***Surface and Interfacial Science at the APS***

Interfacial science by its very nature brings together a diverse scientific community with interests in catalysis, biomembranes, oxide film growth, semiconductors, geochemistry, surface physics, corrosion, nano-science, tribology and electrochemistry. The widespread interest in nano-scale materials has also highlighted the critical role of surfaces and interfaces, where a large fraction of atoms are within close proximity to the surface or interface, and the unique properties of these materials often have greater dependence on interactions with the local environment.

One of many challenges in this highly interdisciplinary field is to understand and control the assembly of atoms and molecules at well-defined surfaces in complex environments. In the area of materials growth and synthesis, the ability to manipulate materials' properties (such as controlling composition or strain in thin-films or nanostructures) is a central theme in engineering many new materials with novel chemical, magnetic, optical, mechanical, ferroelectric, thermoelectric, and electronic properties.

Understanding the balance between mass transport and site-specific reactions at interfaces is critical to advancements in growth techniques (such as MOCVD, PLD, MBE, Laser MBE, ALD, and oxide MBE), and is essential to understanding chemical reactions and geo-chemical processes (such as etching, adsorption, dissolution, catalysis and precipitation).

The relationship between atomic scale structure and catalytic function has important applications in fuel-cells, hydrogen production & storage, and natural processes at biological membranes.

The mineral-fluid interface is the principal site of low-temperature geochemical processes at and near the Earth's surface, and influences the composition of groundwater, surface water, and to some extent the atmosphere. Environmental mediation strategies often require detailed knowledge of the structure and chemistry at these interfaces to establish effective procedures for environmental cleanup.

The role of interfacial magnetism in fabricated magnetic superstructures has received much recent attention, and a grand challenge today in highly correlated electron systems is the determination of the role surface and interface electronic structure in these complex materials. Indeed, the importance of surfaces and interfaces is becoming more widely appreciated in many different areas.

Because of favorable cross sections, x-rays offer a unique opportunity to penetrate many complex environments (gas, liquid, or solid thin-film overlayers) to probe the structure and chemistry of surfaces and internal boundaries from macroscopic lengths down to the atomic level, in environments where traditional electron and other scanning probes are not applicable. High brilliance x-ray sources such as the APS enable these in-situ studies, permit real-time investigations to elucidate thin film growth mechanisms, and allow for molecular scale studies of important chemical interactions at internal boundaries using scattering, diffraction, resonance & absorption, fluorescence, standing wave, and imaging techniques.

Throughout 2006–2007, numerous Basic Energy Sciences Advisory Committee (BESAC) and Grand Challenges Subcommittee meetings and conferences were convened in response to a request from the USDOE Office of Science to identify the most important scientific questions and science-driven technical challenges facing BES. The report, *Directing Matter and Energy: Five Challenges for Science and the Imagination*, identifies 5 Grand Challenges and describes the importance of these challenges to advances in science & technology development, and to our energy and other societal needs. The science and technology of surfaces and interfaces provides a foundation for addressing all of these challenges which are key to making the transition from observation science to control of matter.

The 5 Grand Challenges are:

- How do we control materials processes at the level of electrons?
- How do we design and perfect atom- and energy-efficient syntheses of revolutionary new forms of matter with tailored properties?
- How do remarkable properties of matter emerge from the complex correlations of atomic or electronic constituents and how can we control these properties?
- How can we master energy and information on the nanoscale to create new technologies with capabilities rivaling those of living things?
- How do we characterize and control matter away—especially very far away—from equilibrium?

The DOE-BES has also held a series of Workshops and meetings to identify Basic Research Needs in many areas, including:

- Basic Research Needs: Catalysis for Energy
- Basic Research Needs for Electrical Energy Storage
- Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems
- Basic Research Needs for Solid-State Lighting
- Basic Research Needs for Superconductivity

Important issues involving all five of *the Challenges for Science and the Imagination* can be successfully addressed through surface/interface science, as well as many important aspects of these BES Basic Research Needs. For example, new understanding of materials growth enables designers to control the structure (through strain and composition) at complex interfaces to tune properties such as electronic band gap, magnetism, thermoelectric properties, and even superconductivity.

In a 2007 report, *"CONDENSED-MATTER AND MATERIALS PHYSICS: The Science of the World Around Us"*, the National Research Council of the National Academies Committee on CMMP 2010, Solid State Sciences Committee, identified the prospects for CMMP in the early part of the 21st century. One of the main findings of the report is the identification of six grand challenge areas in which CMMP research is poised to have a large and enduring impact in the next decade.

- How do complex phenomena emerge from simple ingredients?
- How will the energy demands of future generations be met?
- What is the physics of life?
- What happens far from equilibrium and why?
- What new discoveries await us in the nanoworld?
- How will the information technology revolution be extended?

"The design and synthesis of novel systems are the foundation to address all of the CMMP grand challenges." (p. 233). Finally, a National Research Council study, *Assessment of and Outlook for New Materials Synthesis and Crystal Growth,* is expected to make detailed recommendations in a report to be released in the summer of 2008. Indeed, the area of surface and interface science is rich with opportunity and is highly relevant to the Nation's research goals today.

For these compelling reasons, there is significant interest in Surface and Interface Science, and a very active user community at the APS in this area. A new, dedicated X-ray Interfacial Science (XIS) facility at a sector of the Advanced Photon Source with exciting new capabilities such as chemically sensitive 3D atomic mapping and new in-situ materials growth capabilities is currently in the planning stages and has generated broad interest and enthusiasm. Surface and interface science activities have been developed and are ongoing in several APS sectors, and the planned Midterm Upgrade will benefit these distributed capabilities. For example, a canted beam line design will provide improved beam access for MOCVD and EEP programs in sector 12. A new dedicated hutch and canted source is planned for the MBE programs in sector 20, and new focusing optics in sector 6 will greatly benefit the surface diffraction facilities often used for investigating vacancy defects in oxide and metal surfaces. Sector 33 will continue as a center for surface and interface science activities in the APS XOR Strategic Planning, and the Midterm Upgrade provides opportunity to build on the successes to date in this area and extend these to complement the development of a new sector and the distributed surface & interface science capabilities at other APS sectors (12ID, 5ID, 6ID, 13ID, 13BM and 20ID).

While challenging to implement, the opportunity to coordinate these activities to best exploit the APS source and advanced x-ray techniques, together with a close relationship with the scientists and capabilities of the Center for Nanoscale Materials holds great promise for discovery in areas such as interfacial and surface chemistry, fundamental growth processes, and nano-scale sciences.

***New Opportunities in Surface and Interfacial Science at Sector 33***

Enhancements to the APS complex that provide significant improvements in beam line optics, detectors, staffing and infrastructure will lead to exciting new possibilities in surface & interface science. The comprehensive report of the workshop on *In-Situ Characterization of Surface and Interface Structures and Processes* held at the APS in September 2005 highlights forefront interface science, and details many new important scientific directions in this area. This body of work can be separated into two broad categories. The first area addresses controlled growth and characterization of modern materials with nanoscopic to mesoscopic dimensions. The second topic deals with chemically active surfaces and interfaces which govern many natural processes in the environment and in technologically important areas, including sensors and fuel cells. Ultimately, knowledge of atomic and mesoscopic structural arrangements and composition at surfaces and buried interfaces is fundamental to understanding the function and properties of both synthetic structures and reactive interfaces found in nature.

***X-Ray imaging of surfaces and interfacial boundaries***

Techniques that directly image surfaces and interfacial boundaries are positioned to become widespread and readily applied in many areas. Coherent diffraction imaging, x-ray standing wave (XSW) imaging, and phase-sensitive surface structure analysis have emerged and hold great promise for broad application in surface and interface science. The ability to directly image elementary interfacial structures in real-time will open up new opportunities to understand interfacial reactivity in natural environments and under growth or processing conditions. For example, observation of step dynamics (e.g., during crystal growth and dissolution in aqueous solutions at extreme pH) will provide new information about mineral surface reactivity under aggressive chemical conditions that cannot be studied with scanning probe microscopes. Through changes in scattering angle, various aspects of interfacial structures may be highlighted, including defect distributions at buried solid-solid interfaces (e.g., dislocations), film growth, and the nucleation and growth of nano-particles. The use of non-specular crystal truncation rods will provide sensitivity to lateral structures (e.g., reconstructed surface domains). In a similar way, contrast derived from the resonant anomalous dispersion of x-rays can be used to specifically highlight elemental, chemical or magnetic features of an interface. These approaches should be widely applicable as a probe of various interfacial processes such as ion adsorption, corrosion, catalytic reactions, magnetic and ferroelectric domain growth and switching. This can be seen to be useful for any measurement where the scattering contrast can be used to spatially image the surface or interface processes. For example, changes in crystal truncation rods (CTRs) due to steps, film growth, ferro-electric displacements or composition can be imaged in real time. With the APS lattice, and development of specialized optical stages, the spatial resolution of this x-ray reflection interface microscopy technique will approach 30 nm or better.

***Quantum-mediated growth***

Self-organization of nanoscale islands is a bottoms-up approach to fabrication of new materials. While there are many reports of self-assembly of semiconductor quantum dots, these are generally attributed to a strain-induced self assembly mechanism. Indeed, major achievements have been realized by managing and tuning the strain at epitaxial interfaces to improve properties such as the Si band-gap in the gate region of modern devices. Recently, the self-assembly of Pb islands on Si has been demonstrated to be a direct result of quantum size effects. This represents an exciting new strategy for manipulating quantum behavior for directed self assembly. The Pb/Si(111) quantum size effect includes phase separation into a wetting layer and flat top islands with essentially uniform heights, and bilayer oscillations in surface energy and lattice spacing. The Pb islands have been found to have spatial correlation and a narrow distribution of island sizes. The preferred heights and flat tops of the islands act as a surface anisotropy which promotes island ordering. These quantum well effects may be a new driving force for forming a well-ordered array of nanoscale islands of uniform size. In-situ time-resolved surface x ray diffraction measurements produce two-dimensional (2 D) reciprocal space maps that allow metastable states in nanoscale confinement to be identified and studied.

***In-situ, time-resolved measurements of interfaces or surfaces***

Understanding and controlling the parameters that effect growth in equilibrium and non-equilibrium fabrication and in processing environments enables control of structure and therefore materials properties in many different disciplines. For example, pulsed laser deposition (PLD) has emerged as an important approach for the growth of high quality thin films of complex materials. In PLD, the growth is non-equilibrium and occurs as a plume of laser-ablated material is ejected from a suitable target and impinges on the growth substrate to synthesize artificially layered materials and stabilize metastable phases with atomic layer precision and control. The plume consists of a complex mixture of neutral and ionized atoms, molecules, and small clusters with kinetic energies ranging from thermal to a few hundred eV. This versatile thin-film growth technique provides access to a wide range of new materials and properties that are not available using equilibrium bulk material synthesis techniques. A central problem in non-equilibrium materials synthesis is the relationship between deposition parameters and the resulting film structure and epitaxial relationship. Non-equilibrium materials are characterized by structure and composition that are different than the thermodynamically ordered phases of minimum free energy, and epitaxy is a particularly effective synthesis strategy because it can stabilize different crystalline structures and chemical compositions across atomically sharp interfaces. Detailed measurements of the time scales of crystallization, aggregation, and surface evolution are critical for developing a fundamental understanding of the growth mechanisms and for practical applications of nonequilibrium film growth methods. The ability to measure and control interlayer transport can lead to the discovery of new approaches for synthesis of perfectly smooth oxide surfaces that will be required for device functionality. The details of the earliest stages of growth throughout the duration of the plume impingement on the surface are not currently accessible.

***Interface properties and structures***

In the area of materials growth and synthesis, the ability to manipulate materials' properties (such as controlling composition or strain in thin-films or nanostructures) is a central theme in engineering many new materials with novel chemical, magnetic, optical, mechanical, ferroelectric, thermoelectric, and electronic properties. Advances in the science and technology of complex oxide heterostructures are derived from the understanding that strong correlations arise from electron-electron and electron-lattice interactions and give rise to a rich diversity of tunable phases, including spin, charge and orbital ordering, Mott-insulators and high-temperature superconductivity. Precise measurements of the atomic scale structure at surfaces and interfaces are required to understand the properties that result from the delicate structural and chemical balance. These structures are often comprised of only several layers that may be vulnerable to exposure to the environment, and in-situ measurements are often essential.

***Interfacial chemistry***

Oxides in contact with aqueous solution are one of the most common heterogeneous systems, playing a key role in many geological, biological and industrial processes. The properties of the interfacial region, or electric double layer (EDL), strongly differ from the aqueous and solid bulk phases and profoundly influence the stability of colloids, crystal nucleation, corrosion, and many other related phenomena. Theoretical description of the EDL consists of models that consider both long-range electrostatic effects and the specific nature of the surface groups themselves. Recently, various experimental and computational methods have been combined to solve the problem, with macroscopic titration measurements, ab initio calculations, molecular dynamics simulations, and surface X-ray scattering measurements contributing. The X-ray based measurements provide key input into the validation of the computational models, and provide direct information on the interfacial hydration structure and cation adsorption geometry. As these investigations mature, there is increasing interest in more non-idealized crystal surfaces and small facets on natural crystals. Comprehensive studies are needed to allow better understanding of the reactions at natural oxide-aqueous interfaces and the connections between the microscopic structures and the macroscopic properties and behavior.

***Added Value of the Midterm Upgrade***

Improved x-ray facilities for in-situ surface and interface science at the APS that are based on a new canted undulator beam line design, and state-of-the-art beam line and focusing optics will fundamentally change the paradigm for the study of the structure and properties at surfaces and internal boundaries in fabricated systems as well as those found naturally in our environment. Smaller beam sizes, faster detectors, and expanded dedicated capabilities will enable new research in diverse scientific areas.

The opportunity to include integrated imaging techniques, time-resolved measurement capabilities, and the infrastructure to enable experiments in very complex environments to probe interfacial processes holds great promises for discovery in interfacial and surface chemistry, fundamental growth processes & fabrication, and nano-scale sciences. Similar to the way an electron microscopist seamlessly switches from imaging to diffraction, the integration of x-ray imaging optics with scattering instruments will permit researchers to perform scattering measurements and dark-field imaging from the same location on a sample in the same complex environment. This will be the premier instrument worldwide for scattering and imaging characterization of interface structures.

The Midterm Upgrade will also enable experiments with smaller samples, involving *in situ* reactions and structures under non-ambient conditions in controlled and complex environments. As the interest in non-ideal surfaces grows, small beams are often required to probe small crystal surfaces or facets. Improvements and enhancements to existing techniques will provide new capabilities and enable investigations not possible today.

Software will be developed and refined to exploit widespread use of surface/interface scattering geometry and 2D detectors, resulting in improved temporal resolution and dramatically higher throughput. Sample handling, and off-line visualization & characterization infrastructure and associated specialized ancillary laboratory equipment will form an important element of this upgrade activity.

These improvements recognize the competitive advantage of APS, and exploit the great brilliance of this hard x-ray source.

***Expected user communities***

Interfacial science by its very nature brings together a very large and scientifically diverse community with interests in catalysis, biomembranes, oxide film growth, semiconductors, geochemistry, surface physics, corrosion, nano-science, tribology and electrochemistry. The workshop on *In-Situ Characterization of Surface and Interface Structures and Processes* held at the APS in September 2005 brought together experts in synchrotron radiation techniques and various synthesis, processing and modeling efforts to identify future directions in these areas of research, and to assess the applicability of x-ray tools to future research problems. Over 130 participants from 39 different research institutions (plus 8 different ANL divisions) representing 16 US States, 8 countries, and 7 synchrotron light sources traveled to the APS to contribute to the talks, poster session and discussion. There were attendees from universities, industry, and from national and international government-sponsored research institutes, representing the broad, diverse interest in this research area. This represents a significant user community in areas ranging from materials chemistry and condensed matter physics to environmental science and catalysis.

***Enabling technology and infrastructure***

A canted undulator beam line will be optimized for surface/interface experiments. One branch of the beam line will be fully tunable over a wide energy range (4 – 40 KeV) for experiments that require resonant contrast enhancement. The other branch will be based on a double crystal side-bounce monochromator with selectable energy (over a somewhat smaller energy range). The tunable branch will incorporate an upgraded double-crystal monochromator, new focusing mirrors and an expanded experimental hutch for x-ray standing wave (XSW) studies, coherent Bragg-rod analysis (COBRA), resonant crystal truncation rod (CTR) measurements, and MBE growth methods. The new side bounce branch will include focusing optics and an expanded experimental hutch with a new general-purpose diffractometer designed for integrated microscopy and scattering experiments, upgraded and enhanced PLD capabilities, and an upgraded growth chamber. The beam line focusing optics for each branch line will provide excellent spot size at each experimental location (approx 100 um), and can be focused to a secondary source (slit) for re-focusing with drop-in K-B mirrors or Zone plate optics for experiments that require micron-scale beam spots.

The bending magnet beam line will be optimized for surface & interface scattering research that does not require the brilliance of the ID beam lines. For example, CTR measurements, COBRA, thin-film diffraction and reflectivity can effectively studied on many important interfacial systems. The beam line optics and diffractometer will be upgraded with improved focusing, 2D detectors, and specialized environmental cells and chambers that mount to the standard scattering goniometers.

The growth chambers will have enhanced capabilities, including expanded PLD with RHEED and an improved Laser, additional sources (MBE, atomic oxygen, sputtering), sample transfer and separate prep/analysis capabilities, wider temperature-range stages, UHV-GISAXS capability, and provision for high gas pressure and high temperature studies of material surfaces.

Traditional electron and scanning probes will be included in the facility upgrade, including STM/AFM, in-situ SEM for imaging and analysis, and LEEM/PEEM.

***Partnerships***

Effective partnerships are essential for a healthy research enterprise. APS XOR-operated sectors need close ties to the user community – particularly for developing and using sophisticated in-situ capabilities for surface and interface science. Cooperation between CATs and APS in this area represents additional opportunity for collaboration and consortia participation. The synergy between the nanoscience user community and synchrotron scientists identifies another natural partnership opportunity. And finally, the specific recommendation of the National Research Council of the National Academies in the CMMP 2010 report that DOE and NSF should develop distributed national facilities in support of the design, discovery, and growth of new materials for both fundamental and applied CMMP research identifies a natural vehicle to establishing successful collaborations among the user community members and the APS in this area.

***Industry and technology transfer***

While there are no specific industrial partnerships or technology transfer agreements, there are many opportunities for industrial participation in many surface and interface science research activities at the APS, and many opportunities for vendor collaboration – particularly through partnerships enabling technology and infrastructure.

***Estimated Budget***

| | Capital | M&S |
|---|---|---|
| Year 1: …… | 2500 | 100 |
| Year 2: …… | 2500 | 100 |
| Year 3: …… | 1600 | 200 |
| Year 4: …… | 1000 | 100 |
| Year 5: …… | 250 | |
| Total: | $8350 K | |