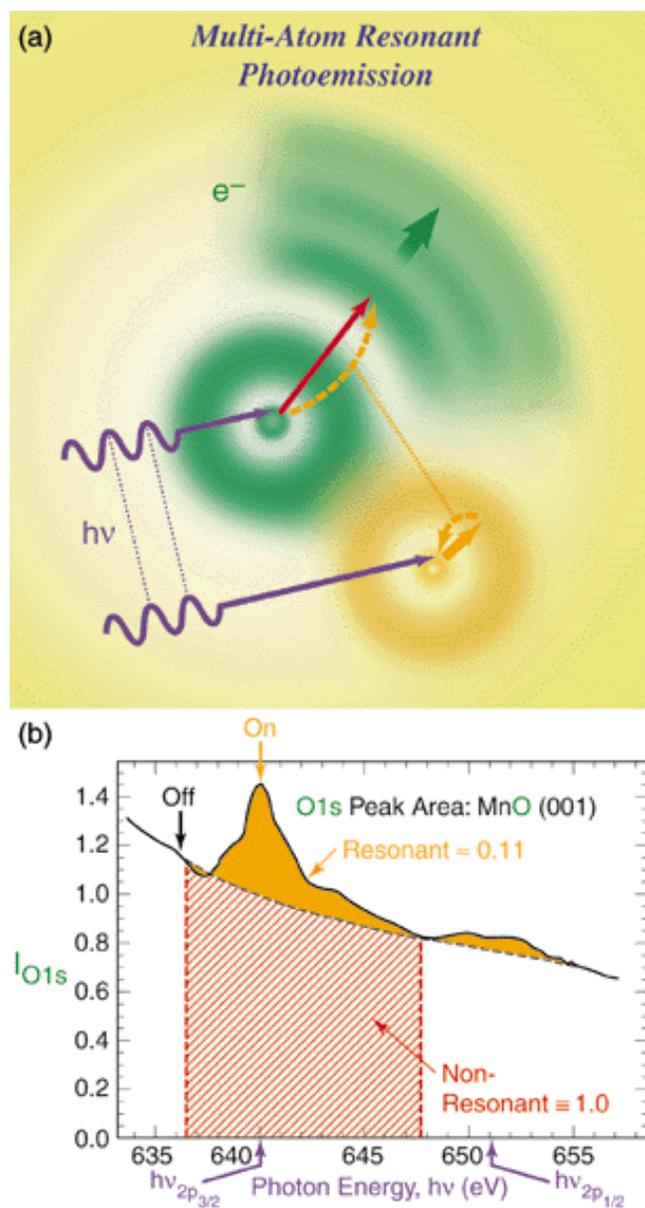


Figure 10. (a) Schematic illustration of a new type of resonant photoemission observed recently at the ALS. If the photon energy can be tuned to a strong bound-to-bound excitation on a near-neighbor atom at right, then the intensity of the photoemission intensity from a core level in the atom at left can be significantly enhanced. (b) Experimental data for this effect, for the particular case of oxygen-1s emission from MnO and the photon energy tuned through the Mn  $L_{2,3} = 2p_{1/2,3/2}$  edge excitations. The resonant enhancement is shown in orange, and the expected intensity in the absence of this resonance is in cross-hatched red. This effect should permit determining near-neighbor atomic identities and thereby provide a new probe of bonding and magnetism. [Figure taken from A. Kay et al., Science, accepted for publication.]

### 3. Achieving New Dimensions in Pressure, Space, and Time

#### 3.1 Fundamental Possibilities

##### 3.1.1 Measurements at Higher Pressures

Carrying out measurements at higher pressures is crucial, and the different techniques discussed have possibilities as follows:

- X-ray emission spectroscopy or x-ray absorption spectroscopy with fluorescence detection or x-ray scattering/reflectivity: up to 1 atm with thin windows (e.g., of SiN).
- X-ray absorption spectroscopy with secondary electron detection: up to approximately 10 torr to 25 torr.
- Photoelectron spectroscopy/diffraction/holography: up to 1 torr and probably up to approximately 10 torr to 25 torr with differential pumping and special electron optics, with preliminary work already at 1 torr, as illustrated in Figure 11.

Of special relevance here are electron inelastic attenuation lengths in the gas phase, which are estimated to yield mean escape or working depths at 1 torr of greater than 1 cm to 10 cm for low-energy secondary electrons, 0.02 to 0.04 cm for primary photoelectrons at 50 eV, and 0.2 to 0.4 cm for primary photoelectrons at 1000 eV. These depths scale inversely with pressure.

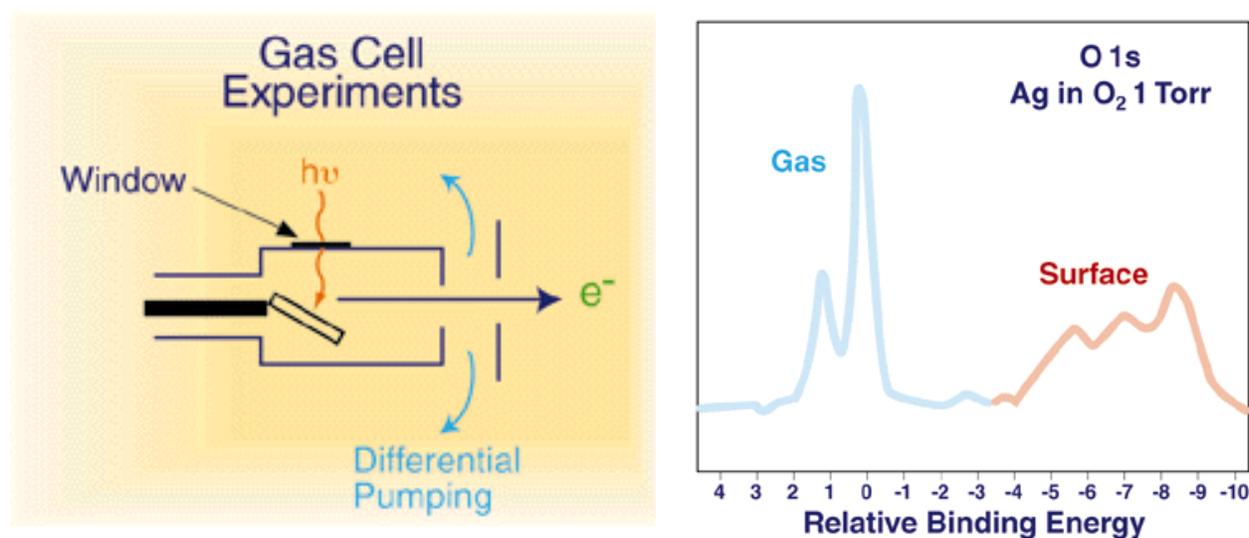


Figure 11. Experimental demonstration of the ability to carry out x-ray photoemission (XPS) measurements at 1-torr pressure. With the aid of a differentially-pumped enclosure surrounding a silver sample, it was possible to measure photoelectron spectra at a 1-torr ambient pressure of oxygen. The schematic experimental geometry is shown at the left, and the oxygen-1s spectrum, with gas-phase and surface species easily resolved, is shown at the right. [Figure courtesy of A. Nilsson, N. Mårtensson, et al. (unpublished results).]

### 3.1.2 Measurements with Lateral or Vertical Resolution

Spectromicroscopy and microspectroscopy with lateral resolution are dealt with in Section 3.2 below. With reference to the techniques illustrated in Figure 1(b), the sensing depths (vertical resolutions) and, where appropriate for atomic-structure probes, atomic-position resolutions are:

- X-ray emission, absorption or scattering: microns (away from core edges) to approximately 100 Å (at core edges), and atomic positions to  $\pm 0.05$  Å or better.
- X-ray absorption with secondaries: approximately 35 Å to 50 Å (metals) to 150 Å (polymers)
- Photoelectron spectroscopy/diffraction/holography: vertical sensing at 5 Å (50 eV to 100 eV) to greater than 40 Å to 60 Å (<10 eV or >2,000 eV), and atomic positions to  $\pm 0.05$  Å or better (diffraction) and  $\pm 0.3$  Å (holography).

### 3.1.3 Measurements with Faster Time Scales

X-ray emission or absorption is approximately 10 to 100 times slower than photoelectron spectroscopy, with the latter now at seconds/spectrum and estimated to go down to msec/spectrum in the future. Using the pulsed nature of the ALS radiation and doing time-delayed pump-probe experiments, perhaps with lasers, could permit doing spectroscopy on the picosecond time scale but with much longer data-accumulation times per actual spectrum.

## 3.2 Spectromicroscopy/Microspectroscopy

The decreasing dimensions of microelectronic and other devices are driving surface and interface science increasingly toward studies with high lateral resolution; that is, being able to do spectroscopy and microscopy simultaneously. Synchrotron radiation sources of the third generation have made it possible to do both “spectromicroscopy” (parallel image acquisition using electron optics) and “microspectroscopy” (sequential image acquisition using a focused beam and a scanned sample stage). Present resolutions are down to 250 Å = 1/40 μm in spectromicroscopy and 1000 Å = 1/10 μm in microspectroscopy (see the illustration of the two methods in Figure 5 of the report of the Working Group on Magnetism and Magnetic Materials). It is anticipated that these resolutions will go down to approximately 100 Å in both cases in the future, and perhaps as low as 20 Å in next-generation spectromicroscopy.

The possibilities and limitations of these techniques are still being studied and thus are not fully understood. Therefore, a few words about complementary techniques are appropriate in order to put potential studies at the ALS into the proper context. Structural and topographic information can be obtained more quickly with low-energy electron microscopy (LEEM) and simultaneous diffraction (LEED); chemical identification can also be accomplished with Auger-electron-emission microscopy (AEEM); and magnetic information can be obtained with spin-polarized LEEM (SPLEEM). The key opportunities for synchrotron-radiation-excited photoelectron emission (or secondary electron emission) microscopy (XPEEM) lie in the areas where the electron methods fail—chemical shift or chemical state imagery via core-level photoelectron or near-edge absorption spectra and element-specific magnetic imaging via magnetic-dichroism effects (see also comments on magnetic imaging in the report of the Working Group on Magnetism and Magnetic Materials).

Some particularly important and technologically relevant fields for applying these methods are magnetic metal multilayers and interactions of semiconductors with other semiconductors, metals, and insulators. Optimum use of precious microscope beam time can be achieved only if the sample or process to be studied by XPEEM has been studied beforehand by complementary techniques, so

that the XPEEM study has to fill only the gaps and the suitability of the sample for XPEEM has been established. This approach is best implemented by having two or more multi-method imaging instruments permanently installed on all branch lines that share the beamline. Specimen preparation and characterization by LEEM/LEED (and/or STM/AFM) before the XPEEM study should be performed before going on line. Similarly, samples prepared at the home institutions of the users should be first studied by whatever electron beam technique is useful—LEEM, LEED, or secondary-electron-emission microscopy (SEEM) (and/or by STM/AFM). When the samples are unsuitable for XPEEM, the beam time can be reassigned to experiments already proven to be feasible. This procedure has been implemented successfully at the spectroscopic LEEM (SPELEEM) installed at ELETTRA and is envisioned also for the ALS SPELEEM instrument, which, according to plans, will be combined with XPEEM imaging by magnetic circular dichroism.

The present state of the art in spectromicroscopy is 25-nm lateral resolution at 0.5-eV energy resolution with image acquisition times in the 10-sec range. In Figure 12, an example of the current state of the art is shown. A small chemical shift of approximately 0.15 eV is resolved between a base

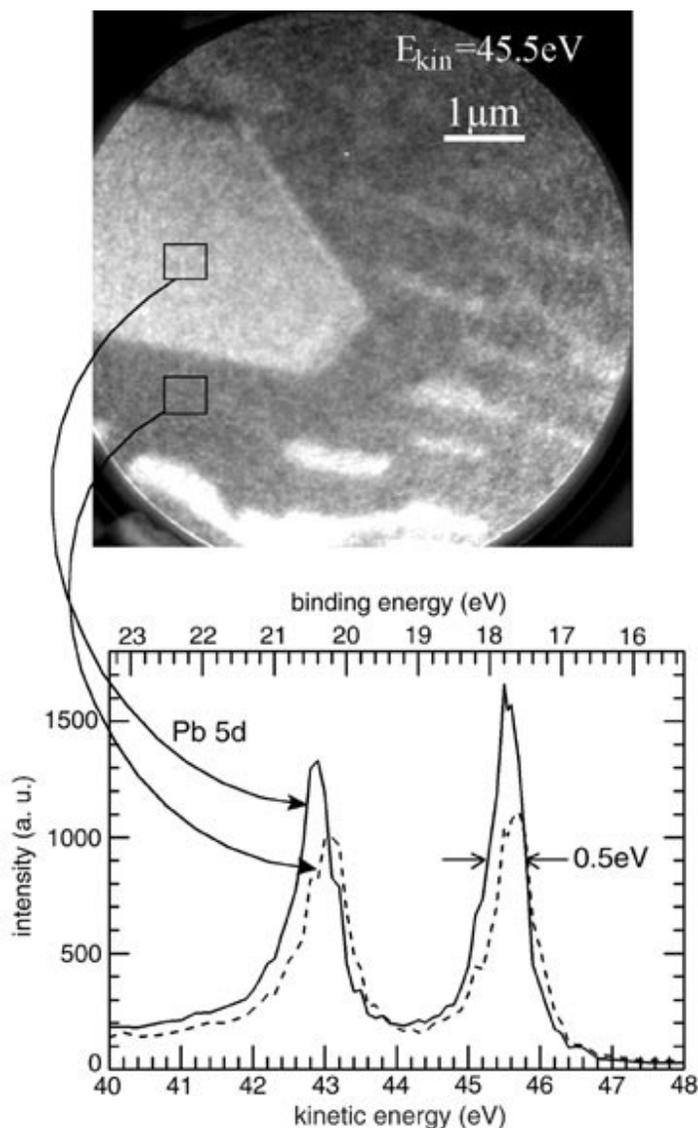


Figure 12. Photoelectron-emission microscopy (PEEM) image of a tungsten (110) surface with a flat one-monolayer “base layer” of lead deposited on it and overlying flat three-dimensional islands of additional lead. With an exciting photon energy of 65 eV, it is possible to resolve a very small chemical shift of 0.15 eV in the lead 5d levels between these two morphologies with a simultaneous lateral resolution of about 70 nm. The same instrument has achieved resolutions down to about 22 nm. [Figure taken from T. Schmidt et al., Surf. Rev. and Lett., accepted for publication.]

monolayer of lead and three-dimensional lead islands growing on top of it, with a concomitant lateral spatial resolution of about 70 nm. Chemical shifts between metal monolayers and thick metal crystals on silicon have also been clearly demonstrated. Photoelectron diffraction patterns from selected areas as small as 1  $\mu\text{m}$  in diameter have also been obtained and used as a contrast mechanism based on internal atomic structure. Future spectromicroscopy measurements using diffraction and/or holography will permit detecting the local atomic structure of small grains or nanoparticles. Imaging the dispersive plane of the energy analyzer allows spectroscopy of areas of the same size. A particularly promising area of application is imaging with the low-energy part of the secondary electron distribution ( $< 1\text{-eV}$  energy). SPLEEM with 1-eV to 2-eV electrons has shown that the magnetic-domain distribution in the bottom layer of magnetic/nonmagnetic/magnetic sandwiches as thick as several tens of angstroms can be imaged because of the large inelastic mean free path of very slow electrons. Similarly, element-specific magnetic imaging of interfaces buried at such levels should be possible.

Provided that sufficient windowing or differential pumping is available between the beamline and the sample region of the microscope, surface reactions and epitaxial growth at pressures as high as the low- $10^{-5}$ -torr range are possible. For example, GaN films have been grown on SiC during observation at temperatures as high as 800°C, and silicon has been nitrided at temperatures as high as 1100°C. Likewise, catalytic reactions can be studied with high lateral resolution. Thus, spectromicroscopy can make valuable contributions to many fields of fundamental and technological importance. Its main limitation is determined by the high field at the specimen, which makes it difficult to study very rough surfaces or powders, and by the charging of insulating samples. The latter problem can frequently be overcome by conductive backing or heating. A superior technique for the study of very rough surfaces and powders is microspectroscopy, which is uniquely suited for this purpose.

In conclusion, both spectromicroscopy and microspectroscopy open up new worlds in surface, interface, and thin-film science.

#### **4. Theory for Synchrotron-Radiation Experiments**

Theory is a pervasive need in studies of surfaces and interfaces, both in enabling data analysis and in providing an understanding of mechanisms and phenomena. There is a high synergism between theory and synchrotron-radiation experiments. For example, the availability of third-generation synchrotron x-ray sources such as the ALS has led to experimental data of unprecedented precision and accuracy, as well as novel phenomena, that challenge theory for their accurate interpretation. Thus, resonant processes in x-ray fluorescence and Auger emission have required new developments in theory and are still controversial in their interpretation. Conversely, advances in theory have permitted the analysis of experimental data to higher precision and suggested fruitful new avenues for experimental exploration. Thus, advances in the theory of x-ray absorption (both NEXAFS and EXAFS) have revolutionized the field and led to greatly improved efficiencies in data collection and analysis by reducing the need for using reference compounds. Similar advances should be possible in many other spectroscopies of interest at the ALS.

Efforts have already been initiated at the ALS to further develop the fundamental theory of optical excitation in matter, as applied particularly to synchrotron-radiation experiments. This effort can also be called “theory of the experiment” or “front-line theory.” That is, the effort aims in part to interpret experimental data that otherwise remain useless, as e.g., diffraction and scattering data. Theory-

of-the-experiment contrasts with what can be called “predictive theory,” which is more aimed at calculating fundamental materials properties than at extracting a maximum of information from a particular type of experiment. Such predictive theory is widespread, with hundreds of groups in the U.S. alone providing it in various forms, from electronic and magnetic structure to molecular dynamics. However, only a few groups in the U.S. (and indeed the world) are dedicated to theory-of-the-experiment as related to VUV/soft x-ray measurements.

Part of the work of theory-of-the-experiment has focused on photon-in/photon-out techniques, e.g., EXAFS (XAFS) and NEXAFS (XANES). Until recently, these methods have been more often used at hard-x-ray facilities than at the ALS, but new experimental efforts in microEXAFS and micro-NEXAFS, as well as more conventional EXAFS and x-ray scattering, implemented at the ALS make these techniques important tools for current and future efforts. Other theory work focuses on photon-in/electron-out techniques, e.g., photoelectron diffraction and photoelectron holography, as practiced more at lower energy storage rings such as the ALS, where use can be made of element- and chemical state-specificity. Many of the techniques mentioned have similar theoretical underpinnings, including a common multiple-scattering interpretation, and hence foster a collaborative interaction between theoretical groups and various experimental groups.

Advances in theoretical developments are often driven by experimental needs and instrumental capabilities. Thus, applications to more varied and more “relevant” materials constitute one major impetus for theoretical progress. And a third-generation facility like the ALS poses new challenges and opportunities for extending existing techniques and developing new ones. Much of this kind of work addresses the basic structure of surfaces and interfaces, with increasing attention to electronic and magnetic properties and response functions (e.g., spin- and polarization-dependent x-ray absorption and photoemission, valence-band photoemission, and x-ray emission spectroscopy).

Future theoretical developments include the following:

- Existing analysis techniques should be extended in terms of generality, capability, and efficiency. It will be particularly important to develop robust, user-friendly codes and user interfaces to permit experimentalists to analyze experimental data rapidly and with confidence. Examples of great potential application are the quantitative interpretation of spin- and polarization-dependent NEXAFS. On-line or before-experiment calculations of photoelectron-diffraction patterns will also increase experimental effectiveness markedly.
- Improvements in fundamental theoretical techniques are also needed. A long-term goal is to develop efficient codes for the calculation of self-consistent, full-potential scattering phase shifts including spin and relativistic effects for the entire range of spectroscopies of interest in synchrotron-radiation experiments. Additional advances are needed to improve the calculation of phonon/vibrational effects, inelastic losses, and many-body effects. Finally it is necessary to couple these theoretical methods with total energy calculations to permit an *ab-initio* treatment of thermal vibrations and disorder.
- Specific applications to various spectroscopies include the development of photoelectron-diffraction theory so as to fully include all effects of radiation polarization, electron polarization, and spin-orbit scattering, and the extension of valence-band photoemission theory so as to be able to treat both the energy positions *and* the intensities of features. Most analyses of angle-resolved photoemission to date have made only qualitative use of intensities, thus throwing away part of the potential information content. This will permit studying the valence electronic and magnetic structure of surfaces and interfaces in a more precise way, with particular relevance to complex

materials. Improved algorithms for holographically inverting photoelectron diffraction and x-ray fluorescence data are also under development. Another development will be the calculation of anomalous x-ray scattering amplitudes for multiple anomalous dispersion (MADD) scattering experiments that are extensively used in the biosciences.

- Calculating core-level energy relaxation effects in XPS will permit the study of electronic structure and bonding properties of atoms and molecules at surfaces and interfaces.
- Calculating x-ray emission spectroscopy of adsorbates; high-resolution, vibrationally resolved XPS; and resonant Auger Raman or x-ray spectroscopy will explore the local nature of bonding, especially for molecules bonded to solids.
- Theoretical models are needed for new phenomena of utility in surface and interface science, as for example, the multi-atom resonant photoemission effect recently observed at the ALS.

## 5. ALS Availability and User Issues

The ALS faces the problem of a severe shortage of high-quality surface-science end stations. This, combined with the fact that surface-science experiments in general require relatively more total experimental time, including both sample preparation and actual data acquisition, imposes limits on (1) the number of groups having access, (2) the success rate of the groups, and (3) the variety of experiments possible.

One aspect of solving this problem lies in leveraging the existing end stations as much as possible. Each end station should have a wide variety of facilities for activities such as sample heating, sample cooling, thin-film growth, and gas handling. Loadlocks to permit easy loading of samples without full-system bakeouts should be present on all systems, and if possible, independently usable preparation chambers should be available, so that one group can be measuring while another prepares specimens. Vacuum suitcases should be provided for groups wishing to bring samples prepared in their home laboratories. In addition, a permanent staff of scientists having long-term continuity with the beamline and its end station should be engaged with the experiments to ensure that outside users, who may come principally knowledgeable about their own sample preparation, can still successfully perform experiments. Although it will never be possible to have as rapid a turnaround in surface-science experiments as in x-ray crystallography, it is crucial to make these systems as user friendly as possible. Finally, it is essential to have available user-friendly data-analysis software that permits rapidly assessing how an experiment is going and where to take it next. In this overall context, we note examples of other experimental techniques, such as nuclear magnetic resonance (NMR) or magnetic resonance imaging (MRI) in which fundamental shifts in usage came about because the equipment became much more useful to a variety of disciplines through automated data collection, fast on-line analysis, and quantitative theoretical interpretation.

A second, although more expensive, part of the solution is to construct another 5.0-cm-period undulator and associated end stations in order to spread out the present very heavy load on undulator Beamlines 7.0 and 8.0. This is much needed.

Another problem often encountered by ALS users is a blessing that can become a curse—a single experiment can produce so much data (e.g., enough for several publications) that it is difficult to analyze and write up in a reasonable period of time. Data analysis thus becomes the limiting step. Faster on-line data analysis and theoretical interpretation tools are required.

## 6. Conclusions and Suggested ALS Roadmap

1. Surface and interface science is crucial to most current scientific and technological developments, and it is expected to become even more important as the scales in devices and materials continue to shrink to the nanometer and even single-molecule scale.

2. Several important frontiers of this field will be advanced by the application of powerful existing synchrotron-radiation experimental techniques and associated theoretical methodologies to more complex and heterogeneous systems, including nanostructures of various kinds, as well as to systems at higher ambient gas pressures. Studying systems that lack long-range order will become more important. However, parallel studies of model systems of a simpler nature will continue to be necessary in order to develop an essential microscopic understanding of the phenomena involved. And new techniques and theoretical ideas will continually be needed to push these frontiers forward.

3. Surface and interface science in its various forms will continue to be one of the most important single areas of endeavors at the ALS or at any other similar third-generation synchrotron-radiation source in its energy regime, and the ALS can make extremely important contributions to the advancement of this field. The ALS provides unique capabilities for studying elements with both low and high atomic numbers, and for investigating lower energy optical excitations, as opposed to the ground-state properties often probed with higher-energy radiation.

4. The further development of photon-in/photon-out experiments that can be used up to higher pressures and/or to study buried interfaces is very important. However, the complementary information obtained from photon-in/electron-out experiments cannot be replaced, and these two types of measurements should be combined wherever possible. In addition, the expanded use of photon-in/ion-out (or atom-out) experiments provides an important avenue for future development.

5. The ALS can optimize its contributions in this field with several specific developments:

- The involvement of and collaboration with scientists from other fields (e.g., surface chemistry, environmental and earth science, chemical engineering, materials science, industrial science, and the biosciences) that have to date been less represented in its user community. The evaluation criteria for research proposals and productivity should also be modified to reflect this larger community.
- The construction of a system combining high-resolution x-ray fluorescence spectroscopy, x-ray absorption spectroscopy with fluorescence detection, and photoelectron spectroscopy/diffraction and in which pressures can be maintained at the highest possible values during measurement (atmospheric for photon-in/photon-out and up to 10 torr to 25 torr for photon-in/electron-out if possible). Such a system would be of very broad utility and would in addition be of great benefit for the environmental sciences.
- The concerted development of new methods and facilities for carrying out surface studies at higher ambient pressures, for example, of water reacting with oxides and minerals, and of liquid film structures.
- The concerted development of new methods and facilities for carrying out studies of buried interfaces, e.g., by means of total internal reflection of soft x-rays and/or soft x-ray emission spectroscopy.
- The construction of a beamline optimized for x-ray absorption spectroscopy in the 1-keV to 4-keV energy range, using both electron and fluorescence yields.

- The construction of another broad-use undulator of approximately 5.0-cm period for use in surface- and interface-science studies.
- The provision of additional sample-handling and transfer facilities, as well as user-friendly data-analysis software, to optimize beam-time utilization and overall productivity.
- The further development and optimization of spectromicroscopy and microspectroscopy facilities, in particular so as to reach resolutions in the 100 Å range or better. This should include ancillary facilities for microscopic investigation and complementary measurements at the National Center for Electron Microscopy.
- The development of new higher speed detectors (e.g. multichannel or two-dimensional for electrons and x rays and spin for electrons) to permit fully utilizing the photons and electrons provided by the ALS. Experiments now often requiring closing down slits to avoid detector saturation.
- The advancement of various theoretical models and computer programs that are necessary for interpreting experimental results obtained. This includes computer availability for on-line analysis of experimental data.