Report on the breakout session

Surface and Interface Science

Joint Workshop for:

The NSLS-II Powder Diffraction Project Beamline

Materials Science and Engineering Strategic Planning for NSLS and NSLS-II

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Charge of the breakout session

This breakout session was convened in order to: (i) review and update the grand scientific challenges related to Surfaces and Interface Science, and begin building a strong science case that capitalizes on the unique capabilities of the NSLS-II, and (ii) review and suggest changes to the organizing committee's straw-plan for the suite of primary beamlines and transitioned beamlines.

1. Introduction to Science Theme

The overall theme of the Surface and Interfaces Science proposed for NSLS-II will be to combine and strengthen existing activities in several areas with an entirely new capability to use focused x-ray beams. In-situ studies of inhomogenous surfaces, thin films, and interfaces will be carried out with spatial resolution down to ~50 nm. A broad body of methods have been devised to probe the characteristics of surfaces and interfaces using x-rays, which are briefly described in the following sections. The capabilities envisioned by the source and instrumentation of the NSLS-II will not only allow world-class surface/interface research in these ongoing areas to continue, but will allow a revolutionary leap in a dimension that has become vital in a host of systems. Specifically, the high brightness will allow us to deliver sufficient photon flux into a spot with small lateral dimensions to probe processes that scatter only weakly. Such lateral dimensions can be achieved even with reasonable working distances, compatible with real processing environments. This revolutionary capability will allow access to surface-specific phenomena on inhomogeneous samples during processing, such as modern electronic devices, catalysts, and growth on patterned media. In addition, for traditional homogeneous 2-D samples, the favorable characteristics of the source will allow extremely high flux to be delivered in grazing incidence; we can then gain access to time-resolved measurements, measure very weak phenomena, and make very rapid determinations of complex interfaces.

Time-resolved studies of thin-film growth and processing

Atomic-level precision in the growth of thin-film heterostructures and novel materials is increasingly required. The ability to characterize samples and control thin-film growth and processing on atomic length scales and in real time is critical to advancing our capabilities. The ability of X-rays to penetrate through process environments and to access atomic length scales make them nearly ideal for real-time structural and chemical studies of thin-film growth and processing. Some of the growth/processing techniques of interest include: sputtering, sputter deposition, thermal deposition, supersonic beam deposition, molecular beam epitaxy, atomic layer deposition, pulsed laser deposition, chemical vapor deposition, and ion beam assisted deposition. To make progress, time-resolved x-ray probes must be incorporated into already sophisticated growth systems. To ensure the integrity of the growth/processing, dedicated systems are required for each technique and, frequently, each material system studied. The high brilliance of the NSLS-II undulator beams is well-matched to the needs of these experiments. It will enable experimenters to utilize all of the x-ray beam in grazing incidence geometries near the critical angle and to focus the beam to 20-50 nm spot sizes.

Rapid structural determination of complex surfaces

Modern condensed matter investigations focus on the interplay of electronic and geometric structure, and surfaces of such materials often exhibit novel phenomena. The behaviors of interest are manifested in relatively complex crystals. Thus, surface crystallography must evolve into a tool capable of making routine measurements of the full, three-dimensional structure of complex systems. Such a tool requires rapid acquisition of large datasets and swift reduction and analysis of the data. Presently, there are bottlenecks in data acquisition that an improved source and advanced instrumentation will bypass, and roadblocks in structural determination that developments in phasing can ameliorate.

In-situ and ex-situ structural analyses can be greatly sped up with advanced detectors and new scan modes. There are no major roadblocks to implementing these, but development will be required. In SXRD, a surface structure factor is typically acquired by conducting a rotation scan to pass the diffracted signal of interest through the detector, and measuring the integrated intensity. Instead, use of an area detector allows one to measure the intersection of of the signal with the Ewald sphere in one exposure, effecting a speedup of about 30 times. Moreover, typical x-ray measurements employ a step-wise scan, where all motor motion ceases and a measurement is made. This measurement may proceed for an extended time to accurately capture weak signals, as encountered in SXRD. However, with a bright source, the count rate will be greatly enhanced, allowing a new acquisition mode to be used effectively. Specifically, a “trajectory scan” can be used, where the motor never stops, but the data are read out continuously. Such a mode would more optimally couple the characteristics of the source to that of the detection system, but requires (evolutionary) advances over detectors currently available. With these improvements, acquisition times will fall dramatically, allowing much larger data sets to be gathered. (Short acquisition times are sometimes imperative for fragile surfaces.)

Inverting these data to find a correct structure determination for relatively simple surfaces can be time-consuming, and for complex surfaces can be extremely nettlesome. Advances in phasing techniques (i.e., direct methods) will be necessary to make sense of the data quickly, allowing an image of the three-dimensional near-surface structure to be constructed within hours of acquiring the data. These methods are under development, but work is needed to increase the robustness and generality of the inversion.

Use x-ray spectroscopy and resonance effects to study surfaces

An emerging theme in research on complex oxides is the use of resonance effects to gain information about the chemical, electronic, and magnetic structure of surfaces and thin films. Techniques such as X-ray Absorption Spectroscopy and Resonant X-ray Scattering are used to study electronic states. Surface sensitivity may be obtained by use of grazing incidence. An example is the use of Resonant Inelastic X-ray Scattering (RIXS) to probe thin films of manganites. Strain localizes 3D electronic states, which can be easily observed by this technique.

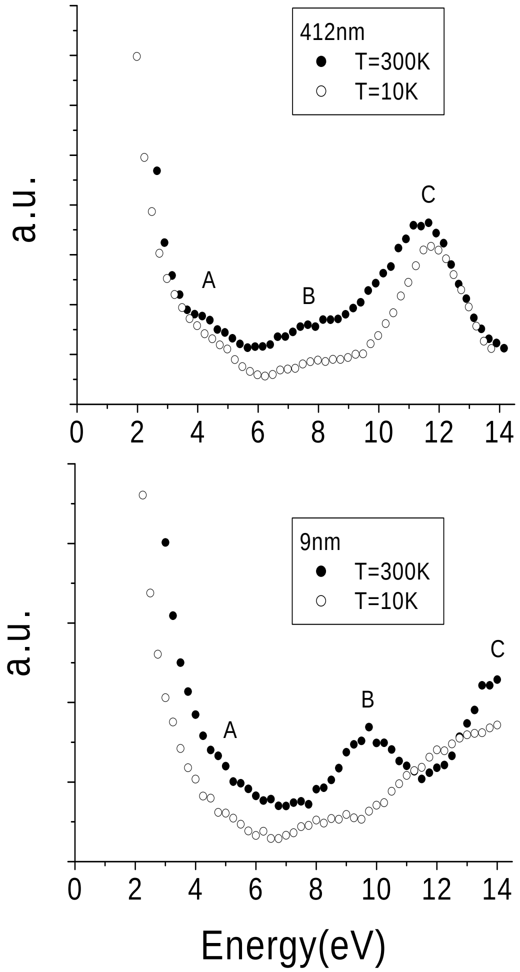


Fig. 1. RIXS measurements of 412nm (top panel) and 9 nm $La_{0.8}MnO_3$ films (lower panel) showing the strain induced localization of 3d band (labeled B) in the insulating phase of the 9 nm film. (APL **90**, 101915 , 2007)

The characteristic feature of correlated oxide system is closely lying structural, magnetic, orbital and other electronic/structural states. This results in spatial inhomogeneities. Hence to understand the properties of these materials, the ability to obtain spatially resolved electronic and structural information is essential. For example, direct comparisons with PEEM magnetic imaging with a current resolution of 50 nm will be quite useful. Utilizing RIXS and high resolution x-ray emission methods with hard, x-ray bulk sensitive information will be obtained and it will be possible to probe buried structures not accessible to the PEEM technique. Serial x-ray diffraction and x-ray spectroscopic (XAFS) measurements will enable both long range and local structural information for the region probed by the ~50 nm beam. Hence both high energy resolution and high flux are essential. Both *in situ* and *ex situ* film growth studies will benefit from this capability. Chambers for high-quality oxide growth that have the capability to perform in-situ RIXS, XAS and GIXD will allow a new generation of experiments in this area.

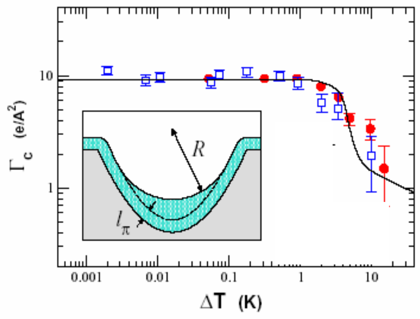
Microelectronics industry research

As microelectronics devices shrink, and new materials and processes are incorporated to improve performance, the behavior of interfaces in thin layers play a major role in the outcome. In-situ diffraction and other measurements, such as resistance and visible light scattering, taken during processing yield vital information about the behavior of thin films and small features. The formation of desired crystallographic phases, grain orientation and size, smooth surfaces, strain, and transition temperatures can all be measured during rapid thermal or laser annealing. Some of the materials of interest include copper for interconnects, metal silicides for transistor contacts, lead-free solders, phase change materials for advanced memory, ultra-low-k dielectrics for insulation of the transistor gate, and diffusion barriers between copper and silicon. While thin films are studied for preliminary assessment for process and materials parameters, arrays of nanopatterned features are measured to determine the effect of size on the same characteristics. Often nucleation or diffusion effects will change the kinetics of phase formation in small features. Complementary measurements will a nanometer-scale x-ray probe are also of interest. Looking at an isolated feature while current is running through it allows investigation of phenomena such as electromigration.

Soft Matter Interface Science

Many problems in soft-matter interface science involve both a solid surface and organic films. An example of such an interface is a thiol bonded monolayer on a single crystal gold surface or an alkyl monolayer directly bonded to a single crystal silicon surface. In this class of problems there is great interest in both the structure of the organic layer and of the arrangement of atoms in the solid. Interdisciplinary science that crosses the boundaries between soft and hard matter, such as the problem mentioned above, is extremely relevant to many scientific issues in nanoscience.

The soft-matter community is also developing a plan for facilities for interface and surface scattering beam lines and it is important for this group to coordinate its plans with those of the soft-matter community. Currently, the two interface beam lines under primary consideration by the Soft Matter Community are a liquid spectrometer, where the sample must remain horizontal, and a Grazing Incidence Small Angle X-ray Scattering beam line. These specialized instruments may not be optizimized for all classes of interface studies and the proposed suite of Materials Science beam lines maybe better suited for certain classes of measurements. The GISAXS station will employ a vacuum vessel to reduce air scattering and may limit some measurements that require larger sealed chambers. The complicated nature of the liquids spectrometer makes it needlessly complicated for thin organic films.



Wetting experiments on nanopatterned surfaces, both from organic liquids and noble gases, maybe sell suited for the proposed beam line. We have carried out wetting studies on topographically patterns with periodic order. The macroscopic description of wetting films is predicted to break down at nm length scales and many theoretical predictions related to these nano-properties have not been tested due to the technical difficulties of measuring the structure of nanoliquids. Our research aims to investigate these nano-liquids by using in-situ synchrotron surface x-ray scattering techniques. We have investigated the wetting of nanopatterned substrates prepared by block copolymer films. More recently we have initiated investigations using patterns created using e-beam lithography. Our initial studies were carried out using parabolic shaped cavities, 20 nm wide and separated by ~40 nm. Our results show that the wetting behavior differs from the predicted $\Delta\mu^{-1/3}$ thickness. The exact dependence, including the cross-over to the filled region, has been well described by simple models by Rascon and Perry and detailed calculations by Dietrich and coworkers, both of which are in good agreement with our results. More recently, we have extended our studies to a pattern of posts, only 100 by 500 microns in size, which were created with e-beam lithography. This is an emerging new metrology for characterizing patterned media, such as those that maybe used in the next generation of magnetic devices.

2. The Growth, Expansion, and Transition of NSLS Scientific Programs

The real-time studies of materials growth and transformation at the NSLS-II will benefit greatly from a strong effort in this area already existing at the NSLS. For example, the IBM beamline X20C has pioneered the time-resolved examination of transformation kinetics in thin films during rapid thermal annealing (RTA), particularly silicides that play a central role in the semiconductor industry. Jordan-Sweet and collaborators at IBM have also examined phase change materials and Si-Ge structures that will likely play an important role in the next generation(s) of technology. On X22, Lyman's group has developed new techniques for determining surface and interface structure. Headrick, Ludwig and collaborators have developed a dedicated UHV facility on X21 for the real-time studies of surface and thin film processes that has been used to examine, among other issues, surface morphology development and nanostructure formation during ion bombardment, the growth of wide-bandgap nitride semiconductors by MBE, Ge nanodot growth and surface/interface evolution during the growth of multilayers by sputter deposition.

To pursue a complementary program of research for those in-situ experiments not needing nanobeam capability, to take better advantage of the existing expertise at the NSLS, and to attract new users to the field, the X21 beamline should be moved to a three-pole wiggler adjacent to the undulator beamline of the in-situ nanoprobe facility. The X21 beamline, with its cryogenically cooled monochromator, can likely be moved with little modification to the 3-pole wiggler NSLS-II line, making this a very attractive option financially. This new beamline would house three in-line experimental hutches with relatively rapid (less than 1 shift) switching time.

An upgraded time-resolved RTA experimental chamber/diffractometer from IBM's X20C effort would move into the first hutch. IBM is planning to rebuild this system to incorporate laser annealing, high throughput (robotic sample handling) and remote access. The second hutch would contain a flexible general-purpose six-circle diffractometer for thin film analysis. This diffractometer could also accomodate small chambers for in-situ studies. The third hutch would house a diffractometer with a similar geometry to that now on X21, so that upgraded chambers could be rolled on and off, and also used on a complementary diffractometer on the undulator line. The existing surface chamber diffractometer on X21 could be used effectively on the three-pole wiggler line. Because it's in the end station, we plan continuous access to the surface chamber for sample preparation and optimation of experimental parameters.

By placing the new beamline adjacent to the undulator line, transportable chambers can easily be moved between them and a community of related researchers can be fostered. Some infrastructure (e.g. office space) could potentially be shared between them. In addition, the limited footprint of the undulator beamline's beamtube would allow sufficient lateral floor space to more optimally use the new 3-pole wiggler line for in-situ chambers.

It is anticipated that IBM will use approximately 20% of the total beamtime and Headrick/Ludwig will use 25% of the total beamtime on the 3-pole wiggler line.

3. Proposed Suite of Beamlines

High-brightness, high-flux beamline

1. For time-resolved measurements, weak signals, small beams.
2. High brightness undulator source.
3. Energy Range 2 – 25 keV.
4. Choice of bandwidth 1%, 0.01%, 0.2 eV.
5. Focussing elements for ~30 micron to ~50 nm at sample inside processing environment.
6. Multiple end stations with various size/complexity growth and processing equipment.
7. Ventillation, gas handling, fume hoods, etc.
8. Beamline extends beyond outer wall of NSLS-II to an “out-building”.
9. Close proximity and easy access to LOB.
10. Desks for students.
11. 3-5 hutches, mainly in a Tandem arrangement, although other configurations, possibly involving canted undulators may be of interest.

3-pole wiggler beamline

Move X21 to a three-pole wiggler. No essential changes to the beamline are envisioned.

4. Beamline Specifications and R&D Needs

The beamline specifications are still evolving. However, the majority of the end stations will require more floor space than will be practical to provide within the currently planned NSLSI-II building. Therefore, an out-building is envisioned.

The flux of the U20 undulator drops rapidly above 20 keV. Other undulators should be considered, such as the U14 superconducting undulator.

Detectors are a key area for research. We envision a suite of detectors will include various strip detectors and area detectors, which will include detector capabilities such as microsecond time resolution and energy resolution.

Other areas for research include vibrations, endstation development, and methods for phase retrieval for surface/interface structure determination. Collaborations with Argonne National Laboratory and with industry may be mutually beneficial.

5. Recommended Transition/Construction Sequence

Real-time in-situ growth studies are currently being conducted at NSLS beamline X21 as a Contributing User Program. In addition to this program that utilizes interchangeable UHV processing chambers, the NSLS SAC recently approved the installation of a psi 6-circle goniometer upstream of the heavy-duty diffractometer that orients the UHV chambers. The psi

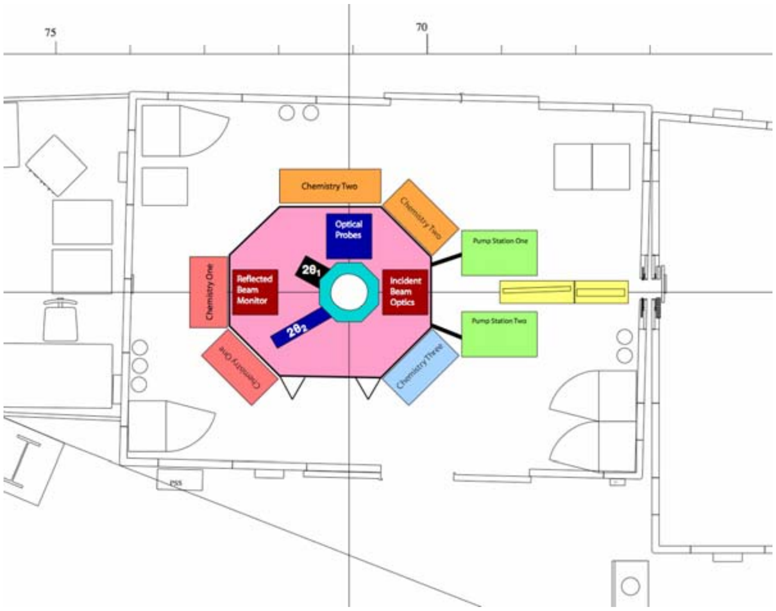
6-circle goniometer will be used for ex-situ measurements as well as small scale environmental sample chambers. These existing facilities will play a key role in the transition plan to NSLS-II, which is proposed to involve both a transition of the existing beamline to a 3-pole wiggler beamline as well as the development of new surface diffraction capabilities on dual undulator sources.

Concerning the transition of the existing facility, the plan of the community is to expand the number of available UHV sample chambers (an organic vapor phase deposition chamber is one possibility), explore ways to refine techniques such as in-situ reflectivity with pixel array detectors so they can be effectively utilized on a 3-pole wiggler device, work with industrial users (IBM or Albany Nanotech) to develop chambers with multiple probes that provide complementary information as samples undergo processing such as thermal annealing, explore how statistical information on arrays of nanofabricated structures can be analyzed and help optimize fabrication processes, systematically train new graduate students and postdocs as potential users, and reach-out to new user communities that are currently not using the synchrotron facility through surface science workshops. In this way, not only will the surface science community be transitioning a beamline to NSLS-II, but also a large and active user community posed to use the new facility.

Concerning the phased construction of the new surface and interface undulator-based facility, the community would first develop one of the two proposed dual undulator beamlines and instrument this line with redesigned UHV chambers as well as a new goniometer that conveniently allows for interchange of UHV chambers and incorporates design features demonstrated to be successful at existing high brightness sources with active surface science communities such as the APS and SLS. It would be particularly beneficial if the APS proceeds with its proposed suite of surface and interface science undulator beamlines since new concepts for the NSLS-II beamline can be tested and refined at this facility. Modes of facility operation would be implemented and improved on X21, for example, the efficient switching of projects between those using moderate scale chambers to those using small scale sample chambers. Use of nano-focused beam for probing surface inhomogeneities, a key new capability at the NSLS-II surface science beamline, would be explored on sub-micron length scales by upgrading X21 to include a K-B mirror pair. The plans for the NSLS-II undulator beamline include an upstream small-scale chamber 6-circle goniometer. The use of this instrument for buried interface samples would be facilitated by developing 'user friendly' software for data acquisition and analysis of surface diffraction features. This software would be fully tested on X21 and be available for use at the NSLS-II facility as soon as it could be constructed.

6. Facility Infrastructure at NSLS-II

This facility will support a number of complex technologies which require the use of hazardous chemicals, high-power lasers, and equipment with a large footprint. The complexity of these instruments requires extensive and time-consuming setup before measurements can be performed. We find the need for several unique facility requirements.



First, we envisage the use of multiple, in-line hutches where the upstream hutch includes a general purpose instrument and the downstream hutch or hutches are occupied by large instruments for extended periods of time. Since the instruments are large, the minimum useable hutch size is roughly 4 meters by 4 meters. Figure FR1 shows the conceptual design of a modern metal-organic chemical vapor deposition (MOCVD) system showing a specific example of how this space might be used. We anticipate that space for the large, multiple hutches required for these experimental programs cannot be accommodated on the NSLS II experimental floor and will need to be located in an ancillary building.

In addition to the physical space requirement, this instrument is typical of the class of instruments envisaged here in that it requires a significant exhaust capability (roughly 3000 cfm) of exhaust for chemical safety, extensive space for gas cabinets and gas handling equipment, utilities such as cooling water, large electrical service, and compressed air supply, and a large ancillary control area. Other chemical growth techniques such as atomic layer deposition will require similar infrastructure.

Experiments such as pulsed laser deposition require less exhaust but significant additional space for a high power laser deposition system. Experiments on catalytic materials require significant space for surface preparation and characterization equipment (e.g. scanning probe microscopy) to be done in conjunction with the synchrotron measurements along with the ability to use appropriate catalytic materials.

Appendix A: Breakout session participants

Name	**Institution**
Karl Ludwig	Boston University
Jean Jordan-Sweet	IBM Research Division US
Lonny Berman	Brookhaven National Laboratory
Syed Khalid	BNL
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Jeffrey Fitts	BNL
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Joel Brock	Cornell University
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Hua Zhou	BNL
Yiping Wang	The University of Vermont
Richard Matyi	SUNY -- University at Albany
Trevor Tyson	NJIT
Abdul Rumaiz	BNL
Joe Dvorak	BNL
Nathalie Bouet	Boston University
S. Smadici	Univ. of Illinois at U.C.
Peter Siddons	BNL
Ben Ocko	BNL
Ken Evan-Lutterodt	BNL
Elaine DiMasi	BNL