

## ***Interfacial Science: APS Midterm Science Case***

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### **1) Executive Summary**

Interfaces are of critical importance for the next generation of energy-related technologies [1]. For example, the chemical, structural and electronic nature of new materials and nanoscale-structured interfaces relate directly to the performance of multilayer solar cells and other energy harvesting media [2], catalysts [3], energy storage materials [4], thermo-electrics, and solid-state lighting [5]. Interfacial stability under extreme chemical environments is critical to numerous energy technologies including the operation of nuclear reactors [6] and the geological sequestration of energy by-products (carbon and nuclear material sequestration) [7]. Interfaces are also critical in the reprocessing of nuclear materials [8].

Central to achieving these scientific goals is our ability to understand the elementary processes that take place at the interface between distinct media, such as adsorption, chemical reactions, growth and processing, within a diverse range of fields, disciplines, materials and environments. Areas directly impacted by such processes range from the efficient use of energy resources, to the creation of novel materials, to the maintenance of our natural environment. Interfacial science is invigorated by the many scientific and technological opportunities associated with matter at small dimensions (typically Å to nm), and is challenged by the need to access interfaces through complex environments.

This report describes transformative opportunities in the area of interfacial science that can be accessed in the next decade through advances in instrumentation and software at the Advanced Photon Source. These advances will enable unique capabilities to observe interfacial processes through complex environments, in real-time, and with  $\mu\text{m}$ -scale fields of view, and Å to nm-scale sensitivity and resolution. These extraordinary capabilities will enable the community to develop a better understanding of the relevant molecular-scale processes, control interfacial composition and structure, and ultimately create novel materials and devices. More generally, these capabilities will enable the study of “realistic” interfaces with inherent heterogeneity at a level previously attainable only for highly homogeneous “model” systems.

### **2) Introduction:**

Interfaces are the boundaries between media (e.g., solids, liquids and gases) with distinct physical and chemical properties. The presence of an interface typically leads to gradients in the chemical potential, perturbs the properties of the two media to a depth controlled by the properties of the individual media, and introduces interfacial states (e.g., structural, electronic) that are different from that of either media. Well-known examples include the formation of Schottky barriers at the metal-semiconductor interface, the electrical double layer at the interface of a charged solid in contact with an electrolyte solution, and the spontaneous symmetry breaking associated with surface reconstructions. Interfaces can also act as kinetic barriers between reactive media, effectively stabilizing materials that are thermodynamically unstable (e.g., passive oxide coatings on aluminum metal inhibit corrosion).

Interfaces are central to many diverse fields of study (See Figure 1). These include: *materials science*, where the control of the composition and structure of an interface can lead to desirable

materials properties; *geochemistry* and *environmental science* where the transport and sequestration of nutrients and contaminants is often controlled by their interactions with mineral surfaces; *chemical science*, where the heterogeneous reactivity of interfaces in “supported” catalysts creates facile pathways that promote chemical reactions; *energy science*, where robust energy storage technologies currently rely on the passivating layers at solid-electrolyte interfaces to prevent catastrophic failure;

*nano-science*, where the nano-material properties are modified by their surfaces due to their large surface to volume ratios; and *bioscience*, in which membrane proteins actively maintain chemical gradients necessary for sustaining life. Solid-solid, solid-fluid, or fluid-fluid interfaces are all relevant. The solids may be either “hard” (e.g., metals or semi-conductors) or “soft” (e.g., organic- molecular or model membranes), and the fluid may range from an aqueous solution to liquid metals or supercritical fluids.

It is apparent, from these examples, that the understanding and control of interfacial processes are central to modern life. A more robust understanding of these areas can therefore lead to significant advances in addressing critical societal needs. For example, continued improvement in memory storage and other electronic devices, maintaining fresh water supplies, efficient production of petroleum based products, renewable production of clean energy, greater energy storage capacity to make full use of renewable energy sources, etc. Yet the ability to understand interfaces, especially those in complex environments, remains both a scientific and technical challenge.

The apparent diversity of disciplines, phenomena, materials and environments within this field masks deep underlying commonalities. Interfacial processes can be understood within the context of a few classes of molecular phenomena. These include: *molecular adsorption and bonding*, in which the presence of the interface leads to the organization and concentration of species from the environment; *chemical reactions and transformation*, in which the constituents of the environment and/or substrate react and transform to new species; and *growth, dissolution and processing*, in which materials are either deposited or consumed. It is at this level that the commonalities become clear. For example, the concepts of heterogeneous epitaxy, originally developed to understand the principles behind the semiconductor and metal film growth, provide the context to understand geochemical processes such as the anomalous inhibition of dolomite growth, a mineral which is often highly supersaturated in natural waters. Epitaxy is also closely related to the concept of wetting which explains the morphology of liquid films and is responsible (through interactions between hydrophobic and hydrophilic regions) for the conformations of biological molecules such as proteins.

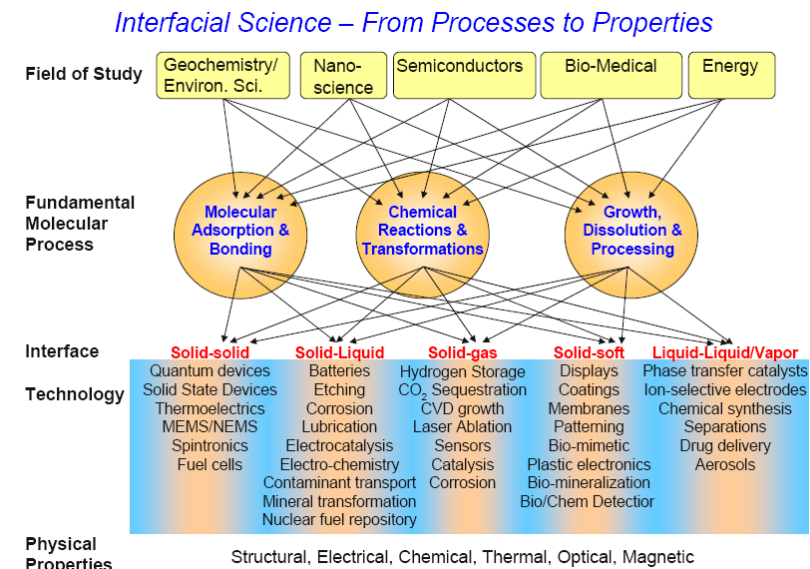


Figure 1: The diversity and commonality of interfacial science.

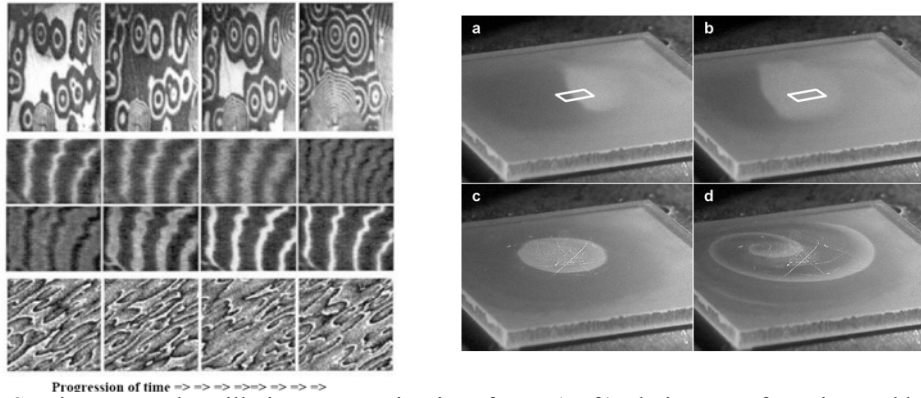


Figure 2: Spatio-temporal oscillations at reacting interfaces: (Left) Platinum surfaces imaged by photoemission electron microscopy during catalytic oxidation of  $\text{CO}_2$  where light and dark regions are associated with oxidized and reduced regions of the surface [From [www.fhi-berlin.mpg.de/surfimag](http://www.fhi-berlin.mpg.de/surfimag)]. (Right) Growth of InN films on GaN under MOCVD growth conditions in which bright and dark regions are InN islands and In droplets, respectively [Jiang et al., *PRL* **101**, 086102, 2008].

### 3) Science Drivers

Given the broad impact and relevance of interfacial science to many fields of study, it is not possible to provide a complete description of the many science drivers in this community. However, it is evident that much of the activity in this area can be illustrated by a few examples that are representative of the broader community.

*3.1) Interfacial Reactivity in Complex Environments:* Differences in the local coordination of interfacial species with respect to that found within the bulk media can substantially modify interfacial reactivity: either by decreasing thermodynamic barriers to enhance the reactions of surface-bound species (e.g., catalysis of chemical reactions) or through the development of kinetic barriers associated with compositionally or structurally-modified interfacial layers that inhibit the transport of material through the layers (e.g., the formation of protective coatings). Reactive interfaces are found in a broad spectrum of technical fields ranging from energy storage (e.g., batteries), to electrocatalysis (e.g., fuel cells), geochemistry (e.g., transport of contaminants), hydrogen storage, catalysis, materials growth and corrosion at liquid-solid and gas-solid interfaces.

Intrinsic to each of these areas are the divergent spatial and temporal scales describing interfacial reactivity. The fundamental step in these reactions involves the formation and breaking of chemical bonds between reactants and with the substrate. Insight into these reactions has normally been obtained by static views of the associated molecular ( $\sim\text{\AA}$ -scale) structures, before and after reactions. Individual defects (e.g., steps, adatoms, vacancies) typically have intrinsic reactivities that are substantially modified with respect to that of an ideally flat surface, leading to substantial lateral heterogeneity (from  $\sim\text{nm}$  to  $>\mu\text{m}$ ) in the reactivity. The idealized concept of a molecularly-sharp interface (i.e., normal to the interfacial plane) is often unrealistic as gradients in the chemical potential across an interface can lead to extended structures normal to the interfacial plane (e.g., extended elemental distributions in an “electrical double layer”, or the development of compositionally modified layers) 10’s to 100’s of nm thick. The relevant temporal scales at interfaces are similarly broad. Reorganization times of individual water molecules at an oxide interface vary from  $\sim 1$  to  $\sim 1000$  ps; the time for catalytic turnover ranges from  $\sim 1$   $\mu\text{s}$  to  $\sim 1$  s; growth or removal of individual layers ranges from  $\sim \mu\text{s}$  to hours.

The coupling of these disparate spatial and temporal scales can lead to unexpected complexities that have been largely unexplored (see Figure 2). A prime example is the observation of temporal oscillations during the catalytic oxidation of CO to CO<sub>2</sub> at Pt surfaces under nominally static conditions, which was a key element in the Chemistry Nobel Prize awarded to Ertl in 2007. Ertl showed that this phenomenon was due to non-linear reaction dynamics associated with the formation of reaction waves, ultimately associated with the differential reactivity of metal surfaces between two distinct surface structures and the associated transport of material between these regions. This is part of a general class of “Belousov-Zhabotinsky” reactions that are known to exhibit an extremely rich range of behavior ranging from regular periodic switching to chaotic dynamics. Spatio-temporal reactions have recently been observed under chemical vapor deposition growth conditions (Fig. 2, right).

These considerations reveal that a robust and fundamental understanding of interfacial reactivity relies on our ability to observe interfacial reactions in real-time, with high spatial resolution, and over large distances so that the complexities of transport, kinetics, and heterogeneities, etc., can be visualized directly. There remains, in particular, a broad need to project this level of understanding to realistic systems in complex environments (e.g., in contact with liquids, or high pressure gases that are opaque to traditional surface-science tools) that are representative of the complex and often heterogeneous interfaces that are central to many technical and industrial activities. The ability to observe such reactions in real-space (both within and across the interfacial plane) will require the development of robust “contrast” mechanisms that image individual components of a reaction (e.g., elemental specificity), or that differentiate chemically distinct regions (e.g., oxidation states), or that can differentiate between the reactivity of idealized terrace sites and spatially separated defect sites.

**3.2) Emergent Materials Properties at Interfaces:** Interfaces are not simply the place where two materials meet, with each of them retaining its own properties. There are abrupt changes in chemical and electrostatic potentials, as well as a lattice-mismatch that exerts significant stress on the material. Ionic and electronic reconstructions can occur at the heterointerface leading to the emergence of entirely new physical properties and phenomena.

An essential requirement for the study of heterostructure interfaces is the ability to image the laterally-averaged three-dimensional structure of buried interfaces, without sample thinning, with atomic scale resolution. This is a formidable problem because only the *intensity* is usually

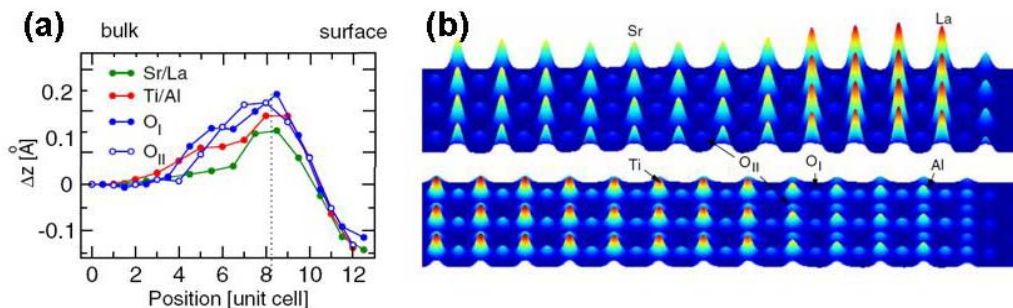


Figure 3: COBRA investigation of a LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interface grown by PLD using a YAG laser. (a): determination, at each layer across the interface, of the displacement of each type of atoms from their reference frame of bulk STO, and (b) electron density maps emerging from COBRA, showing the plane normal to the surface containing the La, Sr, and O<sub>II</sub> atoms and the plane containing the Al, Ti, O<sub>I</sub> and O<sub>II</sub> atoms. [Wilmott et al., *Phys. Rev. Lett.* **99** 155502 (2007)].

measured in conventional x-ray scattering experiments; the *phase* of the scattered x-ray is undetermined. This is the well known phase problem. Recently, significant progress has been made in providing a solution to this problem for epitaxial thin-films and buried interfaces. The importance of these developments lies in the fact that nearly all current electronic and optoelectronic materials applications and devices rely on heteroepitaxial interfaces, including compound semiconductor heterostructures and oxides exhibiting correlated-electron behavior.

The  $\text{LaAlO}_3\text{-SrTiO}_3$  heteroepitaxial interface is a prime example in that it forms a quasi-2D electron gas at the interface between two nominally insulating materials. The class of perovskite oxides to which this system belongs is broadly interesting because it exhibits various important emergent correlated electron phenomena such as novel metal insulator transitions, interface superconductivity and 'colossal' magnetoresistance. Surface x-ray scattering experiments (Figure 3) have revealed the formation of a metallic  $\text{La,SrTiO}_3$  layer at the  $\text{LaAlO}_3\text{-SrTiO}_3$  interface with an accumulation of trivalent Ti at the interface which is responsible for the observed lattice dilation (Fig. 3) and for minimizing the electrostatic energy at the  $\text{TiO}_2$ -terminated  $\text{SrTiO}_3$  substrate surface. The net result of this combined ionic and electronic reconstruction is to lower the conduction band minimum below the Fermi level, as confirmed by density functional band structure calculations. These findings illustrate the importance of heterointerface structure as the basis for the emergence of an electrically conducting interface as well as suggesting interesting directions for the design of epitaxial oxide multilayers with novel electronic properties.

*3.3) Soft Material Interfaces:* Soft materials include small organic molecules, macromolecules, polymers, polyelectrolytes, amphiphiles, block copolymers, colloids, liquid crystals, elastomers, and surfactants. Novel synthetic strategies, some inspired by biological processes, can be used to engineer the properties of these materials to be photo or chemical reactive, conducting or semiconducting, or to have different chemical affinities and localized interaction sites. This ability to tailor functionality has resulted in a wide range of applications such as high-resolution displays, organic light emitting diodes, field-effect transistors, and photovoltaics. Advantages of soft material-based devices include potentially low-cost production, environmentally friendly solution-processing, and roll-to-roll production methods on flexible substrates. Organic monolayers can also be used to modify surfaces for low friction, adhesion, and hydrophobicity, and may be functionalized to have selective recognition and be used as chemical or biological sensors. Soft materials can self-assemble into ordered structures as occurs with liquid crystals, block copolymers, and membranes. These self-assembled structures can be oriented by alignment surfaces and edge interactions (see Figure 4). Soft materials can alternatively be nano-patterned using imprint, dip-pen, electrochemical lithography and ink-jet technology. Hybrid devices in which inorganic nanoparticles or nanorods are oriented in an organic matrix have potential applications as photovoltaic devices.

The use of soft materials in applications often requires a systematic exploration of their numerous processing parameters and molecular degrees of freedom. High efficiency devices have yet to be achieved because of gaps in the fundamental understanding of the underlying interactions and electronic properties. A challenge for the next decade will be to understand what controls local and long-range orientational and positional order in soft materials and the impact of bulk and interfacial structure on transport properties. A representative example is illustrated in Figure 4, where grazing incidence x-ray diffraction (GID) was used to determine how the edge of a confining hexagonal well influenced a thin film of a spherical diblock copolymer as it self-assembled into a two dimensional hexagonal crystal. Numerous scientific



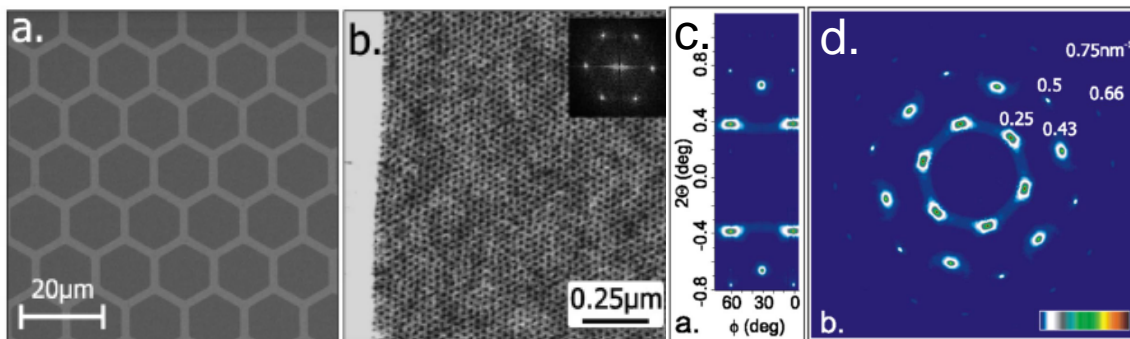


Figure 4: (a) SEM image of the hexagonal wells photolithographically patterned on a silicon substrate. (b) AFM image of the in-plane structure of PS-PVP diblock copolymer spheres adjacent to and aligned by a well edge. (c)  $I(2\theta, \phi)$  data map constructed from GID measurements of the edge-aligned diblock copolymer sample where  $2\theta$  is the in-plane diffraction angle and  $\phi$  is the in-plane rotation angle. (d) Data from (c) shown as a radial plot. [Stein et al., *Phy. Rev. Lett.* **98**, 86101 (2007)].

opportunities in this area include understanding how: processing conditions such as thermal and solvent-annealing affect thin film order; the orientation of organic monolayers affects lubrication or charge mobility; the local crystalline order and orientation of polymer films impacts performance when fabricated into different devices; mixtures of p-type and n-type semiconducting polymers phase separate into nanometer-sized domains; the morphology of these domains and the molecular packing within the domains can be optimized. The concept of biomineralization offers additional synthetic approaches to materials design and fabrication inspired by the complex structural control displayed by nature. The use of an organic framework apparently is central, but the exact role of this framework is poorly understood. Time resolved studies of crystallization under Langmuir monolayers will shed light on the fundamental processes at organic/inorganic interfaces.

Soft materials are also models for understanding biological systems, such as cell membranes. The chemical language of cells conveys information and ultimately has potential to exert control over cellular processes. For example, voltage-gated cation channels (e.g., K, Na, Ca) are integral membrane proteins that are responsible for the generation and propagation of the potentials that underlie nerve and cardiac action potentials. But an understanding of the structural changes within these membranes as a function of the applied transmembrane electrochemical potential is missing. Millisecond time-resolved studies of supported membranes can provide this missing information and make the connection with electrophysiological phenomena. Studies of model membranes at liquid-liquid interfaces offer the additional potential to understand the structural and dynamic properties of model membranes associated with membrane elasticity and membrane-protein interactions.

#### 4) Significance of the APS:

The development of synchrotron based sources had a major impact on interfacial science. First, the routine (if challenging) application of X-ray based techniques to interfaces was first enabled by the development of 2<sup>nd</sup> generation sources, a need arising from the intrinsically weak X-ray scattering cross-sections. This led to significant advances in our understanding of interfacial structure, with some of the first precise ( $<0.1 \text{ \AA}$  precision) determinations of interfacial structures. Second, X-rays opened up the possibility of in-situ studies in complex environments (e.g., the liquid-solid interface). The development of 3<sup>rd</sup> generation sources such as the APS has

led to substantial quantitative improvements associated with its higher flux (measurements in hours instead of days), brilliance (high collimation, spatial coherence, and the ability to probe smaller samples) higher photon energy (i.e., greater penetration into complex environments), tunability (enabling routine application of element-specific approaches such as RAXR and XSW), and stability (making it possible to obtain high quality data necessary for phase-recovery). These distinct advantages have led to a large and mature interfacial science community at the APS.

Of perhaps even greater significance to this community are the potential benefits to fully utilizing the current and anticipated properties of the APS. New and powerful advances in capabilities are available for this community by applying approaches that previously could be applied only to bulk materials. Many of these advances involve “imaging” interfaces, either through traditional microscopy, the use of coherent diffraction, or through phasing of data. Other advances include the application of ultra-fast techniques to this area to extend the temporal sensitivity to as low as  $\sim 1$  ps. Some of the proof-of-principle demonstration measurements have been done, but substantial advances in instrumentation as well as the development of new sources (e.g., for time-resolved measurements) will be needed to make the application of these capabilities routine. It is expected that these capabilities will transform this field, extend its reach to ever more complex and relevant interfaces and allow many scientific technical challenges to be met.

### **5) Scientific Community:**

The interfacial science community was one of the first to capitalize on the benefits of synchrotron radiation. Consequently, the community is both diverse and highly experienced. This community has been quite productive, in spite of the fact that these experiments are difficult, labor intensive, require extensive beam-time, and often involve complex instrumentation. Until recently the community was relatively fragmented, however, in which the various recent technical advances were developed independently through efforts in individual laboratories. It is apparent that this community stands to benefit strongly from having a strong institutional connection with the APS, especially as the community moves forward to make use of advances in optics, sources, software, etc., whose cost and necessary expertise now extend beyond the reach of individual research groups. The establishment of Sector 33 as a sector emphasizing Interfacial Science was an important first step that has substantial potential benefits for this community. The growth and development of this activity, as well as the development of a new X-ray Interfacial Science (XIS) sector, is thought to be critical to enable the various technical and scientific developments discussed in this document.

### **6) Requirements and Capabilities**

In the near term, substantial benefits can be obtained for interfacial science by relatively modest investments in instrumentation. For example, the use of area detectors (e.g., CCD detectors, Pilatus, etc.) has the ability to substantially improve the efficiency of measurements as well as the quality of the associated data. Improvements in the energy resolution and throughput of fluorescence detectors can similarly impact measurements. High energy X-rays ( $E > 40$  keV), a strength of the APS, are generally recognized as being well-suited for *in situ* atomic-scale structural studies. Hard x-rays have two key properties. First, they readily penetrate through centimeters of material, enabling the study of deeply buried structures or surfaces in complex environments. Second, the scattering of high energy x-rays is characterized by a very large

Ewald sphere so that the crystal truncation rods (CTRs) from each of the low index surfaces of a nano-particle can be completely characterized in a single image.

In the longer term, a fundamental understanding of interfacial structure and dynamics relies on our ability to observe the processes in real-time and in real-space. Here, we describe a number of opportunities that, if fully implemented, are expected to have an enormous impact in this community by substantially expanding the spatial and temporal scales over which interfaces can be probed (from  $<1 \text{ \AA}$  to  $>>1 \text{ \mu m}$ , and from hours/days down to ps). To be realized, such capabilities will require substantial investments in infrastructure and staffing to be realized.

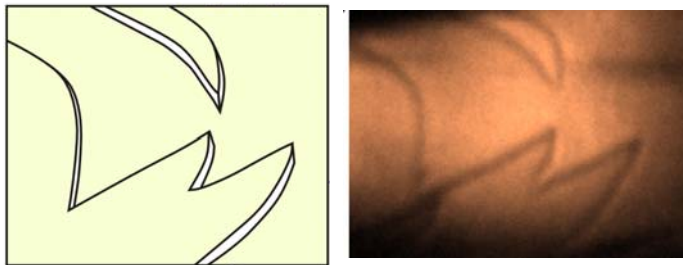


Figure 5: The X-ray reflection interface microscope (XRIM) images elementary interfacial topography through intensity contrast. (Left) Schematic interface topography (Right) XRIM image where dark lines are 0.6 nm high steps. [Fenter et al., *Nature Physics*, **2** 700-704 (2006)]

*Interfacial X-ray Microscopy:* The ability to work in direct space is a broad need in this area. The conversion of reciprocal space intensities to real-space structures has a significant limitation, namely probing properties that are statistically averaged over the sample (e.g., average defect spacing, height-height correlation functions) and this makes it difficult to investigate the behavior of isolated (aperiodic) structures and defects. Imaging elementary topography in real-space demonstrates the ability to probe the behavior of individual structures. This capability has recently been demonstrated with X-ray reflection interface microscopy (or XRIM; Figure 5). XRIM is similar to traditional full-field optical and X-ray microscopes, but uses the weak interface-reflected X-ray beam (with a reflectivity of  $<10^{-5}$ ) to create an image. Since the reflectivity signal is interface-specific, this leads to the ability to image interfacial topography. The differential reactivity of defects vs. ideal terrace areas can be assessed through direct observations. The primary challenge for this approach is that it is significantly photon-limited, especially given the weak reflectivity signal, the relatively low efficiency of the X-ray optics ( $\sim 10\%$ ), and the need to measure statistically significant signals in  $\sim 10^5$  pixels. In the first generation of this instrument, images could be obtained in a few minutes, but only over a relatively narrow reciprocal space range (i.e., where the signals were strong). The spatial resolution is limited, ultimately, by the numerical aperture of the X-ray optics, and was observed to be  $\sim 170 \text{ nm}$  (compared to the expected  $100 \text{ nm}$ ). Improvements of optics, instrumentation, and ultimately the X-ray source itself will lead to substantial improvements in spatial resolution ( $\sim 30 \text{ nm}$ ) and temporal resolution (e.g., video rate imaging of interfacial processes).

Scanning X-ray probe microscopes are complementary to the full field XRIM instrument. Such instruments have numerous contrast mechanisms available by probing various elastic (e.g., Bragg peaks) and inelastic (e.g., fluorescence) signals as a function of position on the sample. Of particular interest is the CNM's nano-probe, which is expected to attain a spatial resolution of  $\sim 10 \text{ nm}$ . This will result in an instrument with exceptionally high photon density that can be used to probe fast kinetics (e.g., ferro-electric switching of individual nano-scale domains in a thin-film material).



*Surface Coherent X-ray Scattering:* Surface coherent X-ray scattering (SCXS) technique is only now being explored due to the relatively low coherent flux of 3<sup>rd</sup> generation sources. Unlike phase-contrast microscopy, SCXS does not use an objective lens and is therefore limited only by the sample and beam characteristics and the sampling of the diffraction images. The evolution of diffraction images can be analyzed to reveal temporal dynamics (e.g., relaxation times) and evolution using X-ray photon correlation spectroscopy (XPCS). Alternatively, direct inversion of the diffraction pattern using phase-retrieval algorithms allows lens-less imaging, known as coherent diffractive imaging (CDI). The XPCS technique has been successfully applied to probe the dynamics of bulk-systems and polymer liquids. CDI has imaged the shape and strain field in micron-size Pb crystals.

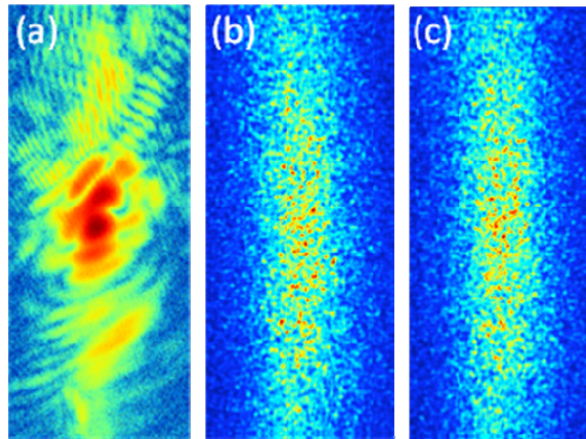


Figure 6: (a) Coherent X-ray diffraction pattern of the Au(001) hex-reconstruction peak (1.2 1.2 0.2) at 25°C. (b) and (c) Time evolution of anti-Bragg speckles at 840°C; two frames are separated by several minutes. [From Pierce et al., unpublished results (2008)]

The brilliance of APS and other 3<sup>rd</sup> generation light sources along with advancement of optics and detectors are just now enabling *interfacial coherent* X-ray scattering measurements. The feasibility of coherent interfacial X-ray scattering to study high-Z (e.g., Au or Pt) surfaces has been demonstrated recently at the highly optimized 8-ID beamline at APS. Pt and Au surfaces are interesting due to their importance as catalysts and the interplay of reactivity and structure that is known to exist on these surfaces (as seen in Figure 2). Interfacial dynamics under catalytic conditions will lead to new insights into the factors that control catalytic activity as well as serve as a test-bed for interfacial SCXS techniques.

Proof-of-principle interfacial SCXS images of a reconstructed Au(001) surface are shown in Fig. 6, including (a) the hexagonal peak, and in (b) and (c) the anti-Bragg reflection. While the hexagonal peak image was taken at room temperature (and is therefore static), the anti-Bragg reflections were measured at 840°C where both hex and (1×1) surface phases coexist and evolve. Here, the speckle structure varies with time providing sensitivity to the temporal evolution of domain distributions. Ultimately these interfacial XPCS and CDI measurements can be combined leading to a real-time *and* real-space surface X-ray imaging technique, providing quantitative measurements of micro- and nano-sized system evolution. Currently, the time scales over which this can be applied is in the range of >30 sec. with the ability to resolve objects >500 Å (e.g., due to the Q-range of the diffraction images). Eventually, the development of nearly fully-coherent hard X-ray sources will allow this approach to be extended to substantially faster time scales (< 1 sec), to smaller spatial resolution, and to the interfaces of low-Z materials.

*Imaging with Phase Recovery and Imaging Elemental Sub-structures:* While the phase problem of crystallography is a substantial impediment for any structural determination, including traditional CTR measurements as well as surface coherent X-ray scattering, once the phase is recovered the structural determination becomes essentially trivial. The seminal work of David Sayre showed that scattering phase can be retrieved solely from measured intensities under certain circumstances. Recent advances in phase-retrieval algorithms have made this possible

for isolated nano-structures. Recently, similar algorithms have been demonstrated the ability to recover *interfacial* structures as illustrated in Fig. 3. Robust phase recovery formalisms would substantially benefit this community by transforming X-ray scattering data into real-space images. It is anticipated that such algorithms could be developed that provide rapid phase recovery, so that interfacial structures can be observed directly and in real-time as the data is acquired.

Complementary to the phase-recovery techniques are approaches that can probe sub-structures (e.g., elemental, magnetic, etc.). Ideally, these measurements are designed to be explicitly phase sensitive so that one can view the scattering measurement as sampling the amplitude and phase of the sub-structure of interest (i.e., its complex structure factor). To date, this perspective has been applied to a few types of experiments, such as Bragg-XSW and RAXR. It is expected that this general formalism can be applied to essentially any scattering technique, providing the ability to “image” sub-structures.

*Time Resolved Studies:* Our fundamental understanding of interfacial and material structures has been advanced primarily by direct measurements of *time-averaged* structures using x-rays. However, matter is not static. The characteristic time for atomic rearrangements is roughly the period of an optical phonon and is typically on the order of a picosecond. Thus, one can expect fundamentally new insights into the dynamics in chemical reactions, phase transitions, and in response to external stimuli if such measurements were to be performed at picosecond time scales. Only optical pulses are short enough to initiate such reactions precisely enough to follow the temporal response in real time. Thus, pump/probe measurements using ultra-fast laser pump beams and time delayed probe beams have been the standard ultra-fast experimental technique for many years.

A substantial opportunity for interfacial sciences at the APS is the plan to build a (2-3) picosecond x-ray source which operates at high repetition rate (i.e., 6.5 MHz) with  $\sim 5 \times 10^{12}$  ph/sec/1% bandpass. Such a source would have a time-averaged flux capable to observe fast ( $\sim$ ps) interfacial processes with  $<1$  Å structural sensitivity. This would substantially extend the temporal resolution available to interfacial processes at the APS with respect to current capabilities. An example of the extraordinary science that can be accomplished combining femtosecond laser excitation with ultrafast x-ray sources is illustrated in Fig. 7. Similar measurements could be performed to probe the perturbation of interfacial structures.

A major challenge to working at high repetition rates is dissipating the

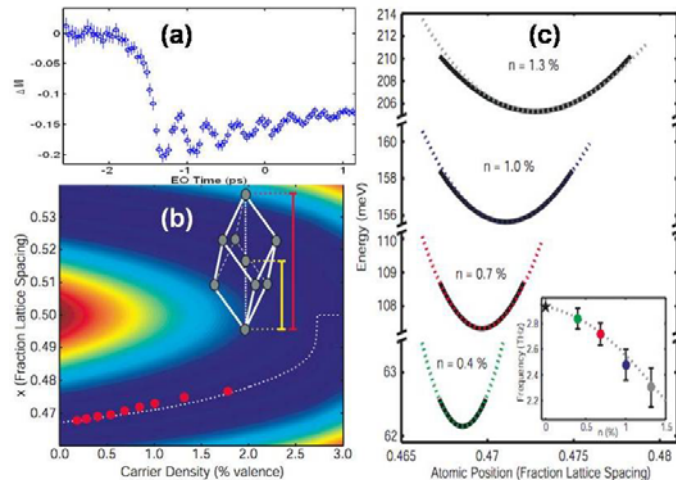


Fig. 7: Ultrafast measurement of lattice potentials. (a) Ultrafast x-ray diffraction efficiency on (111) Bismuth as a function of the time delay between pulses. (b) Experimental (red) and calculated (dotted line) interatomic quasi-equilibrium position as a function of the percentage of photoexcited electrons. (c) Reconstructed potential energy surfaces and phonon frequencies (inset) for different excitation levels. [Fritz et al., *Science*, **315**, 633-636 (2007)]

energy (usually in the form of heat) delivered by the pump laser. In solid samples, the time scale on which heat is dissipated is typically set by thermal diffusion. Thus, in principle, one can shorten the equilibration time by shrinking the volume illuminated by the pump beam. For example, the equilibration time for 10 $\mu$ m length scales in GaAs is on the order of 5 $\mu$ s, enabling the use of higher repetition rates. In practice, the decreasing depth of focus for the optical beam as the beam waist is decreased will set the practical limit for the minimum pump beam waist to be somewhere in the 1-10 $\mu$ m range. In gas jets and liquid flow cells, the heating and radiation damage issues are handled by continually flowing in new sample.

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