One example of a future application of x-ray capabilities is the study of spring magnets, as discussed in Section 2.1.1. Here the elemental specificity of core-level magnetooptic techniques will allow the separation of the magnetic response of the soft and hard materials in the hybrid structure. Not only could the average spin and orbital moments on individual species in different layers be probed, but magnetooptical rotation and other methods could be utilized to measure the hysteresis response of the different layers individually to more fully understand magnetization reversal in these structures. Such studies should provide a better understanding of the unusual twist structure predicted in the soft layer, and they also should provide information concerning the interfacial region where little is know about how the transition from hard, high-anisotropy material to soft, low-anisotropy material is made.

## 4.2 Structure and Magnetic Properties

A key issue in nanoscale magnetics is the interrelation of structure and magnetic properties. Studies of surface and ultrathin-film magnetism are extending beyond elemental overlayers, such as epitaxial iron layers, to surface and thin-film alloy systems, where structural aspects of pseudomorphic or more complex growth modes can influence both structure and magnetism in overlayers. An example of the strong interplay of geometric structure and magnetic properties can be seen in Figure 7, where Invar quenching is observed in NiFe ultrathin films despite the absence of the phase change from FCC to BCC that is observed in the bulk. Here in the ultrathin film, the phase change is frustrated, and instead a decrease in the unit-cell volume is correlated with the loss of magnetization. In turn, understanding these NiFe ultrathin films has a technological significance because they are used as pinning layers in GMR and spin-valve devices. Increased intensities resulting from higher brightness should enable *in-situ* growth studies of layered structures, perhaps with dynamic sensitivity. Being

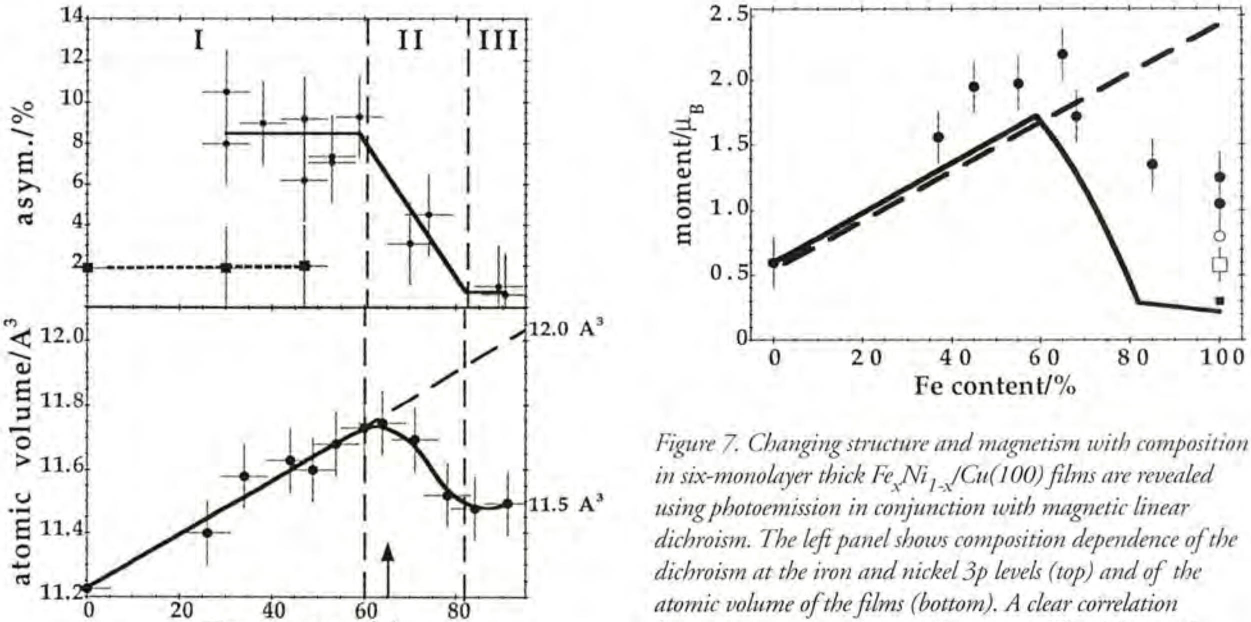

*Figure 7. Changing structure and magnetism with composition in six-monolayer thick* $Fe_xNi_{1-x}$*/Cu(100) films are revealed using photoemission in conjunction with magnetic linear dichroism. The left panel shows composition dependence of the dichroism at the iron and nickel 3p levels (top) and of the atomic volume of the films (bottom). A clear correlation between structure and magnetism is seen. The right panel shows the average atomic moment (solid line) obtained from calibrating the dichroism data. [Figure taken from F. O. Schumann et al.,* Phys. Rev. Lett. ***79** (1997) 5166.]*

able to probe the local atomic structure around each elemental constituent via photoelectron diffraction will also assist in characterizing such structures fully.

Probing magnetic structure both laterally and into the depth of thin-film and layered structures is feasible using scattered or reflected photons. Magnetic scattering in the x-ray range can be thought of as an extension of the magnetooptic Kerr effect common in near-visible regions, but now with wavelengths comparable to chemical and magnetic microstructure within samples. Measurements of scattered intensity as a function of scattering vector can thus probe both chemical and magnetic structure at and above the nanometer size scale in the VUV/soft x-ray range. One early example of these capabilities is that measurement of diffuse scattering away from the specular reflection from a magnetic film has found that the magnetic and chemical roughness that produce this diffuse scattering are not necessarily identical (see Figure 3 in the report of the Working Group on New Directions in Surface and Interface Science). In another example, the magnetooptical sensitivity in the specular reflectivity from a magnetic multilayer has been used to observe an antiferromagnetic multilayer interference peak unobservable with charge scattering alone. Other examples emphasize the compatibility of scattering techniques with variable applied magnetic fields to sense switching of individual layers in layered structures. The above examples have relied on scattered-intensity measurements. However, measurements of polarization changes in reflected (scattered) and transmitted beams have also been demonstrated, thereby extending Kerr and Faraday rotation spectroscopies and hysteresis measurements into the VUV/soft x-ray range. Figure 8 shows hysteresis loops of iron and chromium in a polycrystalline iron/chromium multilayer, revealing that chromium possesses a net moment opposite to the iron moment in these structures.

Careful consideration of the magnetooptical properties and experimental details will allow these emerging scattering techniques to be applied with varying depth sensitivity. Simply increasing the grazing-incidence angle results in increased penetration depth, and so changes in hysteresis loops (e.g., with angle) would indicate changing magnetization of a given element with depth. More sophisticated depth sensitivity might include the utilization of optical standing waves to probe the magnetization in different regions of buried layers. Many opportunities exist to apply these capabilities to study magnetism of the buried layers and interfaces that are often critical in defining magnetic properties of interest for application, as discussed in Section 2. Examples include studying buried layers (including spacer layers) in spin valve and MTJ structures and the antiferromagnetic/ferromagnetic interface where the mechanisms of exchange biasing are not understood. It should be possible to study magnetic fluctuations and inhomogenieties associated with reversal processes and phase transitions with scattering, possibly in a time-resolved fashion.

## 4.3 Spin-Resolved Electronic Structure

Spin-polarized photoemission studies of noble-metal thin films deposited on ferromagnetic substrates provided the first evidence that spin-polarized quantum-well states are available to mediate the coupling in the associated magnetic multilayers. Such states were first observed in Ag/Fe(001) and Cu/Fe(001) systems. These studies focused the discussion of the proposed mechanism of oscillatory coupling on the relative binding energies of the spin-dependent bandgaps in the ferromagnetic layers, thereby providing a mechanism for oscillatory coupling in terms of spin-polarized quantum confinement of electrons in the noble-metal films resulting from the spin-polarized band structure in the ferromagnetic parent materials. When the spacer-layer thickness is varied, the quantum-well states move up to the Fermi level, at which point the total energy of the system reaches a local maximum. The energy of the system is reduced by switching to antiferromagnetic alignment which moves the bandgap away from the Fermi level and reduces the confinement of the quantum-well state.

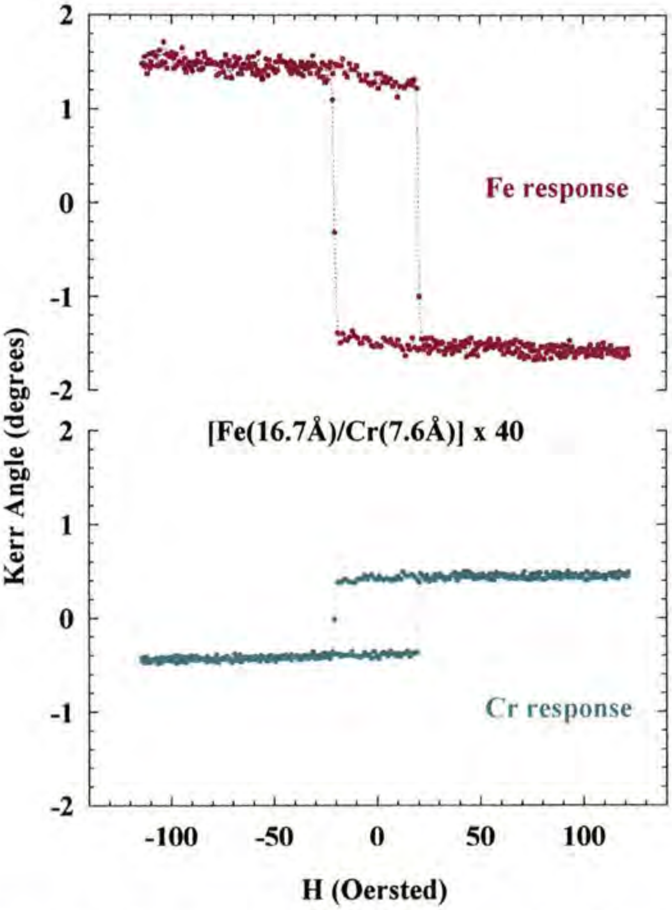

*Figure 8. Longitudinal x-ray magnetooptical-Kerr-effect hysteresis loops of the individual magnetization response for iron and chromium layers in iron/chromium multilayers are obtained by tuning the linear polarizer in the reflected beam to just below the $L_3$ lines of each element (by roughly 2.5 eV in this case). In this polycrystalline sample, the chromium layers possess a significant moment oriented opposite to that of iron, while antiferromagnetic chromium films show no signal by themselves. The net chromium moment observed in the multilayer presumably results from the iron/chromium interfaces where a significant number of chromium moments are uncompensated. Obtained using a low 2° grazing-incidence angle, these curves are primarily sensitive to the in-plane magnetization in just the top iron/chromium bilayer, while similar measurements at higher angles would weight the curves with significantly increased contributions from deeper layers. [Figure courtesy of J. Kortright, Lawrence Berkeley National Laboratory, unpublished.]*

These seminal early measurements have recently been extended at the ALS to include moderate spatial resolution and to investigate coupling between quantum-well states in different spacer layers. These extensions are possible only with small focused beam spots (50 μm to 100 μm at 1:1 focusing), which result directly from the brightness of the ALS, in conjunction with samples grown *in-situ* with laterally graded thicknesses so as to provide an entire range of sample thicknesses for study from one deposition session. High flux and resolution (> $10^{12}$ photons per second at a resolving power of 10,000) then enable combining high-resolution photoemission measurements with lateral scanning of the sample to obtain spatially resolved maps of photoemission spectra. In this case, the diameter of the focused beam spot and film-thickness gradient translated into a resolution of 0.5 monolayers in layer thickness. Single-wedged layers of Co/Cu(001) have been studied, as have more complicated structures consisting of double-wedged structures of Cu/Co/Ni/Co/Cu( 100), where the copper and top cobalt layer were wedged to detect the interference of the quantum well states in the copper and nickel layers. The results shown in Figure 9 clearly indicate how the intensity of the copper quantum-well state depends on the cobalt thickness (copper-nickel separation), thus identifying this interference effect, and the results strongly support the quantum-well model of the oscillatory magnetic coupling in the newly discovered GMR magnetic multilayers. These techniques can be extended by including circularly polarized incident radiation and/or spin-polarized electron detection to more finely resolve the spin-polarized nature of the quantum-well states. They can also be extended to many other classes of magnetic systems and problems.

The colossal-magnetoresistance manganites and related oxide materials exhibit a range of interesting phenomena as a function of doping that demand a microscopic, and ultimately atomic, characterization of structure, electronic structure, and dynamics. At low temperature below the metal-insulator transition, they are predicted to exist as half-metallic ferromagnets. A recent spin-polarized photoemission study has provided the best experimental evidence that this is the case, as shown in Figure 10. More detailed studies of these materials will require spin-polarized studies with energy resolution comparable to $kT_C$, where $T_C$ is the Curie temperature. In the case of $La_{0.7}Sr_{0.3}MnO_3$ for example, this resolution would be of the order of 25 meV, and it can be obtained at a third-generation source such as the ALS by combining high-resolution photoelectron spectrometers with micro-Mott or other spin detectors of improved-efficiency.

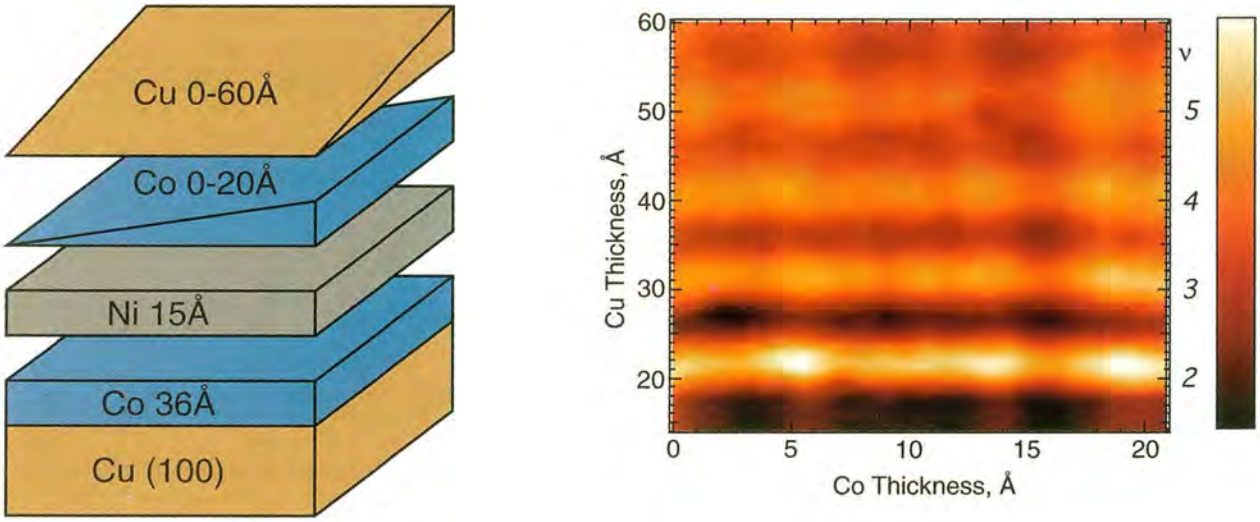

*Figure 9. Interference between quantum-well states in different layers of magnetic multilayers is shown in the image of photoemission-intensity modulations with varying thickness of two different layers (see sample schematic). In addition to the double-wedged sample (grown in situ), an intense x-ray spot 50 µm to 100 µm in size made possible by the undulator brightness was needed to observe these features. The clear dependence of the interference on multiple film thicknesses provides strong support for a model in which spin-polarized quantum-well states mediate oscillatory coupling in magnetic multilayers that in turn exhibit giant magnetoresistance. [Figure taken from R. Kawakami, et al.,* Phys. Rev. Lett. ***80*** *(1998) 1754.]*

Additional important information concerning these materials will come from companion core-level photoemission studies with variable polarization and spin resolution; for example, it should be possible to resolve the two types of manganese ions and to study their short-range magnetic order separately, perhaps using spin-polarized photoelectron diffraction. Clearly photoemission techniques will continue to evolve to higher spatial, energy, angular, spin, and time resolution so as to provide spin- and momentum-resolved electronic structure and magnetic structure for many important problems in magnetic and other materials.

In most cases photoemission and inverse photoemission are the techniques of choice for studies of electronic and spin structure, owing to their high energy and momentum resolution and, in the case of core levels, also their element specificity. In cases of buried layers and interfaces, x-ray emission

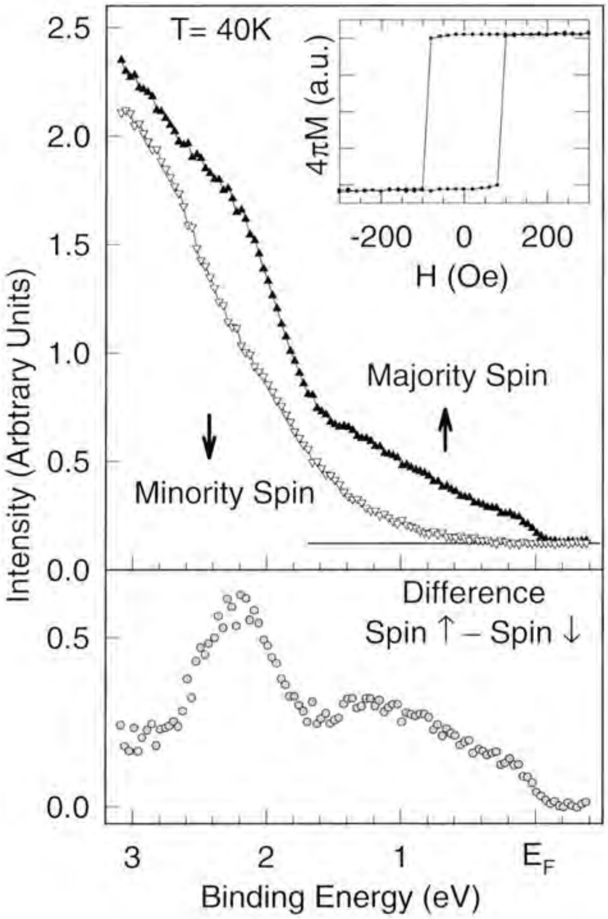

*Figure 10. Spin-polarized photoemission spectra of a 1900-Å thick film of* $La_{0.7}Sr_{0.3}MnO_3$ *taken at* $T = 40$ *K* ($T_C \approx 350$ *K*)*. The photon energy and experimental resolution were 40 eV and 0.2 eV, respectively. A magnetic pulse coil with a magnetic field of about 200 Oe was used for magnetization of the sample. The inset shows the magnetization (M) vs. applied magnetic field (H) hysteresis loop, which was obtained by monitoring manganese* $L_2$*-edge absorption of circularly polarized incident light. [Figure taken from J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan,* Nature ***392*** *(1998) 794.]*

spectroscopy, a technique that has already undergone a renaissance at the ALS, offers unique capabilities. Similar to valence photoemission, the x-ray emission technique probes the filled electronic states, but because of the initial core hole, it does so with elemental specificity. Thus x-ray emission spectroscopy allows an investigation of chemical bonding and hybridization effects. Application of this technique to cobalt/copper magnetic multilayers, for example, has shown the hybridization of the cobalt and copper densities of states at the interfaces, giving direct evidence for the origin of the magnetic moment on copper interface atoms found by XMCD absorption spectroscopy.

In addition to the extensive capabilities of photoemission for characterizing the electronic structure of magnetic materials, XMCD and other core-level spectroscopies are having an impact on magnetism through probing electronic structure. Examples relating to anisotropy are given above. Other examples include alloys, oxides, and compounds in which XMCD spectra of different elements are probed. Induced moments on nominally non-magnetic elements in multilayers and alloys have been observed by XMCD absorption. Moments have been observed on oxygen in $CrO_2$ and the colossal-magnetoresistance compounds $La_{1-x}Sr_xMnO_3$ and on sulfur in rare-earth chalcogenide compounds in K-edge XMCD absorption studies. These intriguing observations have direct relevance to the microscopic exchange mechanisms that are thought to mediate magnetic interactions. This atomic-scale understanding of magnetism in multicomponent structures may be used to test proposed exchange models, in the CMR materials for example, and to motivate further theoretical research in a wide range of materials. Another example is understanding the origin and nature of carrier-induced magnetism in compound magnetic semiconductors. Capabilities of probing both surface and bulk or buried-layer/interface properties are again important considerations in these types of studies.

While demonstrated potential and new opportunities clearly exist to study spin-resolved electronic structure with core-level XMCD spectroscopies, important questions remain about the core-level spectroscopies themselves. The detailed mechanisms of the spectroscopies are quite complicated and may influence the very properties of interest to investigate. In particular, the large MO signals near core levels result from processes in which a core hole is created, which may perturb the final states whose unperturbed spin and orbital polarization are of primary interest. The x-ray physics at ultrashort time scales associated with transition processes and the many-body responses to the creation of the core hole are thus critically important in assessing the degree to which the measurement distorts the system. This implies an essential close coupling of the theory of such experiments with the next generation of such experimental work (see the discussion on theory in the report of the Working Group on Surface and Interface Science).

It is also worthwhile to note that the development of new techniques for probing the atomic and electronic structure of magnetic materials should be possible at a facility like the ALS. One early example of this is the interatomic multiatom resonant-photoemission effect that has been observed for the first time in several metal oxides (MnO, $Fe_2O_3$, and $La_{0.7}Sr_{0.3}MnO_3$) (see Figure 10 in the report of the Working Group on New Directions in Surface and Interface Science). This effect, which couples the photoelectron excitation of one core level (e.g., oxygen 1s in MnO) with a resonant absorption on a neighboring atom (e.g., manganese 2p in MnO), has the unique potential for identifying which atoms are neighbors to a given atom, for doing spectroscopy only on interface atoms that have some degree of hetero-atomic bonding between homogeneous layers, for studying magnetism via XMCD effects in the resonance, and for studying more deeply buried interfaces by using secondary x-ray emission processes for detection.

## 4.4 Time Domain/Dynamics

Some early experiments using synchrotron radiation and accelerator-produced electron beams have studied time-domain issues, but this is a largely unexplored area in the context of synchrotron radiation where interesting opportunities may exist. The issues associated with dynamics are of central importance to research in magnetism and magnetic materials as a whole, where pushing from nano- to picosecond time scales are especially important. One general limitation at these time scales is the ability to produce intense, picosecond magnetic-field pulses.

Nanosecond XMCD spectroscopy has been demonstrated at the European Synchrotron Radiation Facility, where 25-ns and 50-ns magnetic-field pulses with an amplitude of 0.1 T were applied repeatedly to $GdCo_2$ amorphous thin films. Data were collected over three minutes, averaging over 80 million minor hysteresis cycles. Time resolution in the XMCD measurement was achieved through synchronization and delay of electron bunches with respect to the field pulses. The magnetization oscillated in time after the field pulses were applied over the probed area of $30 \times 100$ $mm^2$, going first to negative values. In a second experiment, the dynamics of magnetization reversal at surfaces has been studied using soft x rays emitted from only one electron bunch. This novel time-resolved surface magnetometry measures the spin polarization of the total photoejected electron yield by means of Mott scattering. The first results obtained with this technique are concerned with the magnetization reversal of iron ultrathin films deposited as amorphous low-coercivity ferromagnetic ribbons.

The results obtained so far with picosecond-magnetization measurements generally still suffer from poorly designed magnetic-field pulses needed to initiate the movement of the magnetization vector. For synchrotron radiation to have an impact on this field, the first task would be to find a way to produce appropriate magnetic-field pulses. After that, the brightness of the ALS would be ideally suited to opening up the largely unexplored field of magnetism at the picosecond time scale; we estimate that, with secondary-electron detection, it should be possible to measure magnetization via a Mott detector in a single pulse from an ALS undulator harmonic. If in addition, it could be possible to switch the photon from above to below a given core edge in adjacent pulses, or in some regular way to permit suitable signal averaging, then element- and time-resolved magnetometry could be carried out at the picosecond time scale.

Opportunities for time-resolved work include dynamical studies of fluctuations associated with phase transitions and magnetization reversal generally, and also *in-situ* studies of growth and processing. Techniques capable of high spatial and temporal resolution simultaneously are especially interesting here, including the spectromicroscopies discussed below and possibly dynamic coherent-scattering measurements.

## 4.5 Magnetic Spectromicroscopy

The ultimate goal in magnetic microscopy would be the direct observation of atomic spins and their motions and the correlation of the orientation and size of the atomic spin and orbital magnetic moments with the atomic structure and composition of the sample. The accomplishment of this goal would revolutionize our fundamental understanding and lead to new designs of technological devices. In many ways, these goals of magnetic microscopy underlie many of the research frontiers summarized in Table 1. It is for this very reason that much effort has been exerted to push the magnetic resolution toward the atomic limit.

To put VUV/soft x-ray studies in proper perspective requires noting that magnetic microscopy can be carried out with several different and competitive approaches such as Lorentz microscopy, Kerr microscopy, secondary electron microscopy with polarization analysis (SEMPA), spin-polarized low energy electron microscopy (SPLEEM), and magnetic force microscopy, to name a few. To date the best methods offer magnetic resolutions around 10 nm. In this environment the question arises as to whether synchrotron-radiation-based magnetic microscopy can make unique and important contributions.

It is already clear from the discussion in Section 3 that, in principle, magnetic microscopy based on core-level spectroscopies (spectromicroscopy/microspectroscopy techniques) offer several unique capabilities, most important of which are elemental and chemical- state specificity, the ability to separate the spin and orbital magnetic moments, depth sensitivity varying from surface to bulk, the ability to image antiferromagnetic domains, and the ability to image in the presence of large magnetic fields. An example is shown in Figure 11 where the field-dependent domain structure is observed at a lateral resolution of 30 nm to 40 nm. Despite these various unique capabilities, x-ray-based spectromicroscopy has had little impact on research in magnetism and magnetic materials because its resolution has historically lagged behind the leading techniques. Also, "home based" techniques are more accessible and the instrumentation is less expensive.

Looking ahead, in order for magnetic spectromicroscopy to have an impact on magnetic materials research, unique capabilities of the x-ray techniques must be brought to bear on important problems. One technical improvement here is to push the lateral resolution below 10 nm. In fact, resolutions of about 2 nm appears possible with an aberration-compensated PEEM microscope. Such a microscope, if available in a timely fashion, could have a significant impact on magnetic-materials research.

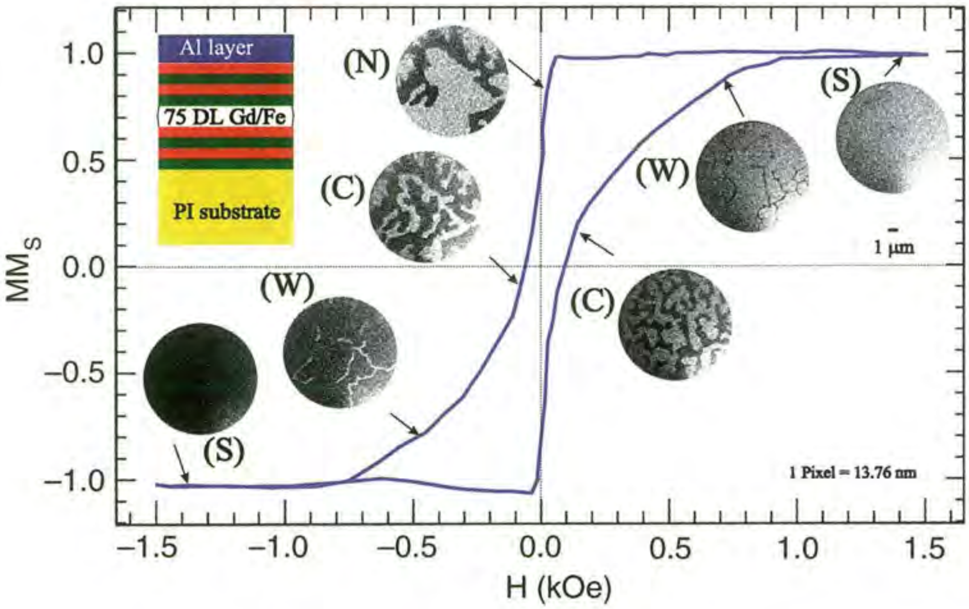

*Figure 11. Magnetic domain pattern of a gadolinium/iron multilayer film measured with circularly polarized x rays at the iron $L_3$ edge as a function of an applied magnetic field, using a transmission x-ray microscope. The domains have magnetization directions perpendicular to the film. The magnetic resolution is between 30 nm to 40 nm. [Figure taken from P. Fischer, T. Eimüller, G. Schütz, P. Guttmann, G. Schmahl, K. Pruegl, and G. Bayreuther,* J. Phys. D: Appl. Phys. *31 (1998) 649.]*

For example, it would help in understanding the stability of the magnetic bits and the magnetic structure of the transition regions between the bits in magnetic-recording media, as shown in Figure 12. Increases in storage density require the design of new materials with domains that are stable to smaller dimensions (i.e., by somehow avoiding the superparamagnetic limit through materials engineering) and that have reduced transition widths (about 10 nm). Such materials will most likely consist of grains of reduced size (< 10 nm) that are separated from each other at the grain boundaries by a magnetically passive material. The ability to obtain element-specific magnetic images of such materials will be of great importance.

A second area of opportunity is to make use of the elemental sensitivity and depth-probing ability to study domains and magnetization correlations into the depth of multilayer structures. Recently this has been demonstrated using a scanning transmission x-ray microscope with XMCD as the contrast mechanism; in this example, domains in the individual layers of an iron/cobalt bilayer film were observed. It appears that only x-ray microscopy techniques can unambiguously image domains in different layers, so they should have impact in characterizing three-dimensional magnetization distributions in nanostructures of both fundamental and applied interest. The transmission geometry should facilitate quantitative magnetization imaging, which will be valuable in testing micromagnetic theories.

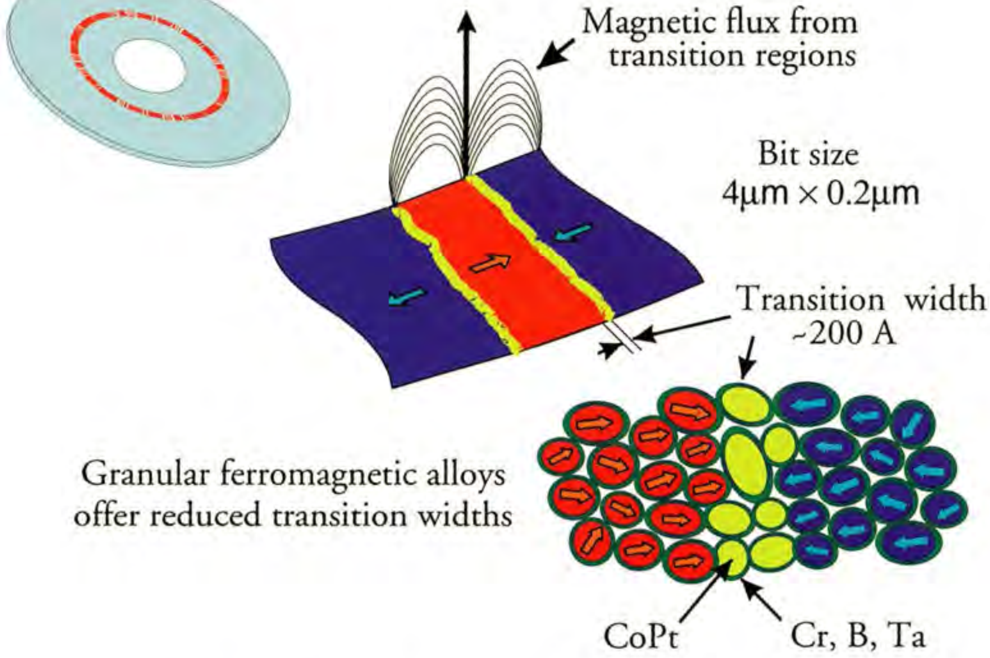

*Figure 12. Advanced computer disks consist of granular magnetic materials like CoPtCr with admixtures of boron or tantalum in order to minimize the transition width between the magnetic domains. In the disk material, the grains are believed to be coated by a non magnetic shell that reduces the magnetic coupling between the grains. A small transition width is required in order to achieve a high magnetic-flux density in the direction perpendicular to the disk surface, as shown. The flux from the spinning disk is sensed by the spin-valve magnetic read head shown in Figure 2. [Figure courtesy of J. Stöhr, IBM Almaden Research Center.]*

A third area of opportunity lies in the ability to image antiferromagnetic domains by means of linear-magnetic-dichroism microscopy and, by a change to circular x-ray polarization, ferromagnetic domains in the same sample. Such studies may well hold the key to solving the important exchange-anisotropy problem discussed in Section 2.1.2. Here and in many other applications, the ability of x-ray dichroism microscopy to probe buried layers and interfaces is essential.

## 5. Conclusions and Recommendations

The importance of magnetism and magnetic materials to society through technological and economic factors is considerable. The magnetic storage industry alone is about one-third as large as the semiconductor industry. In addition, the possible revolution in permanent-magnet materials with the advent of "spring" magnets will have overwhelmingly positive repercussions throughout society. Evolutionary growth in materials-synthesis capabilities is currently linked with vigorous basic research into wide-ranging areas of magnetism and magnetic materials, with clear potential to continue to impact science, technology, and society. The increasing complexity of these materials and the novel phenomena they exhibit require increasingly sophisticated experimental probes to gain fundamental understanding. Of particular importance is the reduction in size of the fundamental elements to the nanometer or even atomic scales.

It is clear that a third-generation VUV/soft x-ray synchrotron source such as the ALS offers new opportunities to positively influence the fields of magnetism, magnetic materials and their application in many ways. Both established and emerging VUV/soft x-ray synchrotron-radiation spectroscopic techniques couple directly and with large signals to the electronic and spin states containing the physics responsible for these unique properties. These techniques can directly probe the valence electrons that lead to magnetism, and through core electronic excitations they provide an atomic-scale sensitivity to magnetism. Together, they provide with spatial sensitivity at the sub-Angstrom level (e.g., through photoelectron and x-ray diffraction methods) and at the nanometer level and above (e.g., through scattering and spectromicroscopy) clear opportunities to move beyond classical models of magnetism (e.g., those based upon the usual Landau-Lifshitz-Gilbert methods) and to establish an understanding of magnetism at a more microscopic and quantum-mechanical level. If time resolution down to the nano- and picosecond domains can also be incorporated into these capabilities, it will dramatically enhance the ability of these techniques to impact the understanding of magnetism at this fundamental level.

Of crucial importance for increased impact is an enhanced coupling of the ALS to the magnetism and magnetic-materials community. This is especially important precisely because magnetism and magnetic materials are very well-established fields, with many groups actively engaged in such research at their home institutions. On the other hand, the unique capabilities offered by third-generation sources of VUV/soft x-ray synchrotron radiation require dedicated development of instrumentation and techniques, as well as on-site support for outside users, by experts who may be separated from mainstream magnetism research groups. This working group thus recommends the establishment of an ALS outreach program to bring these groups together in order to help ensure that the synchrotron-radiation resources are brought to bear on problems that will have a maximum impact in the true frontiers of research in magnetism and magnetic materials. Such interactions are encouraged with the magnetic-storage industry, the permanent-magnet industry, other industries making use of magnetic materials, and university and government laboratory groups.

The ALS should work closely with user groups to push the promising magnetic-spectromicroscopy efforts towards their ultimate nanometer-scale resolutions and to develop other unique spectroscopic, diffraction, and magnetooptic capabilities made possible by the brightness of the ALS. Because of the ALS brightness, spectromicroscopy is a unique strength of the facility, and every effort should be made to exploit this capability. Maximum impact in this area will require the establishment of a user base with deep roots in the magnetics community. The ALS is encouraged to form and work with such a user group to raise the funds necessary for the required instrumental advances toward the ultimate lateral-resolution limits. It is also clear that state-of-the-art facilities for various spectroscopic techniques involving both photon-in/electron-out (e.g., valence and core photoemission with spin resolution and variable polarization) and photon-in/photon-out (e.g., x-ray absorption, scattering, and emission) are necessary complements to maximize the unique impacts of the ALS in magnetism.

# Working Group on Polymers, Biomaterials, and Soft Matter

**Chair: Thomas Russell, University of Massachusetts, Amherst**

**Facilitators: Stephen Kevan, University of Oregon, and Harald Ade, North Carolina State University**

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## 1. Introduction

Polymers and soft condensed matter encompass the world around us. Their applications range from the nanoscopic (e.g., biomolecular material and copolymeric mesophases) to the microscopic (microelectronics) to the macroscopic (high performance structural composites) world. Synthetic polymers have now begun to mimic the biological world of macromolecules, such as DNA and proteins, as well as viruses and cells.

At present, our synthetic capabilities limit us to simple well-defined copolymers of the AB, ABA, BAB, or ABC type blocks where the polymer chains are covalently linked at the end. These polymers form well-ordered, nanoscale morphologies and can exist as liquids, semicrystalline solids, gels, and glasses. They represent ideal model systems for investigating the fundamental chemical and physical principles related to supramolecular formation, folding, and phase transitions. The ability to study hierarchical structures composed of nanoscopic organic/inorganic materials and dynamics on nanoscopic, microscopic, and macroscopic scales, as well as the kinetic processes of self-assembly, have made synchrotron radiation an invaluable tool.

Polymers, biomaterials, and soft-matter science, as subdisciplines of materials science, are of ever increasing importance, both from the fundamental and applied viewpoints. Can the ALS impact these area of science? The answer is self evident. The soft and intermediate x-ray regime is well matched to the spatial and temporal scales relevant to structure and dynamics of polymers, biomaterials, and soft matter. New insights can be achieved by studying the kinetics and thermodynamics of phase transitions involving long chain molecules in bulk, solution, or environments of reduced dimensionality.

# 2. Opportunities in Polymers, Biomaterials, and Soft Matter

## 2.1 Miniaturized Advanced Materials for the New Millennium

### 2.1.1 Biomolecular Materials

An emerging area of science and engineering is miniaturization of materials and structures. The twenty-first century will witness the development of micromachines (e.g., robots tens of microns in size) able to explore extremely hostile environments. One example is micromachine exploration of deep-ocean floors under extreme pressures and temperatures. A second example is biomedical micromachines with molecular-level chemical sensing that will be injected into the body (a truly hostile environment) for non-invasive *in-vivo* diagnostic, as well as chemical and electrochemical treatments.

Self-assembly leads to a highly controlled method of producing nanoscale components for micromachines. Microchannels (Figure 1) can be used to self-assemble biomolecules (e.g., lipids, polypeptides, DNA, and biopolymers) on micro- and nanostructured surfaces. The highly oriented and variable dimension self-assemblies are used as templates for the processing of nano- and microscale inorganic/organic structures; for example, nanowires and nanoconduits.

*Figure 1. An example of variable-width (5000 nm to 500 nm) microchannels (silicon) used for directing the growth of variable-dimension biomolecular self-assemblies. Self-assemblies form templates for nanoscale inorganic/organic structures, e.g., to produce ultrathin wires or nanoconduits to serve as components of micromachines. [Figure courtesy of C. R. Safinya, University of California, Santa Barbara; see also "Structural Studies of DNA-Cationic Lipid Complexes Confined in Lithographically Patterned Microchannel Arrays," Y. Li, G. C. L. Wong, E. J. Caine, E. L. Hu, and C. R. Safinya,* International Journal of Thermophysics *(in press).]*

There is a rapidly increasing demand for biocompatible materials including medical implants and *in-vivo* drug-delivery systems. Companies have reached market capitalizations of over a billion dollars on the strength of simple stent devices. However, it is clear that future development of more sophisticated biomaterials must be based on a precise knowledge of the interactions of organic-polymer surfaces, both with device substrates and with the biological environments in which they operate. Properly designed organic films bonded to silicon, metals, and other substrates may be extremely valuable in preventing immune and inflammatory responses to *in vivo* devices. This applies to products ranging from drug delivery microcapsules to dental implants or more generally, to any material that forms specific boundaries to living surfaces. Conversely, films can be designed that include molecular receptors that promote cell destruction by eliciting strong immune responses at localized sites such as tumors.

Biological systems operate at cell and subcellular dimensions; therefore, material properties including polymer uniformity, thickness, mechanical deformability, permeability, state of hydration, and surface charge must be characterized to dimensions below 100 nm. In a related context, newly developed imprinted polymers are being created with specific features, such as metal ion selectivity, that have tremendous potential use in remediation and sensor technology. At present, these materials lack structural characterization, and thus a better understanding is needed of the metal-ion binding sites within the polymer matrix. What is unique about these materials is that, rather than the local molecular configuration, the long-range polymer structures are the likely key to their behavior. X-ray spectromicroscopy is very well suited to such studies, though enhanced spatial resolution is crucial. Characterization of these advanced miniaturized materials will require the development of an anomalous high-resolution small-angle x-ray diffractometer (5-keV to 10-keV range) with 0.1-μm beam-size capability. It will also require the development of a microdiffraction capability (5-keV to 10-keV range) with spatial resolution of 0.1 μm.

### 2.1.2 Nanoscopic Structures

Slight, nonfavorable, segmental interactions coupled with small entropic gains render dissimilar polymers immiscible. Covalently coupling two polymer chains restricts the separation of the chains to size scales commensurate with the size of the polymer coil. Depending upon the volume fraction of the dissimilar segments in the chain, periodic arrays of nanoscopic structures ranging from spheres to cylinders to lamellae form spontaneously. Controlling the orientation and spatial arrangement of these nanoscopic arrays with electric and magnetic fields and interfacial interactions is key for the incisive use of these structures in applications ranging from electronic devices to membranes to sensors. As an example, consider the diffusion of synthetic or natural macromolecules in solution through a nanoporous membrane comprised of cylinders 2 nm to 3 nm in diameter and tens of nanometers in length. Small-angle-scattering methods, both anomalous and high-resolution scattering, are essential for characterization of the configuration and conformation of the macromolecules in solution and as they penetrate through the membrane. Spectroscopic methods, such as near-edge x-ray absorption fine-structure spectroscopy (NEXAFS) will be key for the *ex-situ* and potential *in-situ* determination of the specific interactions that the macromolecule or associated ions experience at the surface of the membrane and as the macromolecule penetrates through the membrane.

## 2.2 Thin Films

Thin-film polymers have considerable technological importance and have numerous applications (adhesives, low-dielectric insulators in microelectronic circuits, multicolor printing, optical coatings, etc.). As compared to bulk properties, relatively little is known about the properties of polymers when they are processed into thin films. A detailed understanding of thin film properties, such as composition, morphology, viscosity, chain mobility, stability, and possible deviations from bulk properties, is essential for optimization.

Two specific examples are presented. Blends of immiscible and partially miscible polymers can be spun cast from solution onto various surfaces with controlled surface energies. Both the solvent and surface energy will influence the initially formed morphologies during solvent evaporation. Upon annealing, phase separation can occur. In contrast to the bulk, polymer-substrate and polymer-air interfacial energies or kinetic barriers play dominant roles. Experimental and theoretical work on thin films of binary polymer blends suggest large changes in both the phase behavior and dynamics relative to the bulk properties of these blends. A true three-dimensional, quantitative composition-analysis tool would be ideal to study the static and dynamic properties of the films providing a critical test for theories of polymer dynamics. Currently used techniques, such as atomic force microscopy (AFM) can only sense the surface topography and morphology but not the composition. Neutron and x-ray scattering can measure concentration gradients, but they are unable to determine the topography of the polymer-polymer interface unambiguously. Quantitative NEXAFS microscopy (transmission and surface-sensitive modes) provides an excellent complement to more traditional microscopy and reciprocal-space techniques for the elucidation of the properties of thin films.

Another thin-film example is the influence of spatial confinement on the mobility and orientation of polymer chains. In the bulk, the transition from long-range mobility to essentially frozen chains is described by the glass-transition temperature. In small spaces, such as thin films, the chains can "sense" the presence of confining interfaces. Understanding the mobility and dynamics of polymer chains in these situations, as well as the possible influence on material properties, is a considerable challenge that provides great opportunities in polymers, biomaterials, and nanotechnology/nanocomposites involving polymers. NEXAFS, NEXAFS microscopy, and high-resolution scattering and reflectivity can play an instrumental role in these areas.

## 2.3 Surfaces and Interfaces

### 2.3.1 Pattern Recognition

Natural-selection processes rely on intermolecular recognition between molecules that consist, at first glance, of a random sequence of different amino acids. However, an intriguing possibility is that the random sequencing of units actually comprises a statistical patterning of units in the macromolecules. In terms of recognition or interactions between chains or chains and substrate, theory predicts that first-order transitions occur as a function of the composition of the macromolecules and of the probabilities of matching specific sequencing. Synthetic random copolymers in contact with randomly patterned surfaces offer a simple, unique, and quantitative means of understanding rather complex recognition processes. In particular, consider a random copolymer containing only two units where the composition and chain statistics can be varied in the synthesis. Consider, also, a surface that contains complementary interaction sites that are also randomly arrayed on a surface. Maximization of the interactions between the random copolymer and the surface requires optimization of the relative spatial distribution of interacting sites. Elucidation of the kinetics, dynamics, and thermodynamics of this recognition process requires quantitative characterization of the sequencing along the chain and on the surface. The former can be addressed by nuclear magnetic resonance (NMR) methods, whereas the latter requires techniques with the ability to spatially resolve chemically distinct units on a size scale that ranges from one to tens of nanometers. It is also necessary to characterize the specific orientation of chemical units on the surface prior to and subsequent to the chain adsorption. At present, no technique can satisfy these demands. However, x-ray microscopy represents a truly unique means by which these goals can be achieved. The current spatial resolution of x-ray microscopy is on the order of 40 nm. While this resolution is insufficient to address pattern recognition on the molecular level, improving this resolution further will have significant consequences. Even with the current resolution, renormalization of the pattern recognition problem to larger size scales suggests that x-ray microscopy can have immediate impact. The ability to perform site specific spectroscopy with polarized x rays gives x-ray microscopy a significant advantage over any other technique.

### 2.3.2 Polymer Surface Relaxation

The relationship between nanoscopic and microscopic mechanisms and macroscopic spatial- and temporal-frequency-dependent viscoelastic properties of a polymeric material continues to provide an enduring research focus for polymer chemical physicists. To establish and understand this relationship in detail will help to forge a crucial link between polymer structure and properties, thereby facilitating progress in an important array of problems:

- Production of new and useful polymeric materials.
- Understanding the often dramatic ways in which a free polymer surface responds to its environment.
- Optimization of the interfacial mechanical properties of polymer mixtures and ordered copolymer phases.

To formulate this connection requires development of experimental tools having sensitivity over a broad range of both spatial and temporal scales. The primary goal is to determine the microscopic modes of polymer relaxation, such as those that conspire to produce the diverse kinetic and thermodynamic properties often observed. Many such techniques have been successfully developed. Quasi-elastic neutron scattering, for example, has been applied incisively at the length and time scales relevant to entanglement of polymer chains. Dynamic laser light scattering can probe slower phenomena at longer length scales associated with polymer diffusion. Various electron and photon microscopies have been enormously successful in probing polymer morphology over a very large range of length scales but with relatively limited temporal dynamic range. However, no experimental probes have been developed to measure the dynamics of complex fluids on a nanometer length scale at times longer than about 0.1 microsecond. Many interesting and important polymer relaxations (those noted above, for example) occur in this range.

The wavelength range of soft x rays is well matched to the relevant length scales, and the photon energy range of soft x rays is particularly well suited to studies of light elements that are the primary constituents of most polymers. The application of soft x rays to these problems has already started. For example, relaxations near an oriented polymer surface have been probed as a function of temperature and depth using dichroism in polarized NEXAFS spectroscopy. This technique should be further developed and more broadly applied, possibly in a microscopic mode using a focused soft x-ray beam. Another somewhat more exotic experimental approach entails development of dynamic x-ray scattering using a transversely coherent soft x-ray beam. The wavelength dependence of the volume of coherent phase space indicates that, in principle, orders of magnitude more coherent flux is available in the soft than in the hard x-ray regime. In some cases, this translates into an ability to probe dynamical phenomena on much shorter time scales by using dynamic soft x-ray scattering rather than dynamic hard x-ray scattering. Moreover, the possibility of doing dynamic scattering near a threshold for core-electron excitation, the dynamic version of anomalous scattering, will allow selective sensitivity to particular light-atom species and possibly also to particular functionalities. By virtue of its high brightness, the ALS is uniquely suited to develop this new technique.

## 2.4 Engineering Polymers

Engineering polymers have myriad applications: parts for automobiles, dashboards, computer cases, suitcases, etc. The macroscopic properties of these materials are controlled by the nanoscopic structure and chemistry. Key issues in engineering polymers include understanding the microscopic phase structure in blends, compatibilization of multiple phases, fracture mechanics, segregation of additives, adhesion of paints, and adhesion of polymers to other materials. For example, to enhance the adhesion between different polymer phases, a third component is added to strengthen the interface and reduce interfacial tension between the two phases. Soft x-ray microscopy is an excellent method to determine the fate of the compatibilizer. Polymers under tensile stress can be examined *in situ*, allowing the simultaneous tracking of chemistry and microstructure. The kinetics and thermodynamics of the intermixing of phases in polymer blends is also an important phenomena to understand. Other areas include interfacial adhesion in composites and nanocomposites and determining the microscopic structure of these materials. Synchrotron-based analysis techniques can make an important contribution to understanding many of these phenomena.

Scanning transmission x-ray microscopy (STXM) has already made inroads into the quantitative analysis and chemical basis of microscopic phase structure in polyurethane foams used in furniture and car seats. These materials are very complicated, consisting of several different phases. STXM has been applied to spectromicroscopic quantification of polyol, urea, and urethane content in different phases that are sub-micron in size. Currently this technique can be carried out at about 50-nm spatial resolution, whereas many of the interesting phenomena are below 10 nm in size. Achieving 10-nm spatial resolution is based largely on the availability of suitable zone plates. Those currently available do not yet provide the requisite resolution. Advancing the state of the art in zone plate manufacturing is a key technology for advancing STXM and scanning photoemission microscopy (SPEM) at the ALS.

Another area of interest is understanding the spatial variation of crosslink density in gels and other elastomeric materials. Spatial variation in crosslink density may be built into a product, as in the case of super-absorbent polymers. In these materials, a semi-rigid, highly crosslinked shell around the polymer particles helps them to maintain their shape when they are hydrated during use. STXM can be used to determine the variation in the polymer density after swelling the polymer in water. The polymer density, the degree of swelling, and, thus, the crosslink density can be inferred. Studying hydrated polymers is particularly suited to STXM using x-rays in the "water window," the energy between the K absorption edges of carbon and oxygen atoms (285 eV to 540 eV).

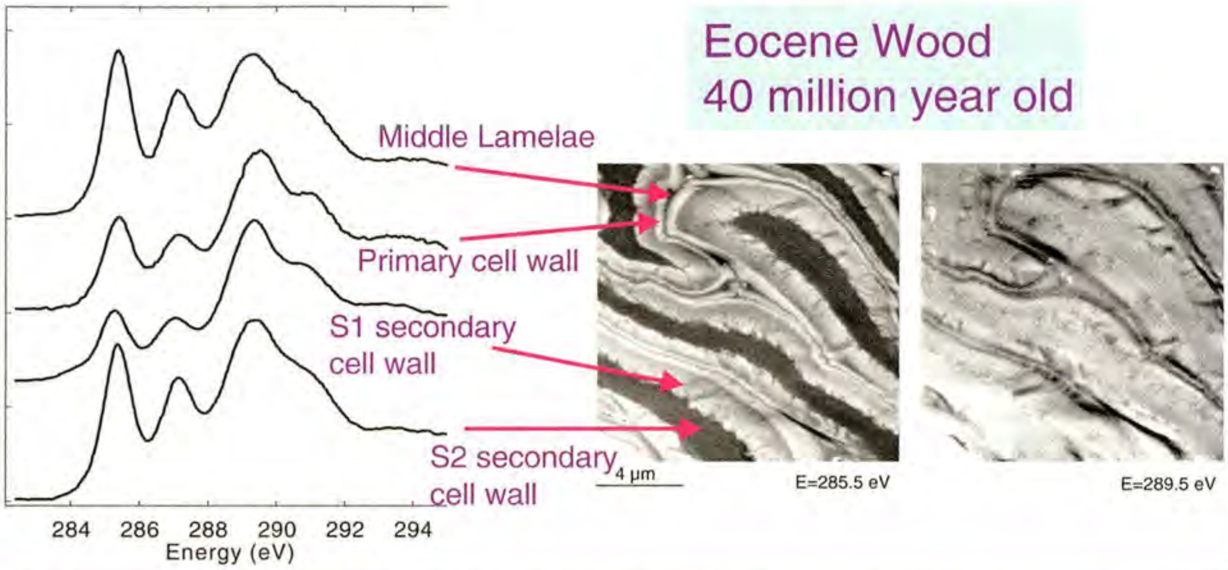
## 2.5 Organic Earth Materials

Chemical characterization of the organic matter included in sediments and sedimentary rocks is of paramount importance to understanding the generation of oil and gas, refining our understanding of the geologic component of the global carbon cycle, and deriving effective strategies for improved technological utilization of solid phase fossil energy resources, e.g. coals. There are currently a number of powerful techniques capable of providing molecular and functional group information on solid-phase organics. However, the chemical structural information obtained is integrated over the entire sample; these methods are incapable of revealing the chemistry within compositionally discrete subdomains. Herein lies the problem, solid-phase organics in earth materials exhibit a high degree of chemical heterogeneity on length scales from tens of nanometers to microns. Understanding the chemistry of these materials requires the ability to obtain molecular structural information at very short length scales. Soft x-ray microscopy and spectromicroscopy provides such a microprobe. Micro-carbon, oxygen, and nitrogen NEXAFS reveals functional group specific information on the appropriate length scales [currently down to 50 nm at Beamline X1A at the National Synchrotron Light Source (NSLS) and 100 nm at Beamline 7.0.1 at the ALS]. The spectroscopic requirements are high energy resolution (0.1 eV or less) transmission NEXAFS on the nitrogen, carbon, and oxygen K edges. Ideally, NEXAFS on either the sulfur K or L edges would also be desirable.

The intrinsic polarization of the synchrotron x-ray beam is also extremely useful in study of progressive graphitization of organic matter in thermally metamorphosed rocks. A related question involves the elucidation of the mechanisms and phase chemistry of nematic phase transitions in organic glasses and heavy liquids (a major technological issue in the fabrication of carbon electrodes and metallurgical cokes). Suppression of nematic phase development is crucially important in petroleum refining. X-ray linear-dichroism studies have the potential to resolve long standing problems in both organic geochemistry and fuel chemistry.

The ability to interrogate the organic structure within carbonaceous chondritic meteorites has become a very important issue in cosmochemistry. It is now well established that a broad range of molecular and macromolecular organic matter was synthesized in the pre-solar nebula. It has been speculated by some that this organic matter may have seeded the primordial earth, leading to the genesis of life. What is poorly understood is the organosynthesis mechanisms. It will be crucially important to characterize the organic matter in these meteorites *in situ*; issues related to spatial chemical heterogeneity and organic-inorganic associations will require the capabilities of x-ray microscopy.

The current instrumental capabilities (e.g., STXMs at Beamline X1A at NSLS and Beamline 7.0.1 at ALS) have already shown the potential to revolutionize the field of organic geochemistry and fuel chemistry. The only limitation is experiment time. The present x-ray microscope facilities are over subscribed—a situation that is guaranteed to become substantially worse. The proposed ALS bend-magnet beamline and STXM, to be dedicated to natural and synthetic polymer research, is designed to address these needs. Even this facility, however, will rapidly become over subscribed. The ALS has the potential to become the home of the premier soft x-ray microscopic and spectromicroscopy facilities in the world. This would ensure the ALS's participation in the rapidly evolving fields of organic geochemistry and fuel chemistry.



- Also, spectacular data on evolution of coke → metallurgical coke, steel production
- Followed evolution of sporopollenin in coal → may address mechanism and timing of oil generation

*Figure 2. The data shown are from wood 40 million years old that was recovered from a remarkable "preserved" deposit of ancient wood in the eastern arctic region of Canada. Although the wood has evolved chemically into a coal-like material, the spectacular chemical differentiation intrinsic to the original cell-wall structure persists. The image on the left was acquired with 285.5-eV photons. Absorption at this energy corresponds to aromatic $1s \rightarrow \pi^*$ transitions, thus the image contrast maps out the distribution of the biopolymer lignin. The image on the right is of the same region acquired with 289.5-eV photons. Absorption in this energy region is largely due to the $1s \rightarrow 3p/\sigma^*$ transitions associated with secondary alcohols in carbohydrates. Carbon NEXAFS spectra of the various chemically differentiated regions reveal the large differences in the chemistry of organic functional groups from region to region. [Data acquired by G. Cody et al. of the Carnegie Institution Geophysics Laboratory on the STXM at Beamline X1A at NSLS.]*

## 3. Requirements for Success

### 3.1 ALS/Industry Partnership: Key Elements for Sustainable Success

The construction and utilization of the x-ray microscopy capability at the ALS has, within a relatively short time frame, enjoyed an outstanding level of success in extending the reach of technologies for the microanalytical characterization of materials. In particular, the spectromicroscopic (< 100 nm) characterization of soft materials (biological and synthetic polymers) has opened the door for exciting value-added research that will most certainly benefit society in many ways. However, before value generation/capture can be optimized, several issues must be addressed that relate to the involvement of industry in the visioning, development, implementation, and sustainability of these x-ray microscopy technologies.

Considering the pressures that industry faces to maximize shareholder value, it should come as no surprise that industry, in general, has aggressively reduced its structural costs, shortened its product-development time horizon, and decreased its tolerance toward higher risk/lower potential-return opportunities. In other words, businesses want it faster, cheaper, and more often—all with increased odds for success. In spite of this, the importance of industry in influencing scientific discovery and in developing value-contributing technologies has never been so high.

With these factors as a backdrop, it behooves the ALS to form multiple and substantive partnerships with a diverse industrial partner base. To this end, it is necessary to:

- Identify key industrial partners early on (i.e., while still in the concept phase of a technology) and work toward cultivating mutually beneficial relations.
- Minimize industry's risk through the "seeding" of key technologies that are jointly identified with potential industrial partners.
- Increase industrial-partner access to ALS facilities. It is not only important to obtain beam time but also to receive it in "packets" that are useful to the industrial investigator, e.g., contiguous shifts rather than singular shifts.
- Increase the quantity of beamline support personnel that can help in the experiment set-up and breakdown, the collection of data, and the maintenance/development of instrumentation
- Encourage the formation of participating research teams (PRTs) between academia, industry, and the ALS, including minimizing hurdles (e.g., cost, bureaucracy, and paperwork).
- Provide rapid access to facilities (i.e., in many cases, the problem needs to be solved rapidly and cannot wait several weeks or months for future access).

## 3.2 Dedicated Science-Driven Beamline for Users

A specialized, dedicated beamline has proven to be more effective for less-experienced users and can save substantial time for instrumentation set-ups where change-overs often require expertise in alignment of x-ray optics and other components. Such is the case, for example, for small-angle x-ray scattering. Thus, beamlines for polymers and soft-condensed-matter research should be dedicated ones which are designed to be user friendly and well supported by staff. A well-run beamline will permit the users to concentrate all of their beam time on science instead of on solving instrumentation problems, thereby improving the effectiveness of the facility. As stated previously, this point is particularly relevant to industrial users, who often have limited time and support personnel to carry out the assignment.

Interesting and unique materials are prepared by scientists and engineers whose expertise is inclined towards chemical and biological disciplines. It is very important to have better communication and to provide educational opportunities for the participants of multidisciplinary experiments so each participant can appreciate the capabilities and the limitations of what the others can do. Aside from workshops, one approach is to provide financial support for user experiments, especially the beginners. In particular, adequate support and encouragement should be made available to those who have good ideas to do important science. By doing so, synchrotron utilization can be expanded to a broader scientific community and more effective use of synchrotron radiation to society will be achieved.

# 4. What Role Can the ALS Play?

## 4.1 Key Techniques for Polymers, Biomaterials, and Soft Matter

The following list gives the key techniques and their currrent characteristics, along with projected performance improvements:

- **STXM** (Scanning Transmission X-Ray Microscopy)
  Zone-plate focusing at 50 nm, improving to 10 nm. C, N, and O edges. Many applications also exist for STXM in the intermediate energy region (1 keV to 5 keV).
- **PEEM** (Photoelectron Emission Microscopy)
  100-nm spatial resolution, improving to 2 nm at the most critical C, N, and O edges.
- **XPS and SPEM** (X-Ray Photoelectron Spectroscopy and Scanning Photoelectron Microscopy)
  High resolution XPS analytical capability and SPEM at 100-nm spatial resolution improving to 10-nm.
- **SAXS and ASAXS** (Small Angle X-Ray Scattering and Anomalous SAXS)
  SAXS and ASAXS in photon-energy range from 2 keV to 10 keV.
- **Microdiffraction**
  Microdiffraction at 1-μm spatial resolution, improving to 10-nm in photon-energy range from 2 keV to 10 keV.
- **Dynamic Scattering**
  Dynamic scattering facility at grazing incidence using coherent soft x-ray illumination.
- **TXM** (Transmission X-Ray Microscopy)
  TXM in short term at 50-nm resolution until high-resolution STXM is available.

## 4.2 Soft X-Ray Spectromicroscopy

As stated in the Birgeneau panel report, "For any polymer that has been processed, x-ray microscopy comes to the fore as an ideal tool for characterization." Soft x-ray spectromicroscopy is one of the most promising ways in which the ALS can have an impact on the scientific issues in polymer science and soft matter that were discussed in the previous sections. Many areas of impact exist based on the chemical and orientational sensitivity at high spatial resolution afforded by transmission NEXAFS microscopy of thin films and microtomed sections. The excellent surface sensitivity and high spatial resolution provided in a PEEM and SPEM, and possibly in STXM operated in total electron yield mode, also hold much promise. Already, there is a strong PEEM project at the ALS; a STXM and SPEM exist at Beamline 7.0.1; a microXPS and microdiffraction facility is coming on-line; and a dedicated Polymer STXM is going to be installed at Beamline 5.3. This will be the most complementary and complete set of instrumentation available for x-ray microscopy of polymers world wide, and the ALS should fully capitalize on this leadership.

However, only the polymer STXM is intended as a facility dedicated to polymer science. The Beamline 7.0.1 STXM and SPEM are available at best for a combined one-fifth of operation time for all subfields of science and the Beamline 8.0 PEEM for about one-third for all subfields of science. Synchrotron-radiation facilities are underutilized by polymer scientists despite their great potential for polymer characterization. While there are several reasons for this, complex multi-user and multi-experiment facilities can be singled out as the major deterrent for a polymer scientist to become a user. It is thus important that sufficient attention and support be provided to the planned dedicated polymer STXM to make it a user-friendly dedicated facility, while microscopy improvements are further pursued at the Beamline 7.0 microscopes and on the proposed Beamline 6.0 STXM. Instrument development and user operation have to be decoupled if the present potential barrier to new users from the field of polymer science and related fields is to be overcome.

Only the ALS is bright enough to use a bend magnet as a source for a microscope based on diffractive optics such as STXM. It is, therefore, the only facility in the nation that will be able to provide much needed STXM capacity. Since a bend magnet beamline is relatively cheap, it is conceivable that several STXM might be operated at the ALS in the future.

It is also desirable that the currently proposed STXM at ALS undulator Beamline 6.0 be co-developed by the various communities at the ALS, including the polymer-science community. A bend-magnet STXM will provide capacity, while only the Beamline 6.0 STXM will provide ultimate performance. Both are necessary and complementary developments.

## 4.3 Microdiffraction, SAXS, and ASAXS

The availability of an anomalous-microbeam-small-angle x-ray scattering and diffraction spectrometer is also critical for research on polymer, biomaterials, and soft matter. The instrument should be capable of probing self-assembling structures on scales spanning 0.1 nm to 1000 nm.

# Working Group on Nanostructures and Special Opportunities in Semiconductors

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## 1. Introduction

Reduced dimensionality and nanostructures, in particular, are themes cutting across several of the reports of the working groups. Nanostructures are low-dimensionality material systems whose size is intermediate between that of atoms or molecules and that of bulk solids. (A nanostructure may be defined as any structure with at least one dimension of order 1 nm.) These novel materials, which modern techniques of synthesis and processing can now produce, have physical and chemical properties that are different from those of the bulk parent compounds and also from those of the constituent atoms and molecules. The properties are strongly dependent upon size and shape. These properties are controlled by quantum size effects, altered thermodynamics and, modified chemical reactivity.

Generally, the interest in understanding nanostructures is focused on the ability to modify materials so that they have properties unavailable in bulk-process materials. These include the electronic, structural, magnetic, optical, superconductive, transport, ferroelectric, and electron-lattice properties of the materials. Examples of nanostructures include quantum dots; nanocrystals and clusters; large molecules and buckyballs; onions; nanotubes, nanoropes, and nanoribbons; and a variety of materials with reduced geometry. They can be free standing, capped by protective layers, or embedded in matrices.

Nanoscience is evolving at a fast pace, and the number of projects in nanoscience research being undertaken by physicists, chemists, materials scientists, and biologists is increasing rapidly. Because this area of inquiry is concerned with a length scale that is of interest to all these disciplines, there are excellent opportunities for collaboration. In addition to the basic scientific questions of how materials behave at the nanometer scale, research in nanostructures opens new opportunities for the design and optimization of properties for specific technological purposes and applications.

An understanding of electronic structure in small confined geometries has obvious importance in electronic, optoelectronics, and memory devices (Figure 1). Structural properties of materials and knowing how to influence their bulk properties are of interest. In addition, the general area of understanding inorganic structures related to biological materials is of great importance.

This working group considered the possible applicability of the ALS to probing these properties of nanostructures on, or beyond, the performance level of currently available techniques. (Examples of currently available techniques are scanning probes, various means of studying transport, lasers, conventional spectroscopy with soft and hard x-rays, electron microscopy, and optical reflection and absorption.)

In addition to nanoscale studies of materials, the ALS offers novel opportunities for studies of small material samples at extreme hydrostatic pressures in diamond-anvil cells over a wide range of photon energies (infrared through soft x-ray). The ALS also enables tunable-ultraviolet studies of wide-bandgap materials, especially the Group III nitrides. Scientific opportunities in the infrared (IR)-visible-ultraviolet (UV) continuum are especially attractive for two reasons: first, only a simple, inexpensive beamline is needed; and second, the Berkeley location of the ALS offers excellent opportunities for collaboration with researchers in many different disciplines.

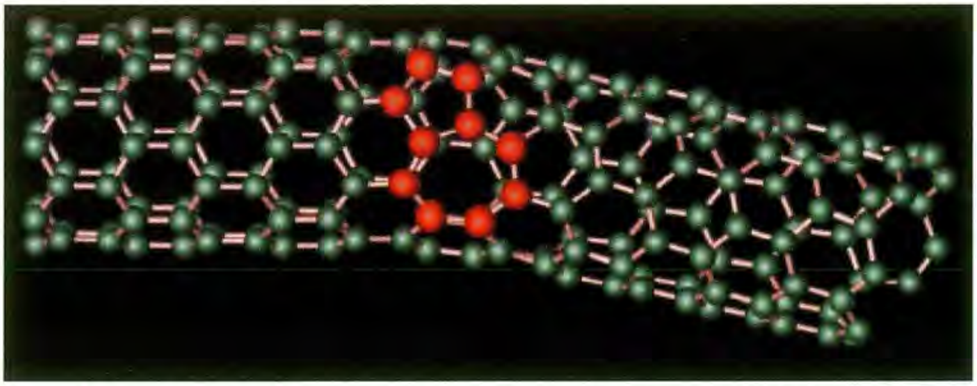

*Figure 1. A metal-semiconductor junction of carbon nanotubes. Theoretical calculations [L. Chico, V. H. Crespi, L. X. Benedict, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. 76 (1996) 971] show that a pair of five- and seven-membered rings changes the helicity of the carbon nanotube and thus joins a metallic segment to a semiconducting segment to form a nanoscale Schottky barrier. [See also "Mixing Nanotube Structures to Make a Tiny Switch," R. F. Service, Science 271(1996) 1232.] Recently there has also been experimental observation of such on-tube device behavior by A. Zettl's group at the University of California, Berkeley. [Figure courtesy of the research groups of M. L. Cohen and S. G. Louie at the University of California, Berkeley.]*

# 2. Opportunities in Nanostructures

## 2.1 Tailored Properties

Franz Himpsel (leader), University of Wisconsin–Madison; Christoph Bostedt, Lawrence Berkeley National Laboratory; Wolfgang Eberhardt, Forshungszentrum Jülich; Steven G. Louie, University of California Berkeley; Jan Luening, IBM Almaden Research Center; Bruno Reihl, Paul Scherrer Institute; Tony van Buuren, Lawrence Livermore National Laboratory.

### 2.1.1 What Are the Interesting and Important Scientific Questions?

We earlier defined a nanostructure as any structure with at least one dimension of order 1 nm, whatever its extent in the other two dimensions. However, conceptually there are two types of nanostructures. One type of structure is based on confining electrons by changing the boundary conditions. The size of such an object is of the same order as the wavelength of an electron. The other type is even smaller and may be viewed as a large assembly of atoms in which not only the boundary conditions but also the Hamiltonian differ from those of a bulk material. It may be thought of as an object consisting only of interfaces with no bulk behind them. This interface nature has ramifications, such as optical properties determined by surface states and many-body effects, that give such materials different properties than bulk materials that are nanoscale in only one dimension.

The lower dimensionality of some structures (e.g., one-dimensional lines) causes qualitative changes in the way electrons behave. For example, in one dimension, the Fermi-liquid model does not apply, and electrons can separate into charges and spins. In essentially zero-dimensional objects that are confined in all three directions and are of size comparable to an electron wavelength, the electronic structure is a function of the number of atoms and electrons in the system.

In nanostructures, one can exert a level of control over structural detail (e.g., electron wavefunctions) that is not available in bulk materials. An example is making a $C_{60}$ (or other fullerene) film instead of a diamond or graphite film. Much of the appeal of making nanostructures is the ability to tailor a material's properties by manipulating wavefunctions. One way to do this is by confining electrons to physical dimensions comparable to their de Broglie wavelength (Figure 2). This occurs in quantum wells, for example.

Even structures larger than a quantum well, such as clusters, can be dominated by electrons at surfaces and interfaces that are in completely different electronic states than would be encountered in bulk materials. Covalent bonding can change to metallic bonding and vice versa. Screening and other many-body electronic interactions can also dramatically change.

Which electrons are relevant? For some properties, the ones within kT of the Fermi level are of greatest importance—for example, in a Stoner-criterion model for ferromagnetism and in the conventional formulae for the critical temperature $T_c$ of superconductors. For other aspects, such as optical properties, electron states at the band edges and multi-electronic excitations like plasmons are the important contributors. This is a key difference between metals and semiconductors. For the smaller types of clusters, the full orbital structure will become important. Strain and local crystallography can be used to tune properties of embedded nanostructures.

These are questions of great potential importance to science and technology. By tailoring electronic structures, we can control the behavior of materials, including their magnetic, optical, superconductive, transport, and other physical properties. For example, the first nanostructures created by man (as we know in retrospect) were stained-glass windows and other colored glasses. A recent high-technology example is the giant magnetoresistance (GMR) technology used for the latest hard-disk read

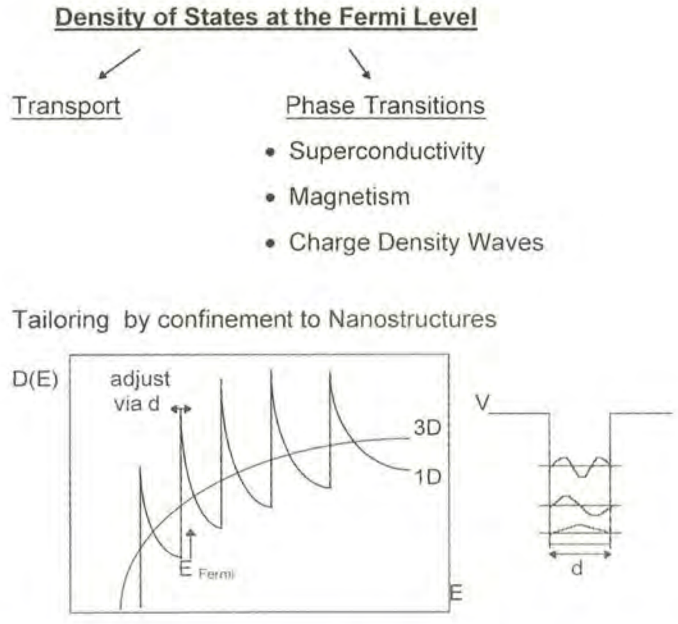

*Figure 2. The density of electron states at the Fermi level determines many properties of materials. By physically confining electrons to small areas in one or more dimensions (nanostructures), the density of states, and thus the materials properties, can be tailored. [Figure taken from F. J. Himpsel, J. E. Ortega, G. J. Mankey, and R. F. Willis,* Advances in Physics *47 (1998) 511.]*

heads (Figure 3). The gate oxide in silicon MOSFETs, as used in most integrated circuits, is another example. A third example is the quantum-well laser that has become ubiquitous in modern life. Nanostructures will be even more important in future devices that are based on single-electron switching.

Chemical reactivity in the most general sense is an electronic-structure effect. And we merely note in passing that the Working Group on New Directions in Surface and Interface Science is reporting on heterogeneous catalysis, which occurs on nanostructured surfaces.

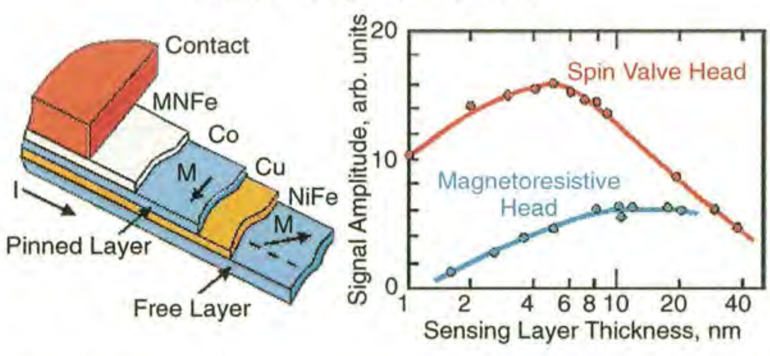

*Figure 3. Structure of a giant-magnetoresistance spin-valve read head for hard disks. It exemplifies the way that nanostructures are becoming ever more important as enabling technologies behind the items of everyday life. [Figure courtesy of Ed Grochowski and Virgil Speriosu, IBM.]*

### 2.1.2 What Role Can the ALS Play in Advancing the Field?

Some critical applications of synchrotron radiation in nanostructure science are:

- Identifying the atomic structure of interfaces, wires, and nanoparticles. Soft-x-ray scattering reveals just the right Fourier components, the ones that are most relevant to the confinement of electrons. The ALS is particularly appropriate because it readily produces radiation whose wavelength is about the size of nanostructures. Particularly useful in soft-x-ray scattering are the L edges of the magnetic metals in the IIId column of the periodic table; these edges make it possible to determine the atomic and magnetic structure of interfaces, in element-sensitive fashion, via resonant x-ray scattering.
- Determining the relevant electronic states at the Fermi level by high-resolution photoemission spectroscopy. Here again, resonant photoemission at the M edge of the IIId metals and the d-to-f resonance of the rare earths and actinides allows experimenters to achieve elemental specificity.
- Determining magnetism of nanostructures via soft x-ray magnetic circular dichroism (XMCD). A critical issue will be the sensitivity of XMCD to sub-monolayer quantities and to buried interfaces. One suggestion is to use XMCD in conjunction with core-level fluorescence spectroscopy. XMCD can provide semi-quantitative data on the orbital and spin moments, separately for each element, in nanostructures. This is impossible with traditional techniques, such as neutron scattering, that require a macroscopic amount of material.

Soft-x-ray emission spectroscopy as an experimental technique benefits tremendously from the brightness advantage of a third-generation synchrotron light source such as the ALS. This technique is ideally suited to studying the electronic structure of nanostructures on surfaces, embedded clusters, clusters with a ligand shell, or buried interfaces. The experiments that can be performed include measuring energy levels and band offsets that are not accessible to traditional optical experiments.

All of these techniques have thus far been applied to arrays of nanostructures all the same size. It seems likely that the ALS will soon have unique spectromicroscopy techniques that can examine individual nanostructures.

## 2.2 Synthesis/Fabrication of Nanostructures and Architectonic Materials

Stan Williams (leader), Hewlett-Packard Laboratories; Jason Guo, Stanford University

### 2.2.1 Scientific Issues in Synthesis/Fabrication

New functionality that depends upon size and shape emerges as materials are prepared with nanometer dimensions. These new characteristics may involve electronic, optical, structural, chemical, or even biological properties of matter. Quantum confinement strongly perturbs the energy level structure of semiconductors, metals and ferroelectrics, and can enable their properties to be tuned to optimize them for particular applications. Elemental carbon can be made semiconducting, metallic or even superconducting, depending upon the atomic structure of the individual moieties (chemical states) and the doping of aggregate configurations. Organic nanostructures may be created that can transport medicines through the bloodstream or even through cell walls to target specific organs or diseases. Composite nanostructures that combine two or more functionalities provide fascinating possibilities for totally original applications.

Each class of material presents unique challenges for the fabrication of nanostructures. For most of the systems currently under consideration, one ideally wants to manufacture large amounts of nanostructures with essentially identical sizes and shapes (Figure 4). For the most part, this involves

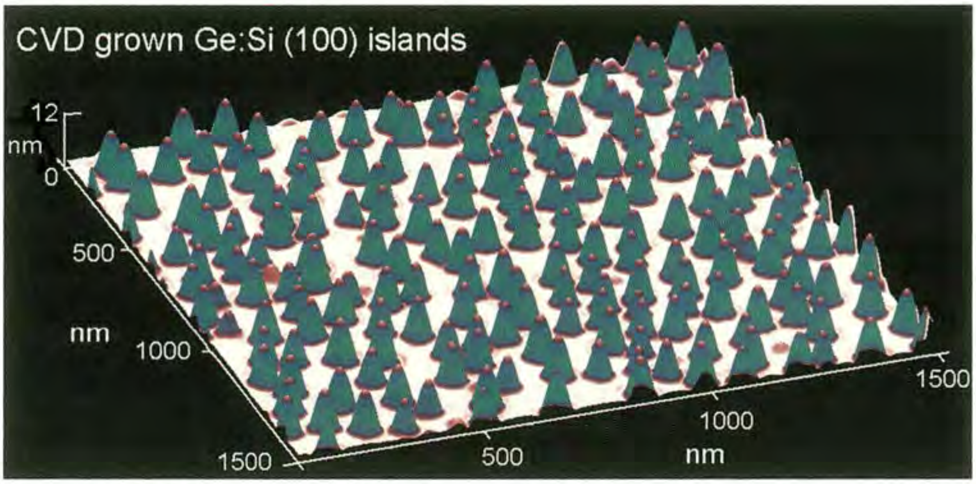

*Figure 4. A thick film grown by CVD and measured ex-situ by atomic force microscopy (AFM) shows very good size uniformity. [Figure courtesy of the research group of Stan Williams, Hewlett-Packard Laboratories.]*

chemical syntheses that are sometimes described as "self-assembling" if they can be designed to produce the desired products simply by the control of reaction conditions. It may also be desirable to fabricate structures that can change their size or shape predictably under the influence of an external stimulus. For some applications, independent nanostructures will be sufficient, but for many others it will be necessary to position specific nanostructures at well-defined locations on a substrate or to create larger-scale constructions to form architectonic (purposely designed) materials that may in turn be a part of a larger device or system. In these latter cases, the connectivity of the superstructures will be extremely important, and if connectivity is achieved by controlling the interaction chemistry of the nanostructures, the process is known as self-organization.

As with any synthesis process, there must be rapid feedback between the steps of the synthesis and the characterization of the intermediates, as well as the final target structure. Ideally, the characterization procedure provides direct physical or chemical information on the desired properties of the nanostructures—information that can be used to select or adjust synthesis conditions and that also yields data that can improve the theoretical understanding of the process for planning future syntheses. For example, at the present time, those who synthesize nanocrystal semiconductors use optical absorption and fluorescence to characterize their materials, since often the optical properties are the most relevant. The positions of peaks in the spectra are related to the size of the nanocrystals, and the width of the peaks can contain information about the size dispersion. However, other materials do not have such convenient optical signatures, or the signatures may be ambiguous, and for those a direct determination of the size, shape and arrangement of the nanostructures is necessary. For these systems, direct imaging with either transmission electron microscopy or scanning probe microscopy are the primary methods currently employed (Figure 5). However, both techniques are fairly slow, and the analysis of the data can be labor-intensive and cumbersome.

### 2.2.2 The Role of the ALS

The ALS can play a very important role in optimizing procedures for synthesizing and organizing nanostructures. The scattering of soft x rays, which have wavelengths on the order of nanometers, depends very strongly on the size, shape, and connectivity of nanostructured samples and automatically provides information on averaged properties of the scattering target. Also, the extremely low emittance of the ALS allows the use of beams with very high intensity with small spot sizes. These are

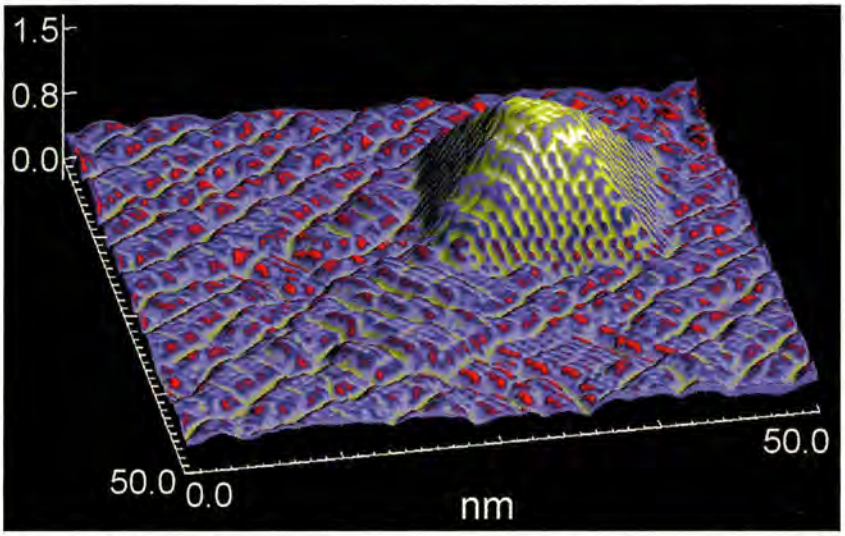

*Figure 5. High-resolution scanning tunneling microscope (STM) image made under ultrahigh vacuum after growth of a 4-µm-thick film of germanium on a silicon (001) surface. [Illustration courtesy of the research group of Stan Williams, Hewlett-Packard Laboratories.]*

necessary to analyze large combinatorial libraries of nanostructures in reasonable times. Using techniques currently under development for drug and materials discovery, it will be possible to prepare substrates that hold more than 100,000 discrete samples, each of which is of order 10 µm square. Using a soft x-ray scattering system at ALS, it will be possible to collect forward- and back-scattering data on all of these samples and utilize a computer-automated analysis and sorting process to rapidly identify promising leads from the library. Depending on the samples and the properties for which one is screening, the soft x-ray scattering can be made specific to elements and even to chemical states by using radiation at a particular absorption edge, as discussed in Section A. The scattering can also be made sensitive to other properties, such as dichroism. After selecting the most interesting samples from the library, they can then be examined at or near the individual nanocrystal level using high-resolution photoelectron spectroscopy and other techniques, depending on the properties of interest. Again, the soft x rays in the photon-energy range from 100 eV to 1000 eV are ideal for limiting the collected photoelectrons from the outermost nanometer or so of the structures.

In order to accomplish these objectives, new end stations and sample-handling techniques will be required. In general, an end station cluster that can handle large wafers will be required for the soft x-ray scattering and other techniques. Also, sample transfer and cleaning techniques will be required. In general, the syntheses and library construction will be performed at a remote location, perhaps even in a different country. The samples then need to be transported to the ALS in a clean environment, perhaps in a container known as an ultrahigh-vacuum suitcase. Such suitcases need to be compatible with the ALS end station, so that samples can be transferred into them without exposure to atmosphere. In addition, it may be necessary to clean the samples once they have been introduced into the end station, to remove some contaminants. Careful thought in the design of end stations and sample handling can make the ALS accessible to a very large community of scientists, who in principle could send their samples to the ALS by means of an overnight-shipping company and receive their data through the World Wide Web. This makes possible the screening of millions of possible systems per year in each of a large number of laboratories. Such analytical feedback would have a profound effect on the progress of nanostructure and architectonic materials synthesis.

## 2.3 Embedded Nanostructures and Synergy between the ALS and the National Center for Electron Microscopy (NCEM)

Uli Dahmen (leader), Lawrence Berkeley National Laboratory; John Spence, Arizona State University

### 2.3.1 Properties of Embedded Nanostructures

It is now well known that nanostructured materials exhibit many novel, useful, and often exotic properties. However, it is less-widely appreciated that when embedded within a solid, nanostructures may have very different properties. A solid matrix may be used to distribute, orient, or constrain an array of nanocrystals, to isolate them from their environment, or to aid in their synthesis. In turn, a dispersion of nanoscale inclusions has a major effect on the host matrix, an effect that is the basis of dispersion hardening in alloys. Understanding embedded nanostructures is therefore of great fundamental and technological interest.

Unlike free nanocrystals, nanocrystals embedded within a crystalline solid are subject to elastic and crystallographic constraints from the confining solid, which can have a large effect on their behavior. For example, noble gases such as xenon, under confinement in an aluminum matrix can form solid nanocrystals at room temperature. Similarly, while free-metal and semiconductor nanocrystals exhibit a strong depression of their melting point, embedded nanocrystals often show a large superheating that depends on orientation, size. and shape. The size and shape of small inclusions must conform to the embedding matrix: the size must be compatible with the constraints of the two discrete lattices (the inclusion and the matrix, as in Figure 6), and the equilibrium shape must conform to the bicrystal symmetry given by their orientation relationship. In the nanoscale regime, size and shape in turn control the properties. Advances in understanding of the fundamental properties of embedded nanoscale structures opens up opportunities for the discovery of new phenomena and could hold the key to the development of new material.

Nanostructures that are embedded within a solid are of great practical and fundamental scientific importance. Nanoscale precipitates control the strength of all dispersion-hardened alloys such as aluminum- or copper-based alloys, lightweight alloys for energy-efficient transportation, or in some cases high-temperature alloys. Dispersion hardening remains a topic of great importance for materials science. Because of its high spatial resolution, electron microscopy (TEM) is the tool of choice for direct observation of individual nanocrystalline inclusions. However, the environment of solute atoms before or during nucleation of a new phase is not accessible to TEM techniques and hence far less is known about clustering that occurs before the formation of a critical nucleus, which is an embedded nanocrystal. The immediate environment of solute atoms before precipitation is an important unresolved question. The average size, shape, and atomic environment of a pre-precipitation cluster of host-lattice vacancies and solute atoms are of fundamental importance to understanding the nucleation of new phases. Any technique that could shed new light on solid-state nucleation would have a major impact on materials science.

Intergranular films are nanostructures under solid constraint from the adjacent grains in a polycrystalline material. The understanding and control of intergranular films is of tremendous importance for bonding, solidification and sintering of materials. In ceramics, intergranular films control the mechanism of sintering during synthesis and the mechanical, thermal, and electrical properties during service. To understand the relationship between the physical and chemical properties of such films and their constraint in the nanoscale space between solid grains would allow important advances in joining, processing, and performance of ceramics. It would therefore be of great value to determine the structure of such intergranular films, especially at elevated temperatures where their interaction with the adjacent crystals establishes the microstructure.

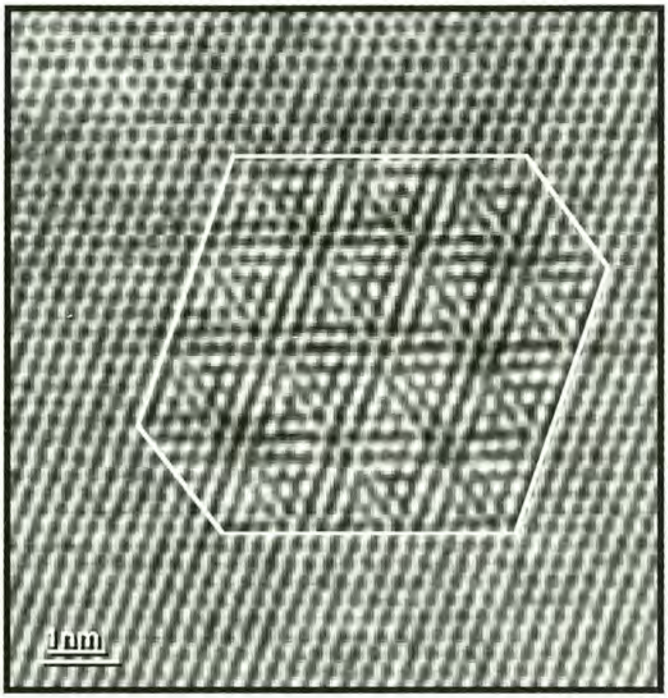

*Figure 6. Atomic-resolution electron micrograph of lead nanoparticle 5 nm in size (outlined) embedded in an aluminum matrix. Because of constraints from the solid matrix, such embedded nanoparticles follow a magic size sequence, are aligned with the matrix lattice, adopt faceted equilibrium shapes, and superheat by up to 100° C before melting. [Figure courtesy of Uli Dahmen, Lawrence Berkeley National Laboratory.]*

### 2.3.2 Opportunities for Synergistic NCEM/ALS Research

At present, very few investigations take full advantage of the combined characterization capabilities that exist with synchrotron and microscopy facilities. There are many opportunities for such synergistic research wherever the high *spatial resolution* of TEM imaging and the statistically averaged accuracy of x-ray spectroscopy with high energy resolution from x-ray diffraction complement each other. This includes all research where microstructure is important, i.e., most of materials science. An atomic-resolution image of a nanoscale structure is often an invaluable complement to an x-ray study. TEM can resolve structure to the 1-Å level and is excellent for global imaging. However, TEM does not provide good statistics and has only moderate [e.g., 0.5 eV for energy-loss spectroscopy (ELS)] spectral and temporal resolution. Combined experiments using TEM and synchrotron facilities would be of great advantage for understanding surfaces and buried interfaces, defect structures and the mechanisms and dynamics of solid-state phase transformations.

Perhaps the best way to illustrate the synergy between x-ray diffraction techniques and TEM is via the mechanical properties of crystals, which are determined both by a crystal's structure and by its defects. X-ray diffraction is the best tool to determine crystal structure, while TEM excels at determining its defect distribution. Both are necessary to understand the deformation behavior of crystals. A similar synergy exists for many different characteristics of materials, and some specific examples are outlined below.

One of the most important features of engineering materials is the structure of internal or buried interfaces and their defects. Internal interfaces, such as grain boundaries or heterophase interfaces, control the mechanical, magnetic, electrical, and corrosion properties of materials. While the structure of interfaces is responsible for many of their global characteristics, it is the interfacial defects that often control their behavior, in much the same way as dislocations control the mechanical behavior of bulk crystals. Thus, opportunities for combined projects exist in the general area of solid-solid interfaces where synchrotron radiation can solve global structures and TEM can identify the local structure and distribution of defects. The challenge in this field is to match the enormous advances of surface science that were made possible by new surface-science instrumentation and techniques in the last two decades. Solid-solid interfaces may be considered a joining of two surfaces, resulting in phenomena that parallel those of surfaces plus an additional set of new phenomena that result from bi-crystallography (the color crystallography of two single crystals joined with a given orientation relationship). As a consequence, interfaces should exhibit the full array of phenomena now known for surfaces, such as roughening, faceting, premelting, adsorption, and reconstruction, plus a new set of phenomena specific to interfaces, such as translation, dissociation, strain fields, slip transfer, interfacial films, special bonding states, and new features yet to be discovered.

Opportunities for synergistic TEM/synchrotron research extend to the study of dynamic phenomena such as domain motion in ferroelectric, magnetic, or martensitic crystals, and phase transformations, such as corrosion, wetting, or melting. For example, high-temperature, high-resolution TEM is able now to observe a size-dependence of melting in nanocrystalline inclusions. However, the dynamics of this process are beyond the current temporal resolution of the technique, and it is unclear whether the observed effect is due solely to size or also depends on shape. Pulsed x-ray diffraction and spectroscopy resolution would be able to provide complementary accurate information on the melting process with better than nanosecond resolution. Conversely, domain configurations evolving during the growth of magnetic thin films could be followed dynamically in a spin-polarized low-energy electron microscopy (LEEM), while complementary spectroscopic information is obtained by photoelectron electron microscopy (PEEM). This would combine the high spatial resolution and global-imaging capability of electrons with the spectroscopic capability of the ALS and thereby afford a unique opportunity for understanding fundamental questions in the rapidly emerging field of thin-film and surface magnetism.

Other opportunities for the complementary use of synchrotron and TEM facilities exist in the area of defects and their atomic, electronic, and elastic structure. In most circumstances defects control the properties of materials, and it is of fundamental importance to understand their structure. The atomic structure of defects may be solved in some cases by atomic-resolution TEM. By synthesizing model samples containing a high density of similar defects, complementary high-resolution spectroscopic information may be obtained on the synchrotron. Both types of information, atomic and electronic structure, can then be used to refine electronic-structure calculations. Similarly, convergent-beam electron diffraction may be used to map elastic strain fields on the nanometer scale by TEM. Microdiffraction using hard x rays may be used to study the same system on a sub-micron scale. Both types of information, on the sub-micron and nanoscale, are needed in many industrial applications. In crystallographic studies, TEM may be used to characterize the defect structure of crystals whose structure is to be "solved" by x-ray diffraction In addition, for the study of bonding in crystals, one may use electron diffraction to measure low-order structure factors (where it is more sensitive than x rays), but use x-ray methods to measure the high-order reflections, where they are most sensitive.

## 3. Special Opportunities for Semiconductor Research at the ALS

Eugene E. Haller (leader), Daniel Chemla, and Steven Louie, University of California Berkeley; Joel W. Ager, Michael Martin, Wei Shan, and Wladyslaw Walukiewicz, Lawrence Berkeley National Laboratory

The ALS offers continuously tunable, high-brightness radiation from the infrared through the ultraviolet. The relatively low cost of exploiting this frequency range, together with the broad appeal to researchers in many fields, makes semiconductor research a high priority for the ALS. In the following sections we discuss two especially attractive areas of research that are of current interest and that take advantage of the unique attributes of the ALS.

### 3.1 Wide-Bandgap Material Studies at the ALS

Optical properties of wide-gap materials present new challenges to researchers who have studied standard semiconductor systems at photon energies below 3.5 eV. "One-electron" (weakly correlated) systems with wide bandgaps include the group III-V nitrides, $SiO_2$, $Si_3N_4$, SiC, and MgO. Strongly correlated "many electron" systems with wide gaps include NiO and $Cr_2O_3$ (discussed in the report of the Working Group on Complex Materials). The properties of these materials are determined by strong electron-electron correlation. Despite the vast number of color-center studies with alkali halide crystals that were performed over 30 years ago, the bulk optical properties of these materials are still poorly understood. In fact, all the wide-bandgap materials have been less well studied than the smaller bandgap materials, in part because of the lack of experimental tools that function in the appropriate spectral range. Optical studies with intense, continuously tunable UV radiation (time resolved as well, for certain experiments) hold great promise for discoveries of new phenomena, new properties, and new device technologies.

### 3.1.1 Scientific Challenges

Intrinsic properties of importance include fundamental bandgap energy, optical response, band structure, and piezoelectricity. Relevant extrinsic properties include energy levels of dopants and impurities, point and line defects, precipitates and clusters (often on the nanometer scale) and, in alloy systems, alloy composition fluctuations. Recently, the scientific and technical focus in wide-gap materials research has been on the group III-nitrides, wide- gap II-VIs, SiC, and diamond. Open scientific questions concerning these materials include:

- Structural instability of II-VI materials under intense UV illumination (diode lasers self-destruct!).
- Effective acceptor and donor doping (in most cases either only acceptors or only donors can be introduced but not both).
- Nature of impurity and defect-induced deep levels.
- Properties of free and bound excitons with small Bohr radii (strongly localized).
- Radiative and non-radiative recombination processes (e.g., Group III-nitride based lasers function in spite of huge defect densities).
- Large red-shift of electroluminescence/photoluminescence (EL/PL) compared to the optical gap in InGaN.

### 3.1.2 Technical/Experimental Challenges

To study these materials, it is necessary to have probe radiation from the far infrared up to and beyond their bandgaps. To study intrinsic properties, infrared radiation is useful to probe the local environments of point defects [spectroscopy of local vibrational modes (LVM)]. Finally, useful information may be obtained from exciting electron-hole pairs with higher energy, more penetrating radiation (e.g., soft x rays). It is critical to perform these experiments with carefully applied external perturbations. Standard methods that have proved extremely valuable for smaller bandgap materials include pressure (hydrostatic with a diamond anvil cell, uniaxial), temperature (down to liquid helium), and intense light illumination (as in pump-probe experiments). These experiments often require using very small samples, e.g., tens of microns square in a diamond-anvil cell (DAC) of volume $\leq 10^{-6}$ $cm^{-3}$. Because of small sample sizes, it is highly advantageous to have a strongly collimated light source, as in a synchrotron or laser. Infrared studies of such small samples have not been possible using conventional black-body sources. In addition, some of these perturbations (e.g., hydrostatic pressure) produce large changes in the material's bandgap and intrinsic and extrinsic energy levels. To follow the material's changing properties during these experiments, a tunable UV source is required. For the study of wide-gap materials, it is necessary to have a source that functions well in the range from 3.5 eV 15 eV. This is beyond the range of most tunable laser sources.

Wide-gap materials also present challenges on the spatial scale. For example, in Group III nitrides, there are quasi-grain structures, phase separation (in alloys), and segregation in epitaxial layers on the sub-micron scale. These affect the optical properties in ways that are not yet understood (e.g., InGaN quantum wells). For this reason, it would be highly desirable to have an intense light source that can be focused to very small spot sizes without losing photon flux.

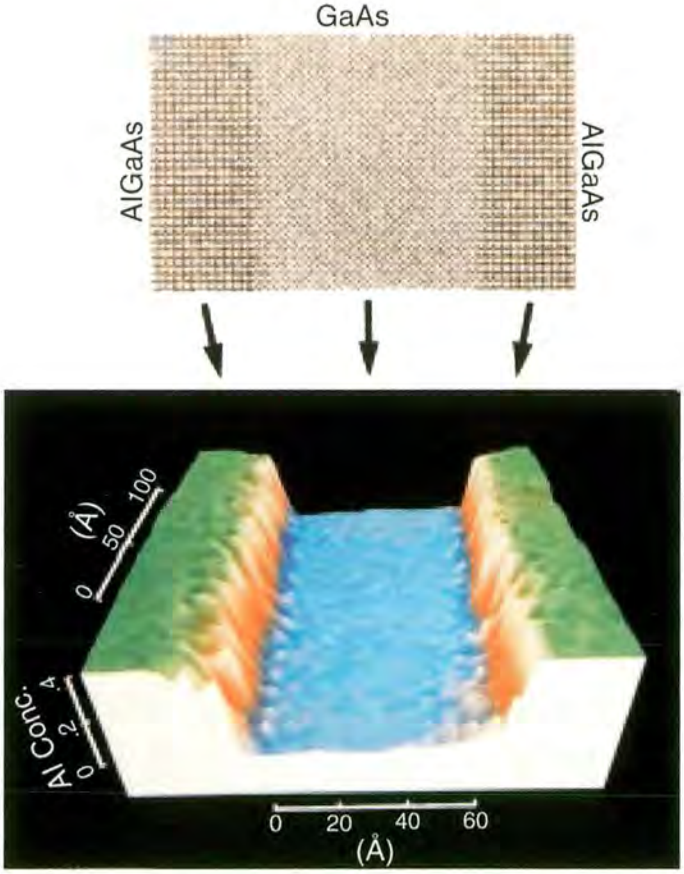

*Figure 7. An atomic-resolution electron micrograph of a GaAs/AlGaAs quantum well (top) and the energy landscape seen by an electron in the structure. [Figure courtesy of A. Ourmazd, Institute for Semiconductor Physics, ODER.]*

### 3.1.3 Challenges for the ALS

Bright, continuously tunable UV excitation is required for:

- Resonance Raman scattering out to the limit of optical materials, i.e., $\lambda \approx 100$ nm or $h\nu \approx 12$ eV. This would help determine the band structure in wide-gap materials.
- Photoluminescence excitation (PLE) experiments in diamond-anvil cells to 5.5 eV (diamond bandgap). Ordinary laser sources are not easily tunable in this range.
- Origin of large Stokes shift (EL/PL red-shifted from optical gap) in InGaN alloys. (e.g., indium clustering, piezoelectric effects, local stresses).

Small spot size is required for:

- Focused UV plus microscopy [near-field scanning optical microscopy (NSOM)]. Could map variations in bandgap be due to stress or alloy fluctuations?
- Focused x rays for spatially resolved microdiffraction; the relevant length scale is 1 μm and below. Potentially could map grain structure in Group III nitride epitaxial layers.
- Focused IR microspectroscopy for "optical" conductivity and local vibrational-mode studies at high pressures.

Short pulses (sub-100-ps) of tunable UV and soft x rays are required for:

- Time resolved photoluminescence (UV, soft x-ray).
- Transient photoconductivity with tunable radiation using the time structure of ALS radiation (UV, soft x-ray). Carrier dynamics in wide-gap materials (e.g., the effect of "grain structure" on mobility and lifetime in GaN and associated alloys).

And infrared (IR) beamlines are needed for:

- Spectroscopy of local vibrational modes (LVM) with very small samples (10 μm) under large hydrostatic pressures.
- Spectroscopy of shallow donors and acceptors with very small samples (10 μm) under large hydrostatic pressures.
- A diffraction-limited beam of IR radiation is ideally suited for the above-listed studies of micro- and nanocrystals because of its high brightness.

## 3.2 Far-Infrared Studies in Very-High-Pressure Diamond-Anvil Cells at the ALS

The application of large hydrostatic pressures in combination with infrared spectroscopy provides a powerful combination of controlled external perturbation and spectroscopic analysis of modern solids. The value of using large hydrostatic pressures in materials analysis is obvious for materials which are used in high-pressure applications. However, high pressures offer significantly more. For example, the band structure of GaAs changes with hydrostatic pressure in the same general way as when GaAs is alloyed with AlAs at ambient pressure. The band structure of AlGaAs with one percent AlAs corresponds to the band structure of the pure GaAs under 1 kbar hydrostatic pressure. This behavior is observed for many crystalline solids and it is of powerful predictive value for alloy design as well, as for the detailed understanding of thermal, electronic, and mechanical properties.

Large hydrostatic pressures can be produced conveniently in a diamond-anvil cell. Consisting of two jewelry-grade diamonds with their tips ground off, it can produce very large hydrostatic pressures of up to 550 GPa ($\approx 5.5\text{x}10^6$ atmospheres) by compressing the small volume formed by a hole in a metal gasket. The diamonds are close to ideal transmitters of electromagnetic radiation from the far infrared to the deep ultraviolet. Samples studied in diamond anvil cells are typically small, a few tens to hundreds of microns in diameter and a few tens of microns thick. This relatively small sample size poses severe limits on optical studies of properties of solids in diamond anvil cells, especially in the mid- and far-infrared range of the electromagnetic spectrum, which is characterized by weak broadband sources and severe throughput problems. It is only very recently that local vibrational modes of impurities in crystalline solids have been successfully studied as a function of hydrostatic pressure in diamond-anvil cells [see for example "Formation of a DX Center in InP Under Hydrostatic Pressure," J. A. Wolk, W. Walukiewicz, M. L. W. Thewalt, and E. E. Haller, *Phys. Rev. Lett.* **68** (1992) 3619].

The unique opportunities offered by optical studies of solids under very large hydrostatic pressures will be extended to ever smaller and purer structures, particles of solids so small that a large fraction of all the atoms in one particle are part of the surface. The band structure, melting point, dopant energy levels, defect structures, and several other properties of such small particles have been shown to deviate significantly from bulk properties. The exploration of the mid- and far-infrared properties, especially of impurities and defects (vacancies, interstitials, etc.) in very small particles, offers a broad and most promising field of materials studies that has remained largely unexplored because of usual limitations encountered in the far infrared, including weak sources, throughput problems, and detectors.

A diffraction-limited beam of infrared radiation from the ALS is ideally suited for the studies mentioned above because of its high brightness. The small product of the beam area and solid angle allows a significantly larger number of far-IR photons to pass through a sample in a diamond-anvil cell than from a standard far-IR source. The blackbody equivalent temperature of the ALS beam has been estimated to be of the order of 200,000 K averaged over all the electron buckets in the beam and it approaches 700,000 K in the buckets. These high source temperatures combined with the broad tunability make the ALS an IR source of unprecedented performance.

In order to exploit these extraordinary ALS IR-source properties, we plan to use the two FTIR spectrometers that are currently commissioned at Beamline 1.4. One of the spectrometers (Bruker IFS66v/s) has an unapodized maximum instrumental resolution of 0.125 $\text{cm}^{-1}$ and operates in a vacuum. It belongs to a family of second-generation instruments used worldwide in materials, solid-state physics, and chemistry research facilities. In addition to the mid-IR standard KBr:Ge beam splitter, the spectrometer will be equipped with a set of mylar beam splitters that allow operation in the far IR from 50 $\text{cm}^{-1}$ to 1,000 $\text{cm}^{-1}$ and a quartz beam splitter to allow visible-light spectroscopy from 8,000 $\text{cm}^{-1}$ to 25,000 $\text{cm}^{-1}$. The second FTIR set-up, a Nicolet 760 instrument with a Nic-Plan IR microscope, has already demonstrated a 10-$\mu$m spot size in the mid IR, which is sufficient to perform microscopy of small samples in diamond-anvil cells.

In order to reduce background radiation, a majority of far-IR spectroscopic studies are performed at low temperatures. The cryostat can also accommodate diamond anvil cells of various designs. We propose to equip the facility with two commercial cells for general use. In addition, cells will be fabricated at Berkeley by several groups with extensive experience in the design and manufacture of such cells.

The choice of detectors to accommodate the various wavelength ranges and the widely varying photon-flux conditions requires special attention. In addition to the proposed set of commercial detectors, we foresee an intensive development effort for new, well-matched IR-detection devices. Again, there exists broad local experience in semiconductor- and superconductor-based IR detectors. For example, the first successful study of local vibrational modes of silicon donor impurities in GaAs under high pressure was performed with a copper-doped germanium photoconductor that was built and integrated with the diamond-anvil cell at the University of California, Berkeley. It is anticipated that this new IR facility at the ALS will stimulate highly interactive and fruitful collaborations between experts in the spectroscopy of solids, in materials properties, and in detector physics and technology.

# Working Group on New Directions in Surface and Interface Science

**Chair: Gabor Somorjai, University of California, Berkeley**

**Facilitators: Charles Fadley, University of California, Davis, and
Michel Van Hove, Lawrence Berkeley National Laboratory**

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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-µm diameter but only 15-Å 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.

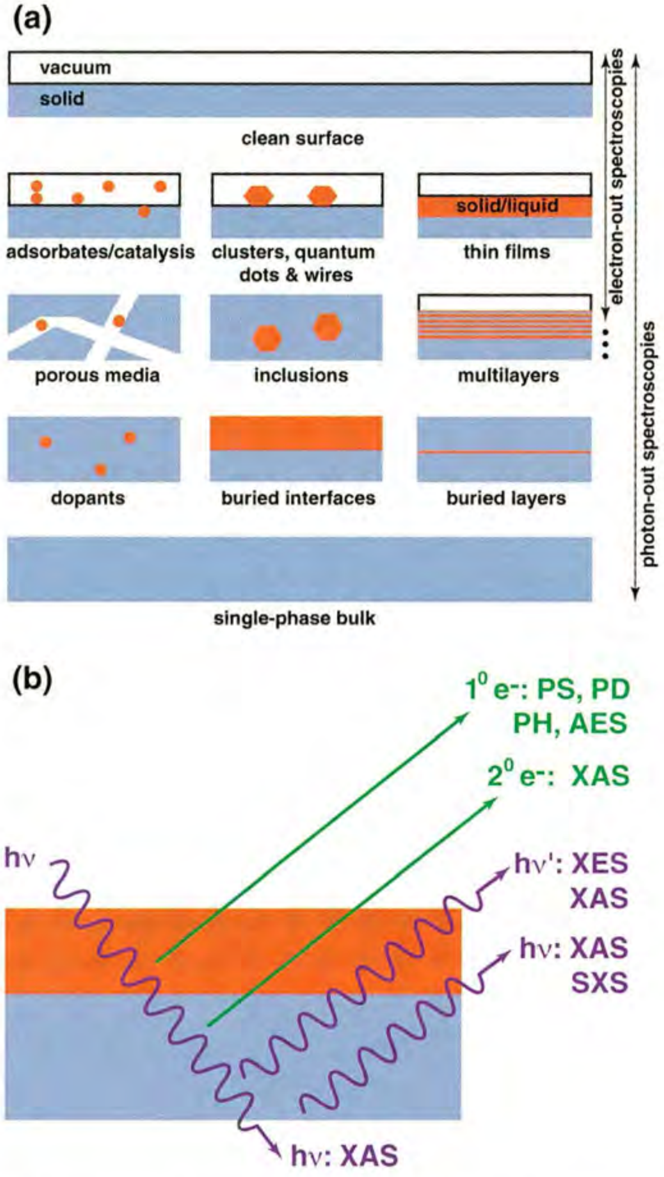


*Figure 1. (a) Various surface and interface morphologies of current interest, with the approximate ranges of vertical sensitivity using electron detection or photon detection indicated. (b) Schematic illustration of some of the most important VUV/soft x-ray techniques and their approximate ranges of 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 surface/interface x-ray scattering (SXS), including reflection and transmission experiments.*

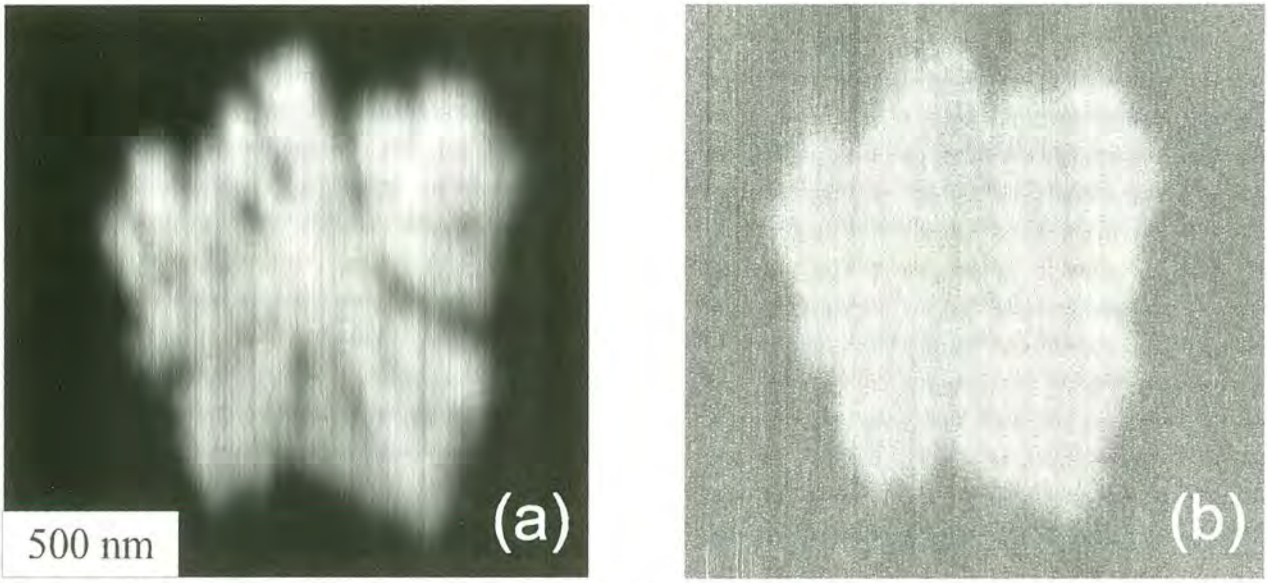


*Figure 2. Images of ice crystals obtained with scanning atomic force microscopy. The ice crystals have approximately 1000 nm = 1 μm diameter and 1.5 nm = 15 Å thickness (about two lattice constants) as grown on a cooled mica (0001) single-crystal substrate. The temperature is –25° C, and the water vapor pressure is 0.43 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 $10^{-18}$ 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 spectromicroscopy). 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 techniques 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.

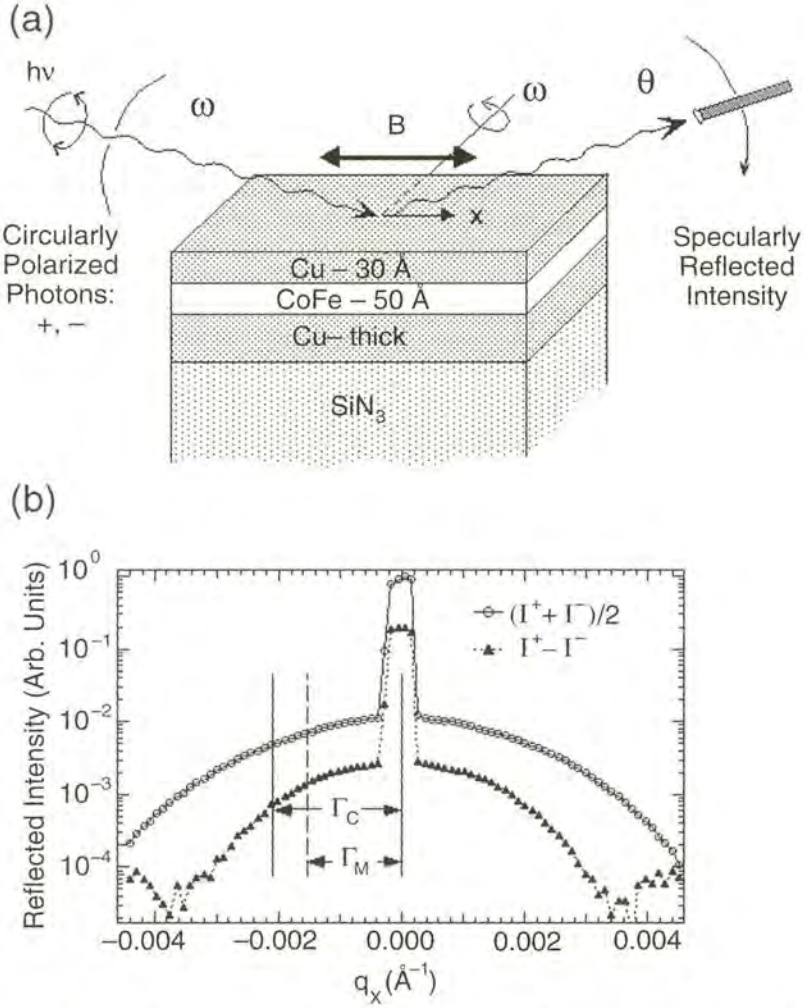


*Figure 3. Specular and diffuse soft x-ray reflectivity measurements from a metal-metal interface. Reflected intensities for right and left circularly polarized radiation ($I^+$ and $I^-$, respectively) have been measured from the top Cu/Co$_{95}$Fe$_5$ interface in a trilayer, with interface sensitivity 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 $La_x(Ca, Sr)_{1-x}MnO_3$, $Mn^{3+}$ and $Mn^{4+}$ 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., $VO_2$, $V_2O_3$) 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.

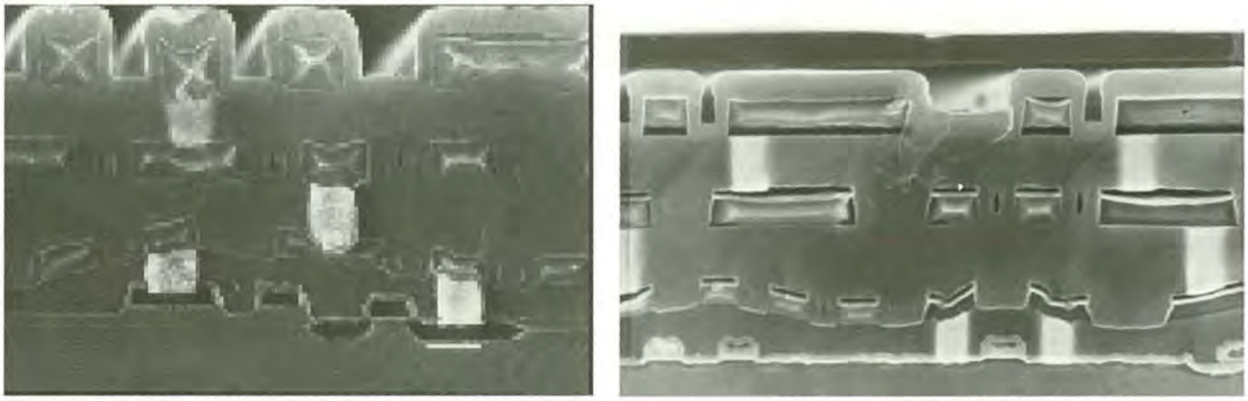
The intense radiation at the ALS may permit measurements of both interfacial geometric and electronic structure by accessing the interface beneath several nanometers of overlayer. X-ray absorption and emission spectroscopies, perhaps making use of total internal reflection at the interface, have the 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.

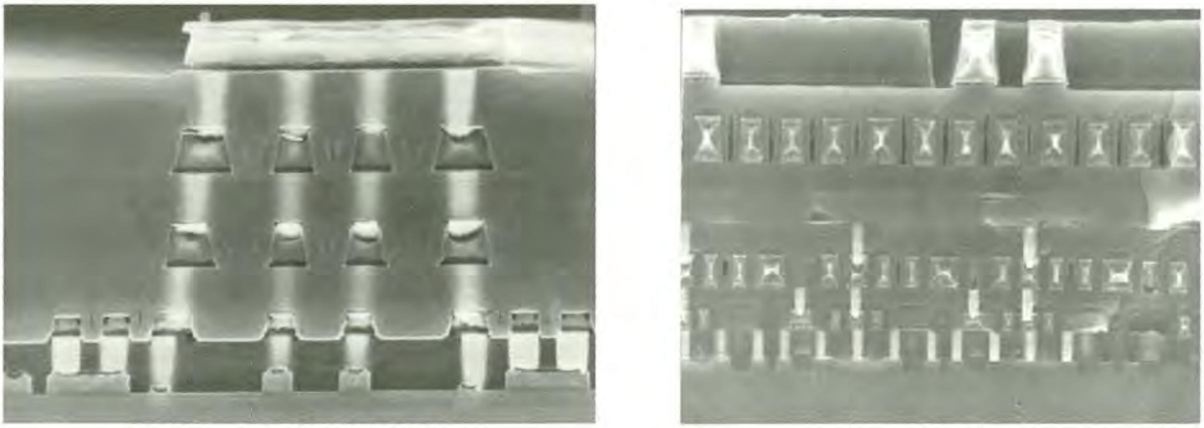
Of equal importance are determinations of the thermal stability of metal-oxide and oxide-oxide interfaces, interdiffusion across the interface, and interfacial segregation. Here also the possibility of interrogating buried interfaces with the intense radiation at the ALS during thermal cycling make such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



0.8μ - (486DX2 Processor)    0.6μ - (75 - 120MHz)



0.35μ - (133 - 166MHz)    0.25μ

*Figure 4. Transmission electron micrographs of cross sections of PC microprocessor integrated circuits representing recent trends in Intel development from 0.8-μm to 0.25-μm 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 $Si_xN_y$ and/or silicon oxynitride is being developed to replace $SiO_2$ 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 $SiO_2$ (with dieletric 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 dieletric 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-dieletric/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).

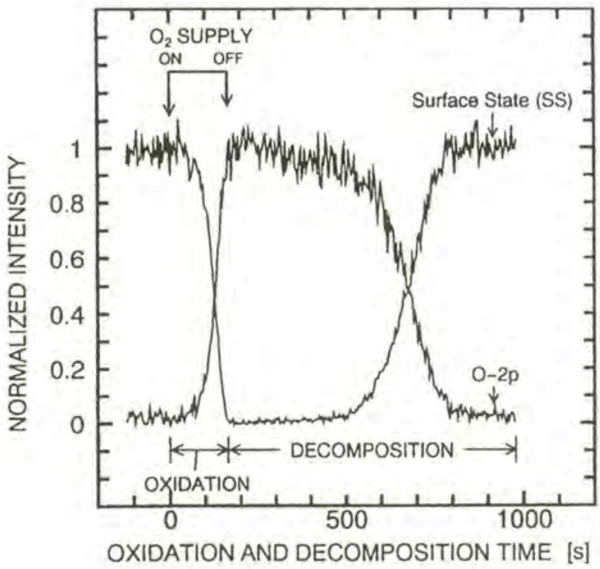


*Figure 5. Time-dependent valence-photoemission study of the oxidation of silicon (001). The intensities of oxygen-2p and silicon-surface-state (SS) features have been used to monitor in real time oxide growth and decomposition after the oxygen supply is turned off. For temperatures above 760° C, there 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.

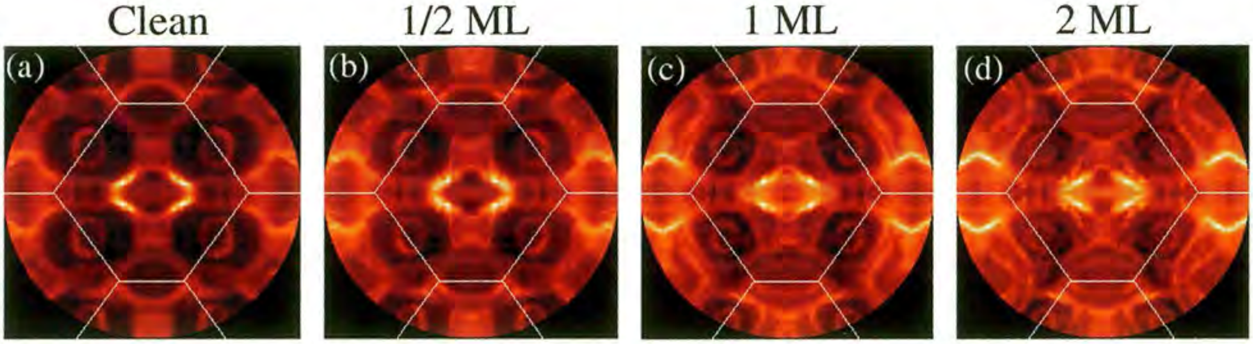


*Figure 6. The dependence of the electronic states at the Fermi level of a transition metal (tungsten) on the adsorption of an alkali metal (sodium). Here, the angular distribution of photoelectrons excited from the Fermi energy of tungsten (110) is shown for the clean surface (a) and for the surface 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.]*

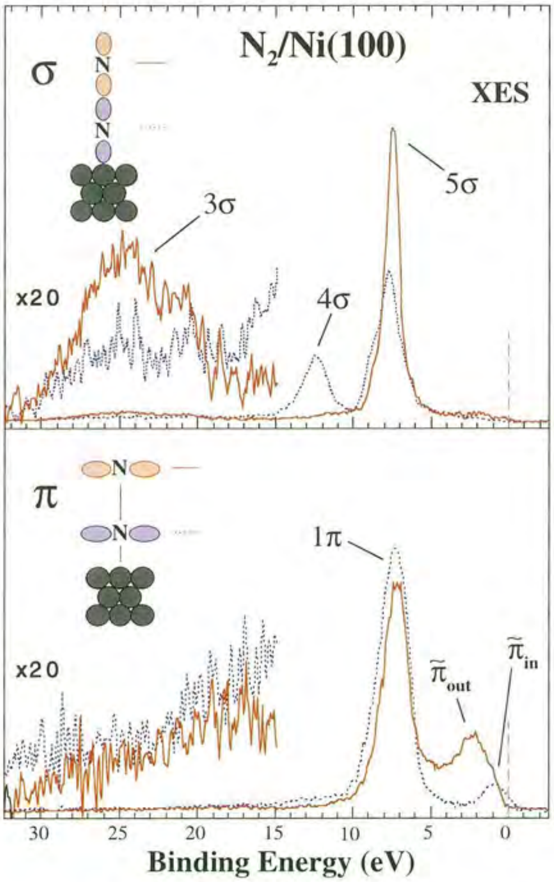


*Figure 7. X-ray emission spectra for nitrogen adsorbed on nickel (001). The spectra were obtained at the ALS with the exciting radiation in two different polarization orientations so as to be sensitive to either the 2p-derived $\sigma$-bonding character (upper panel) or the 2p-derived $\pi$-bonding 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

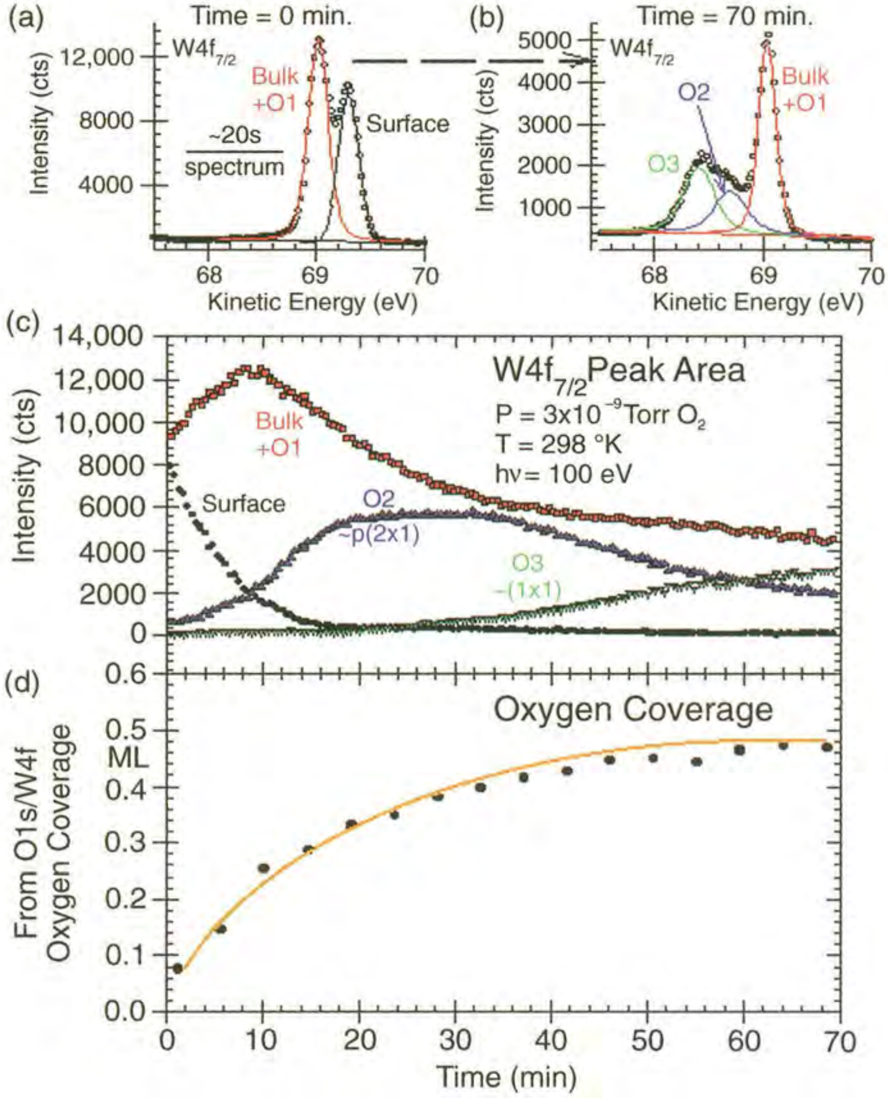


*Figure 8. Chemical-state and time-resolved photoelectron spectra obtained during the reaction of oxygen with a tungsten (110) surface. (a) and (b) Four distinct chemical states of tungsten can be resolved in tungsten-4f spectra [atoms at the clean surface (Surface), bulk atoms underneath the surface, 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

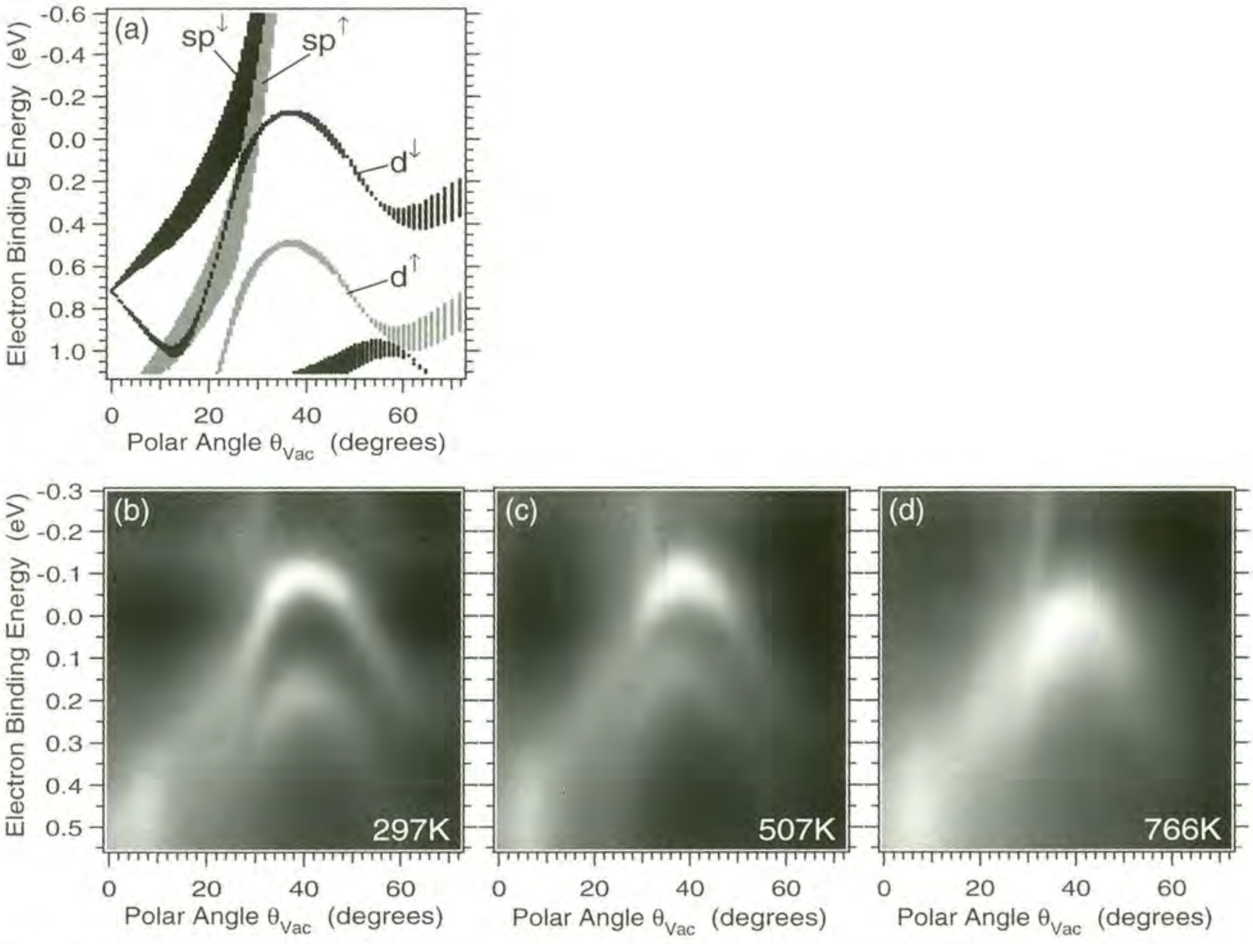


*Figure 9. Temperature dependence of the electronic energy bands of a ferromagnet. A section of the electron energy bands near the Fermi energy for ferromagnetic nickel is shown as a function of emitted photoelectron angle relative to the surface normal (or equivalently wave vector parallel to the surface). (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. Kreutz, 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.

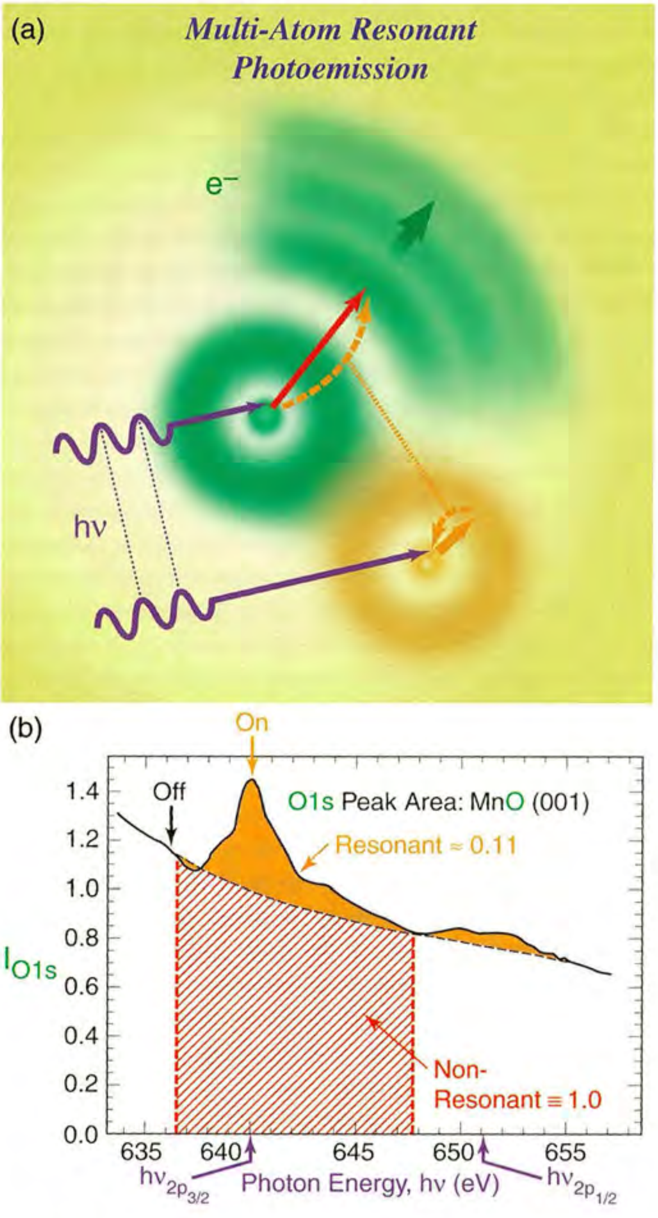


*Figure 10. (a) Schematic illustration of a new type of resonant photoemission observed recently at the ALS. If the photon energy can be tuned to a strong bound-to-bound excitation on a near-neighbor atom at right, then the intensity of the photoemission intensity from a core level in the atom at left 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.

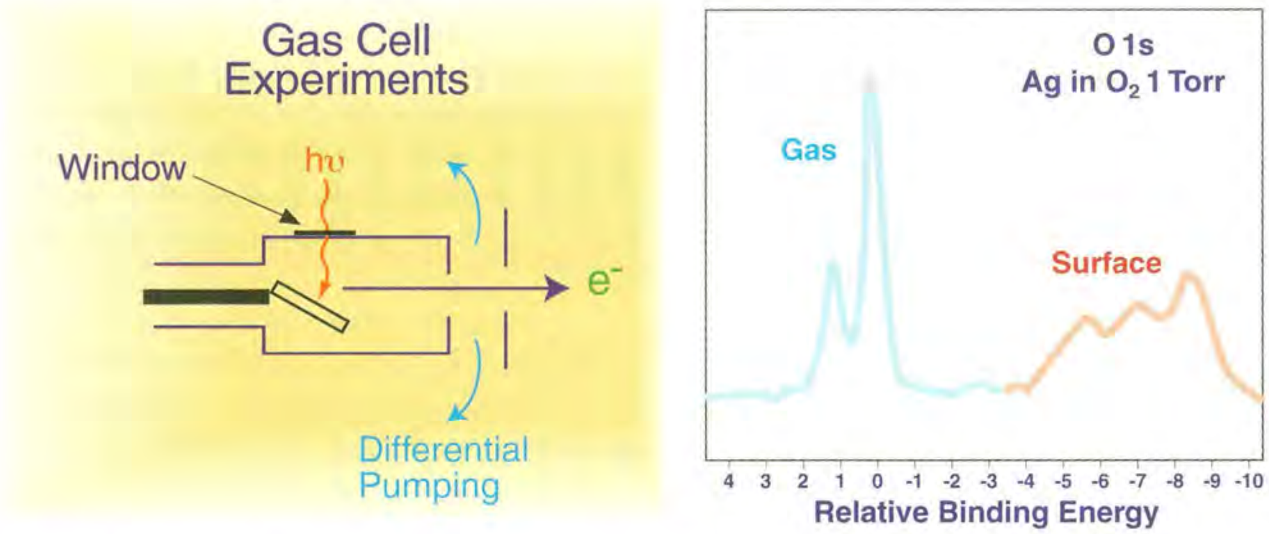


*Figure 11. Experimental demonstration of the ability to carry out x-ray photoemission (XPS) measurements at 1-torr pressure. With the aid of a differentially-pumped enclosure surrounding a silver sample, it was possible to measure photoelectron spectra at a 1-torr ambient pressure of oxygen. The schematic 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 ± 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 ± 0.05 Å or better (diffraction) and ± 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 SPLEEM 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

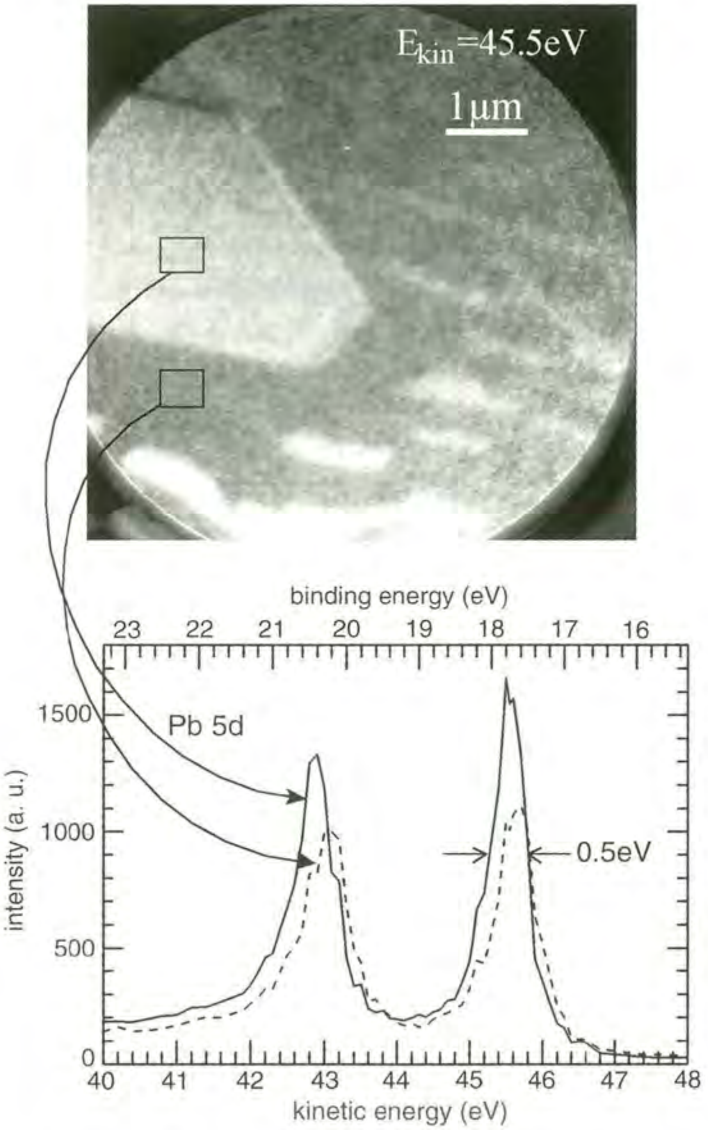


*Figure 12. Photoelectron-emission microscopy (PEEM) image of a tungsten (110) surface with a flat one-monolayer "base layer" of lead deposited on it and overlying flat three-dimensional islands of additional lead. With an exciting photon energy of 65 eV, it is possible to resolve a very small chemical 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 μm 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-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.