Argonne NATIONAL LABORATORY

... for a brighter future

APS Renewal Open Forum

9 January 2009

Surface Probes

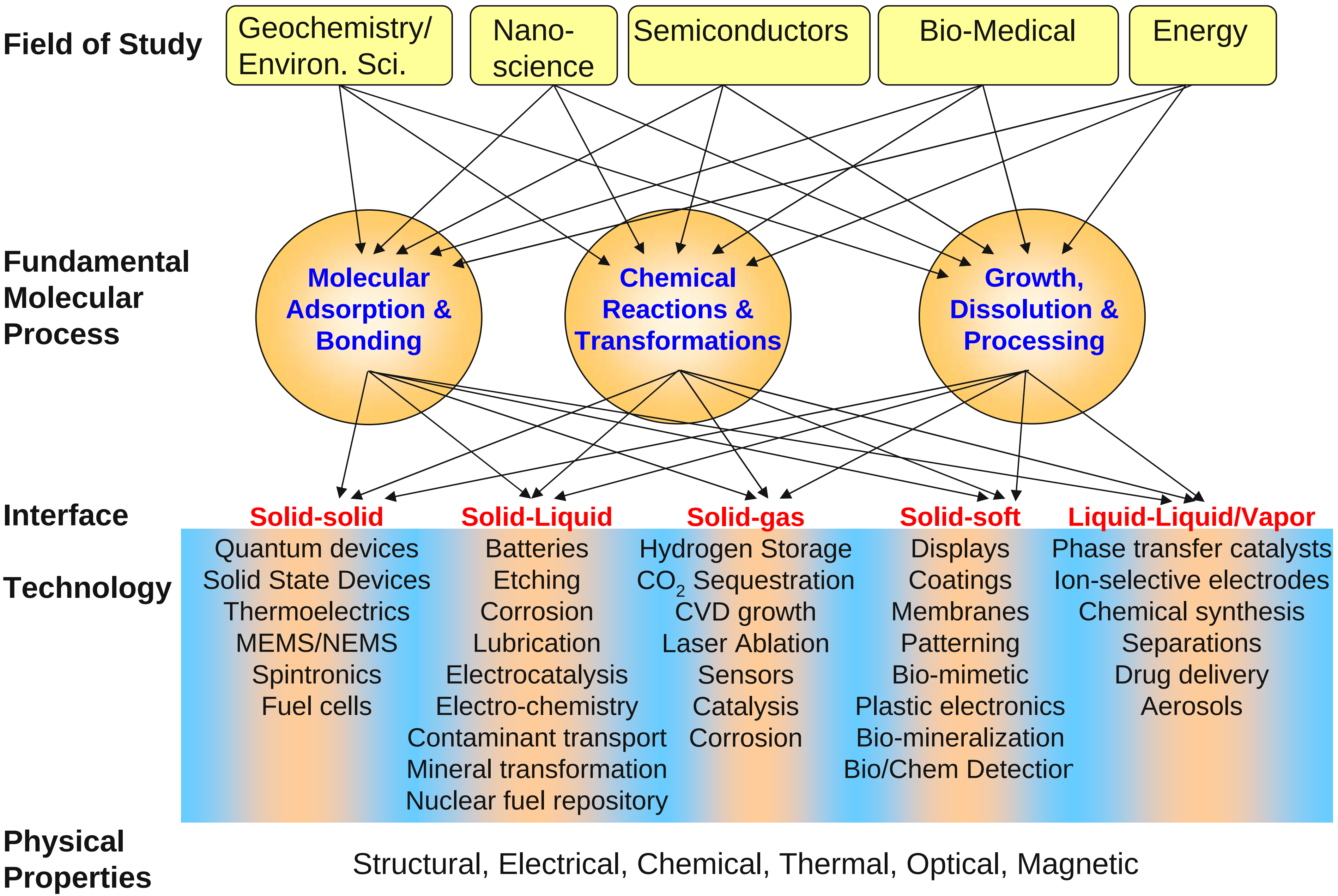
including:

Reflectivity
Standing Waves
GISAXS
Surface & Interface Scattering
Liquid Surface Scattering

P. Zschack, X-Ray Science Division, APS

J. Wang, X-Ray Science Division, APS

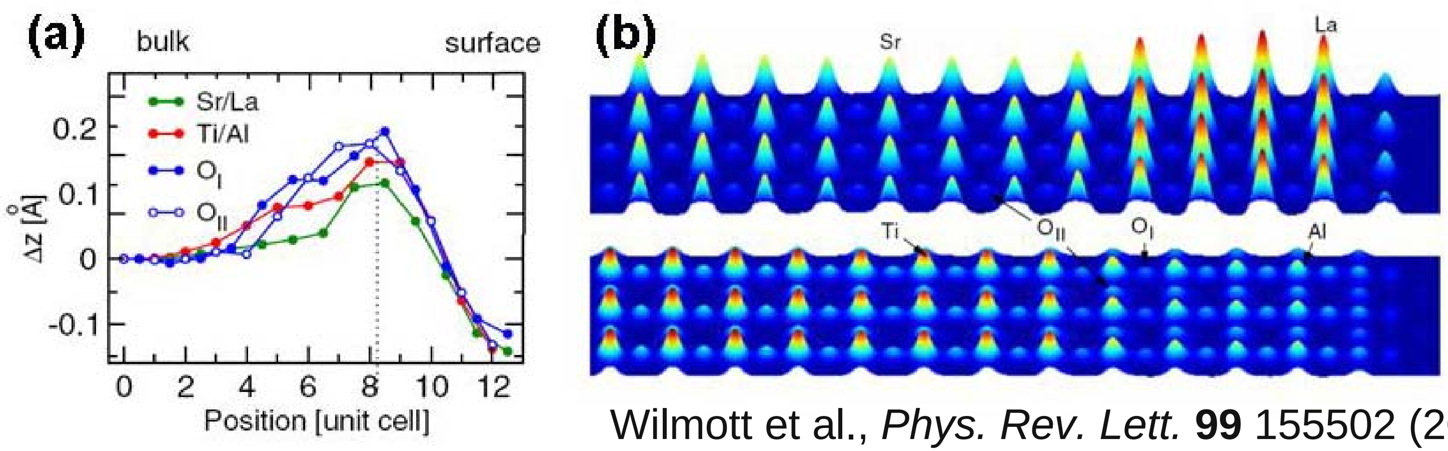
Interfacial Science – From Discipline to Processes to Properties



Major science themes: Emergent Materials Behavior at Interfaces

- metal insulator transition
- interface superconductivity
-'colossal' magneto-resistance
- 2D interface conduction

Structure imaged using CoBRA algorithm: 4-layer film of $LaAlO_3/SrTiO_3$



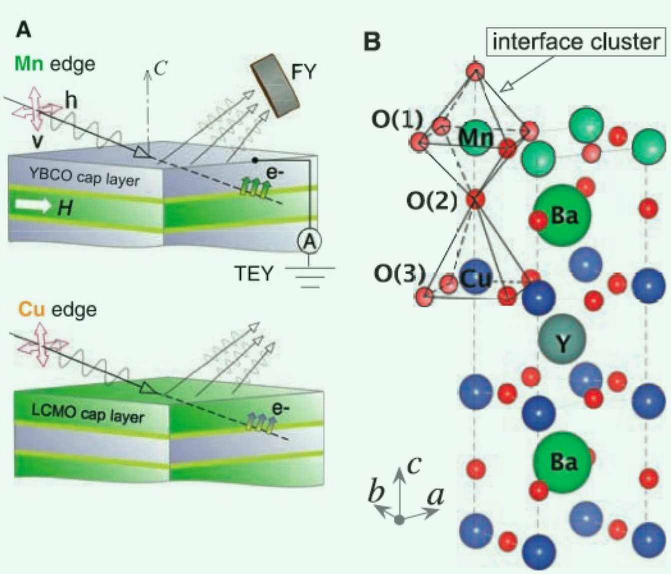
Wilmott et al., *Phys. Rev. Lett.* **99** 155502 (2007)

Currently: only understand laterally averaged static structure
→ Need to image structure and element-specific sub-structure
→ Real-time measurements during film growth

Interfacial magnetism: Magnetic Reflectivity

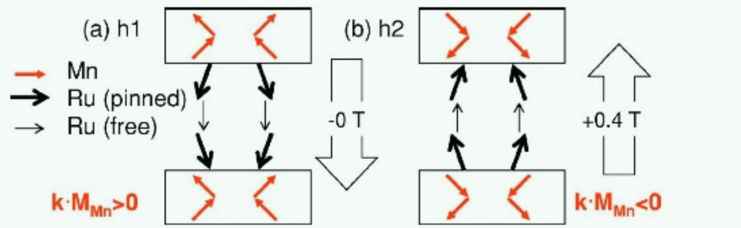
- Manipulating electronic structure at interfaces central to “materials by design” quest.
- Hybrid structures of superconducting, metallic, insulating, magnetic, non-magnetic materials key to advances in information- and energy- technologies (spintronics, solid state lighting, etc).

LaCaMnO3/YBCO
CMR-FM/Superconductor



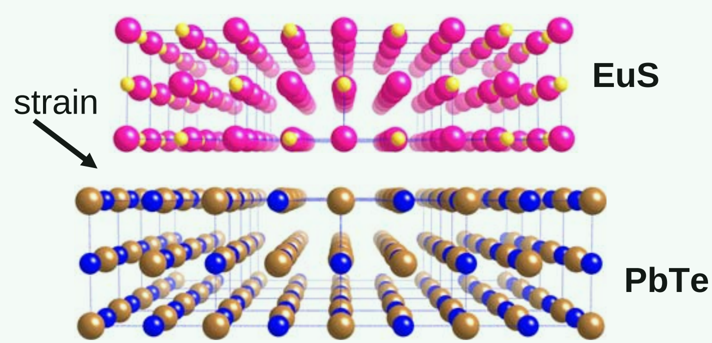
Science 318, 1114 (2007)

SrMnO3/SrRuO3
AFM/FM

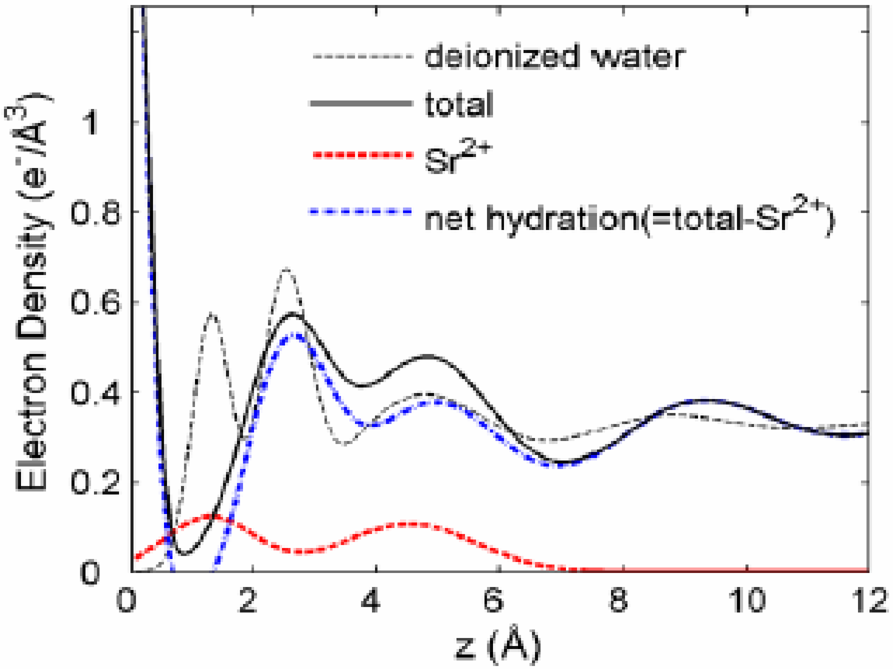


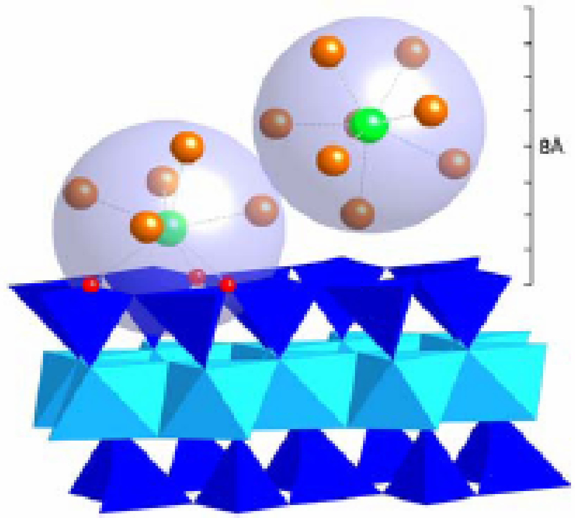
APL 91, 022503 (2007)

Epitaxial strain to control magnetism



Progress in understanding interfacial geochemistry of solute ions



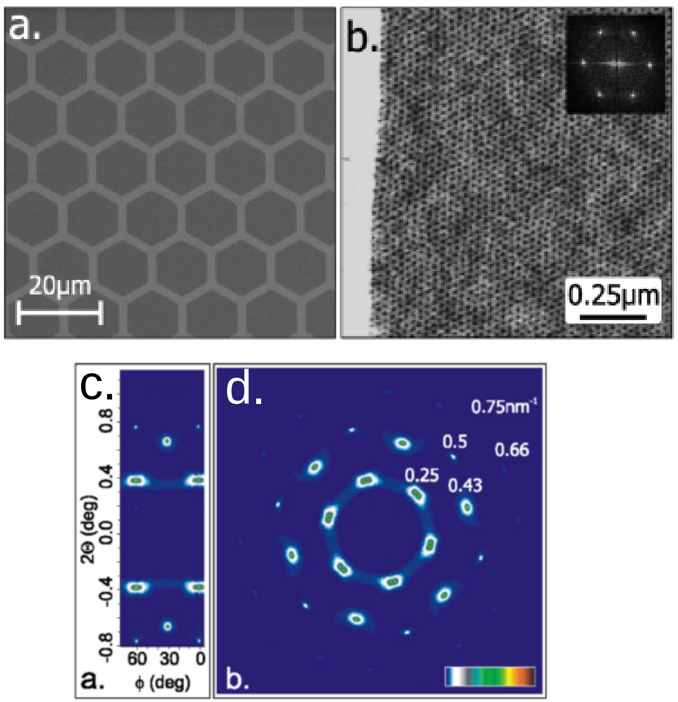


Using RAXR to characterize distribution of adsorbed ions at mica-water interface – finding roughly equal amounts of both inner-sphere and outer-sphere Sr (Park et al., *Phys. Rev. Letters*, 2006)

Major science themes:

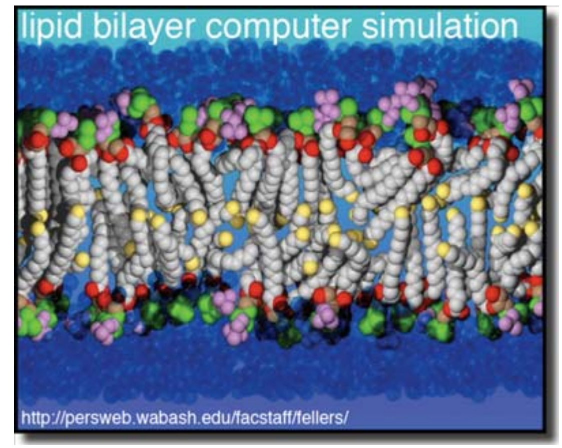
Soft-material interfaces: organization and complexity

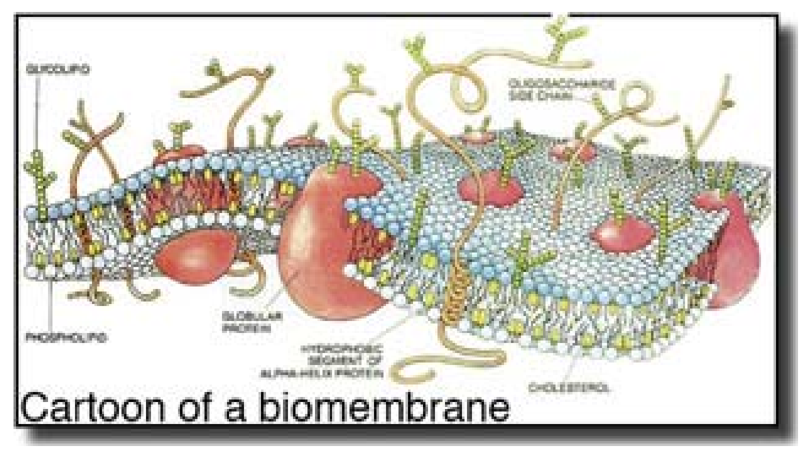
Control of long-ranged orientational and positional order in organic films:



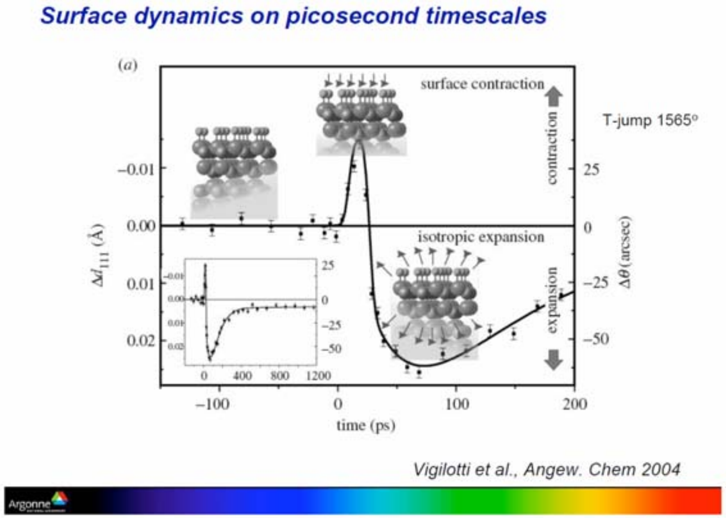
Stein et al., *Phy. Rev. Lett*. **98**, 86101 (2007)

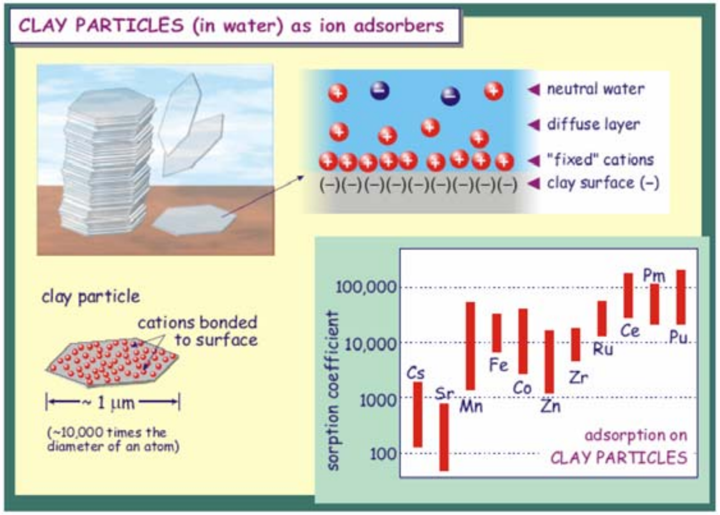
Membrane science: temporal/structural response of voltage-gated ion channels:

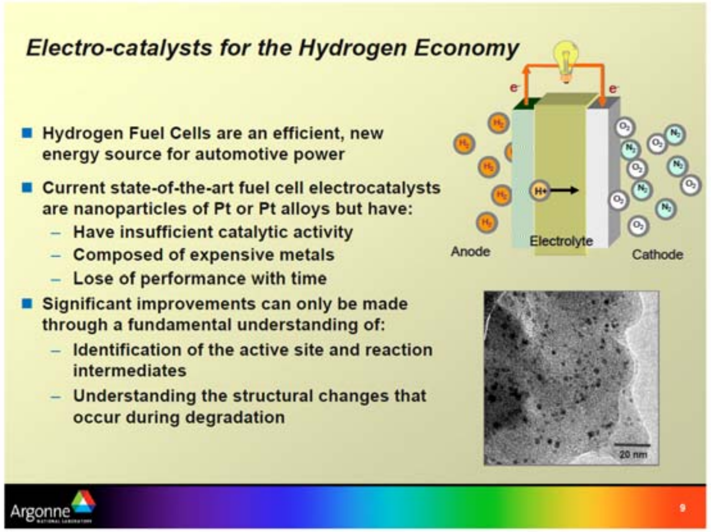


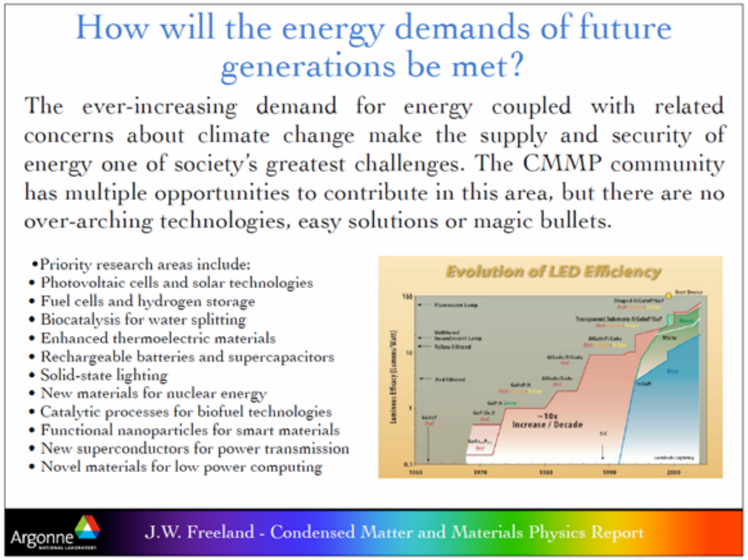


Examples that connect “Surface Probes” to Renewal Science





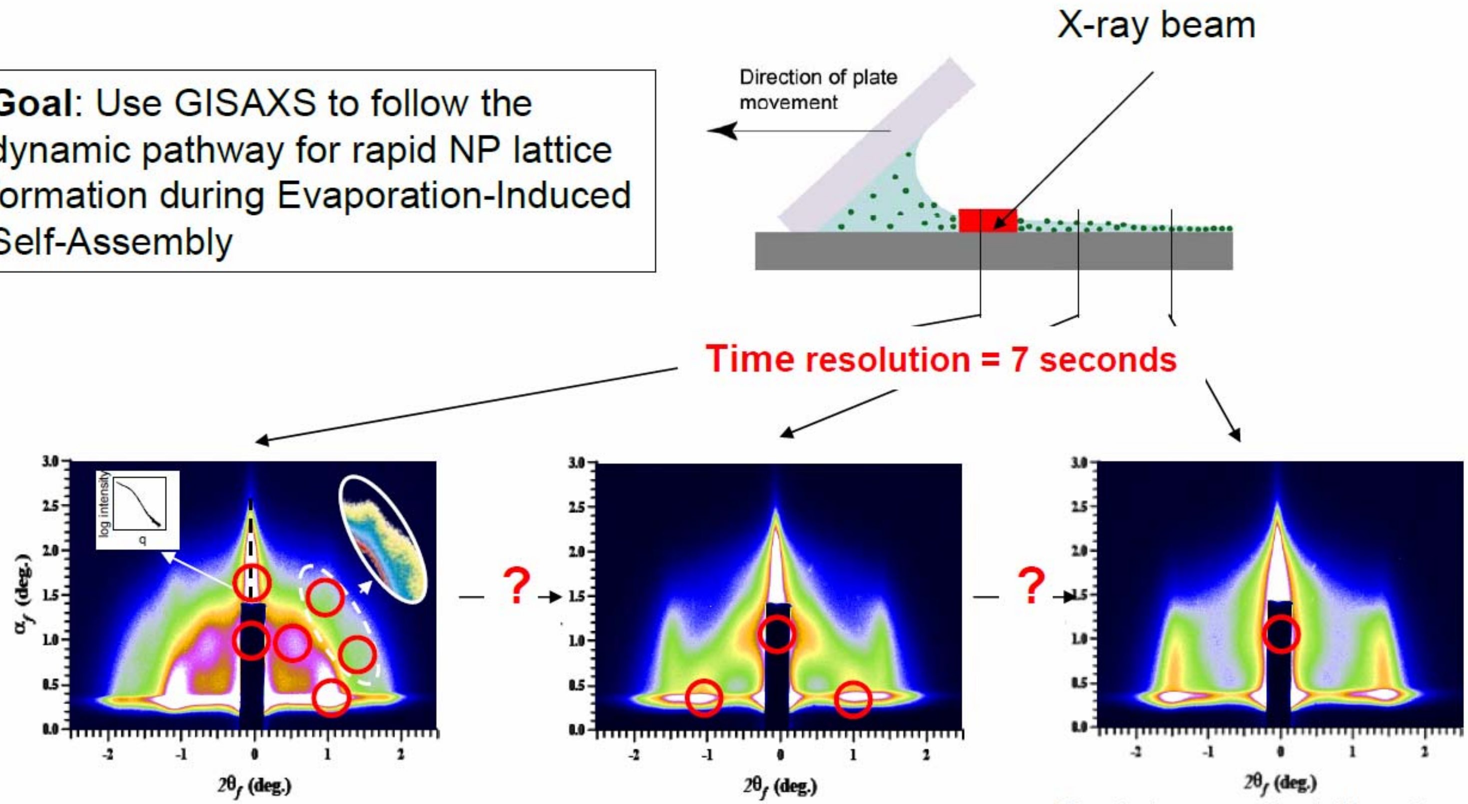




Examples that tie Surface Probes to Renewal Science (con't)

In-situ GISAXS studies of nanoparticle lattice formation

Goal: Use GISAXS to follow the dynamic pathway for rapid NP lattice formation during Evaporation-Induced Self-Assembly

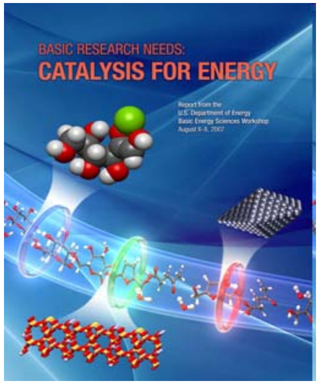


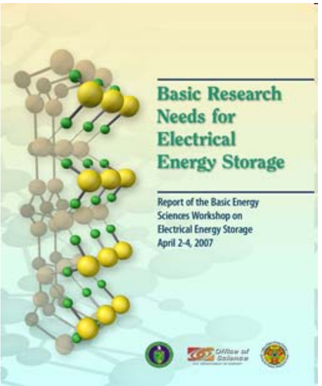
Initial non-close packed (bcc) phase **Simple cubic transition state** **Final close-packed film after drying**

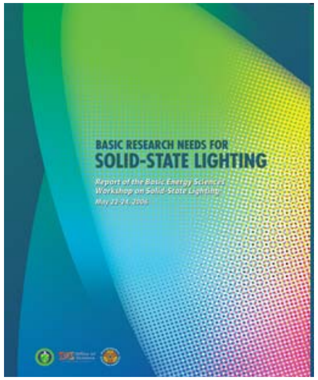
Better time resolution is needed to understand the relationship between these lattice structures

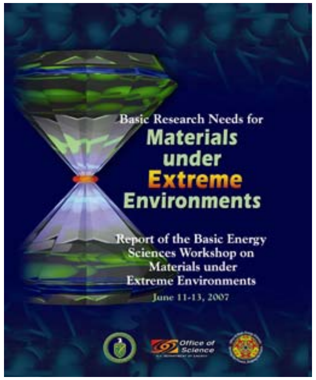
The Renewal Case for Interfacial Science:

- Energy Storage (stability of interfaces):
  - more stored energy, longer lifetime, safer batteries
- Catalysis:
  - observe reactivity of supported nano-particles
- Materials Growth:
  - create novel materials
  - electronic materials
  - solid-state lighting
- Materials Chemistry:
  - corrosion
- Geochemistry:
  - sequestration of energy by-products:
    spent nuclear fuel, CO_2
  - transport of contaminants in the environment
- Actinide Science
  - reprocessing nuclear fuel





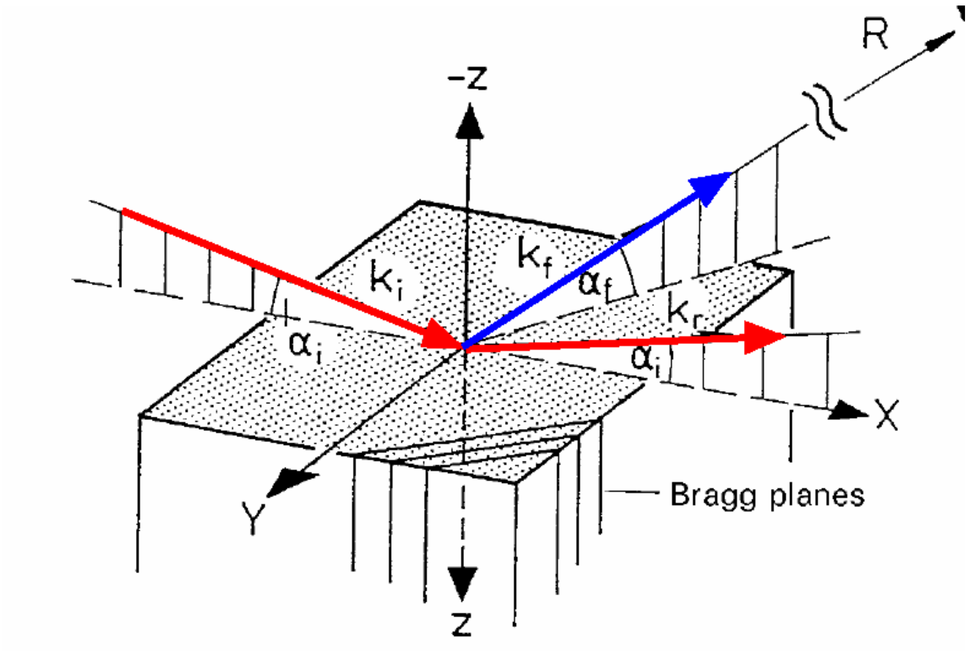




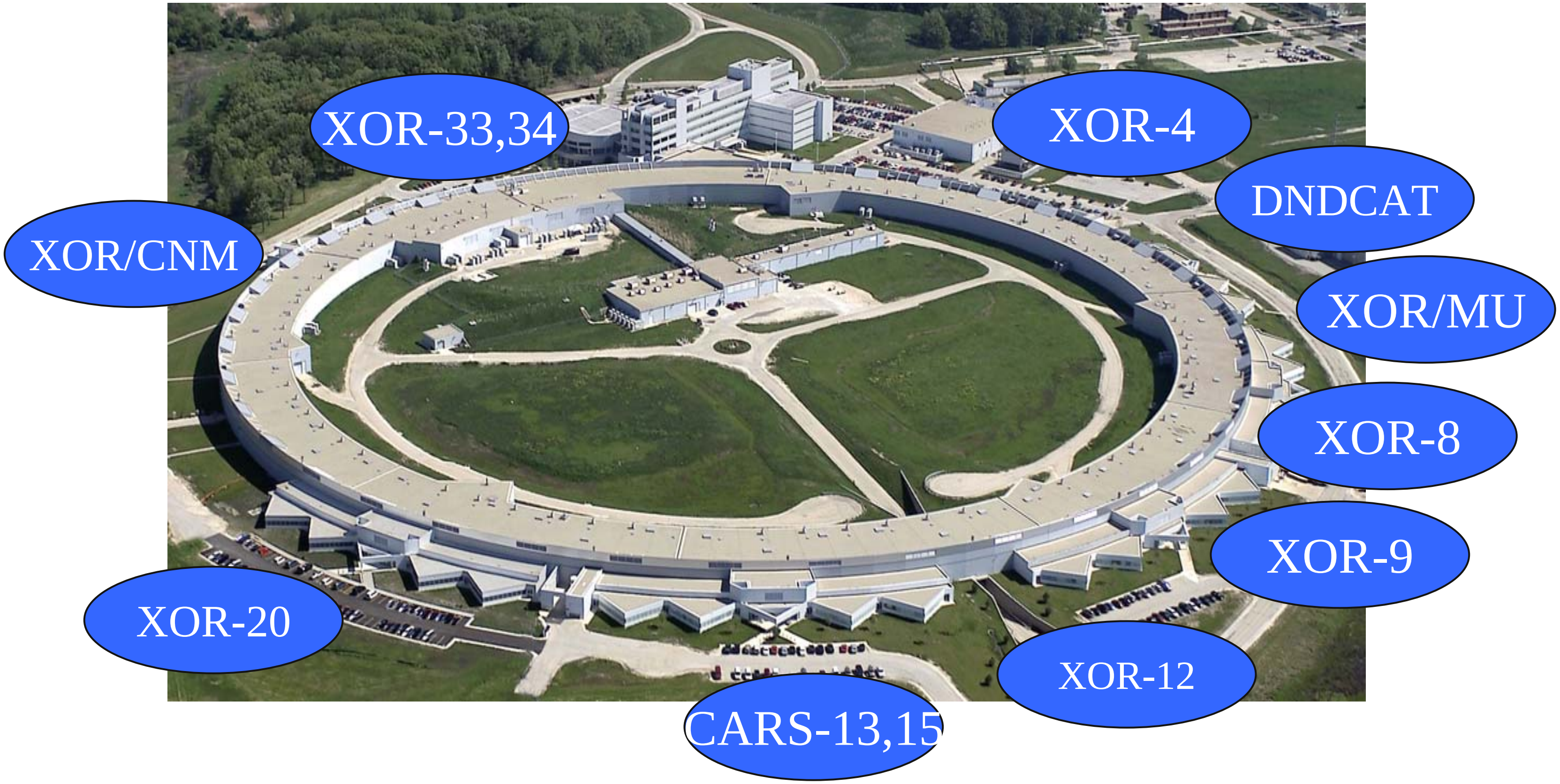
Instruments needed at APS to address science & technology opportunities

- GISAXS
- Surface & Interface Diffraction/Scattering
- Resonant Scattering
- X-ray Standing Waves
- Reflectivity
- Liquid Surface Scattering
- XAFS
- ***In-situ capabilities***

- Some centralized, some distributed



Current Surface & Interface Science Activities at APS

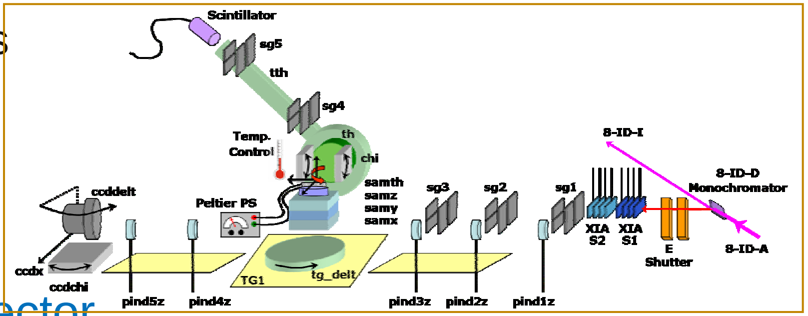


- Where are we today?
- What needs to be done in next 5-7 years to make aps premier facility
- Why aps?

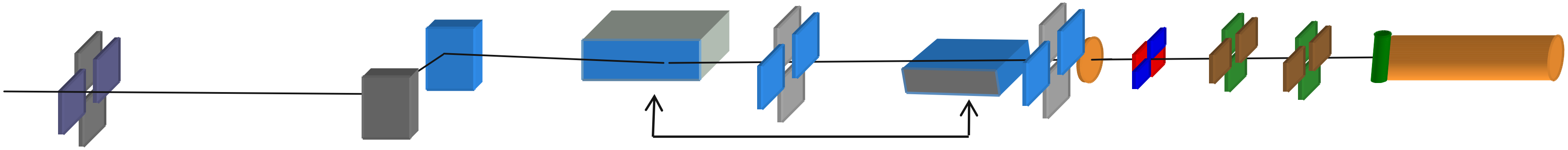
Current APS Capability (GISAXS)

- ***The APS GISAXS capability is currently the world's best***
  - ***Polymers, thin films, phase transitions in low-dimension …***
- Dedicated instruments in two sectors
- Sector 8ID-E: High-resolution GISAXS
  - studying real-time kinetics in nanocomposites
  - High-q resolution for structures > 10 µm
  - Wide-range in situ sample environment
  - Air/liquid interfaces
  - Complementary to XPCS at the same sector
- Sector 12
  - Nano particles and catalysis
  - Currently in the upgrade phase

Sector 8ID-E

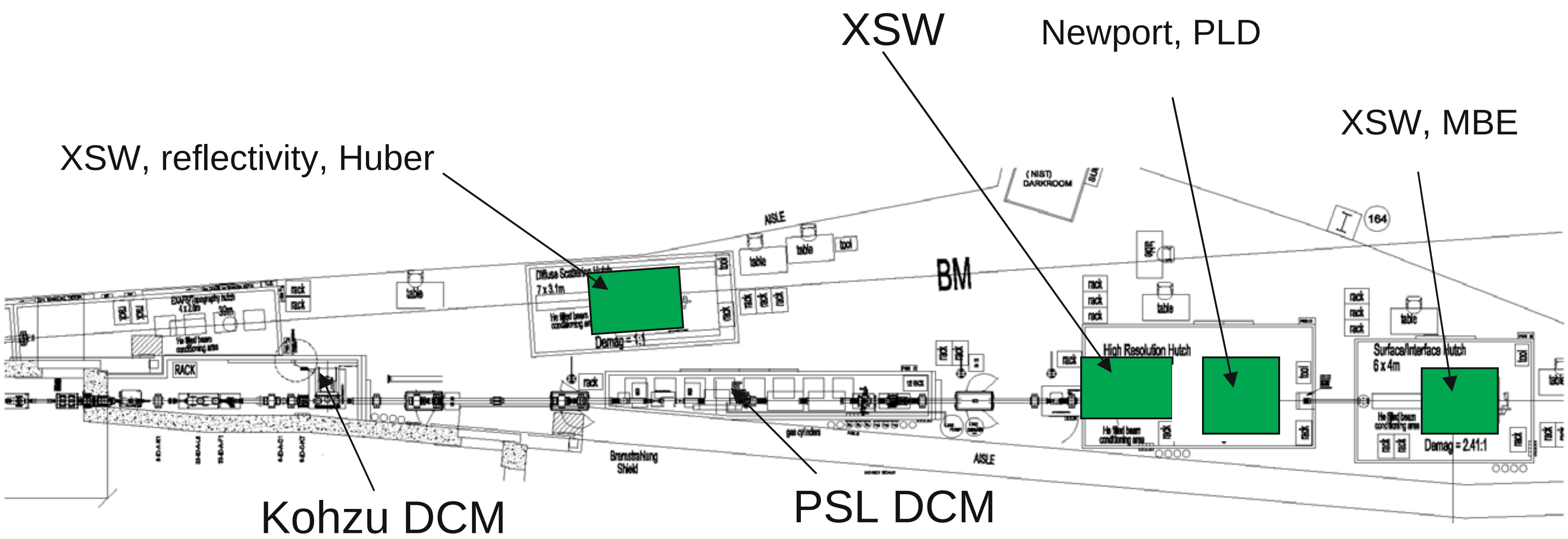


Sector 12: B Branch



Micro focusing optics for GISAXS and SAXS

Sector 33 is Designated for Surface & Interface Scattering

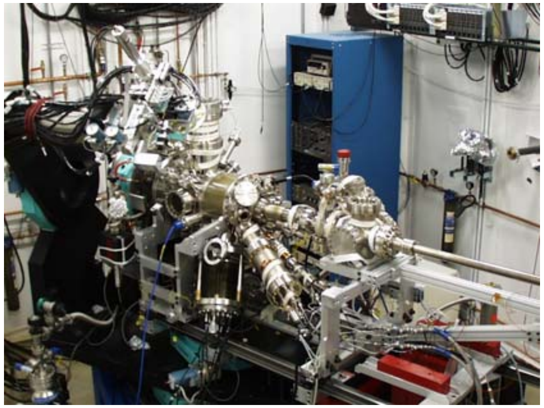


- Continued activity in PLD & MBE materials growth
- Growing General User Program in Surface & Interface Science
  - COBRA
  - Interfacial Chemistry
  - X-Ray Standing Waves
  - Interface Structures
  - Ex-situ thin-film structures

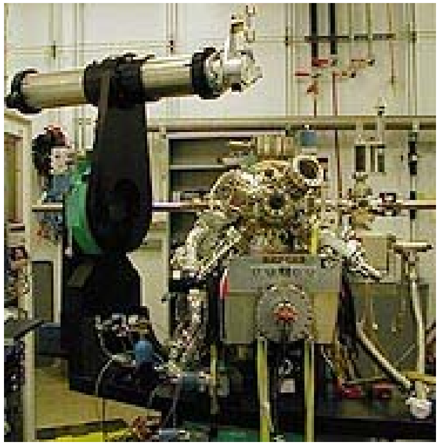
Other distributed facilities

- Large user community, but somewhat dispersed
- Facilities under-utilized (timeshare with other techniques)

- Reflectivity (5ID, 1BM, 12BM, 8ID)
- XSW (5ID)
- Liquid Surface Scattering (6ID, 9ID, 15ID)
- Interface/thin-film scattering/diffraction (11ID, 20ID, 13ID, 4ID)
- Surface Diffraction (5ID, 13BM, 12ID, 6ID, 20ID)



6 ID-C UHV surface scattering chamber



5 ID-C surface science chamber and diffractometer

Proposals that address the scientific needs for "Surface Probes" in next 5 – 7 years

Initiatives for full-time dedicated interface science facilities

- XIS Letter of Intent & XIS Proposal – large comprehensive sector
- 33 Upgrade – expand surface/interface mission & will compliment XIS
- 12ID Upgrade – GISAXS & surface diffraction
- 8ID Upgrade – GISAXS & surface XPCS
- 9ID Upgrade – Liquid surface scattering

Other essential interface science proposals

- 4ID Upgrade – interfacial magnetism
- 5ID Upgrade – XSW, reflectivity, surface diffraction
- 6ID Upgrade – thin-film & interface structure
- 13ID Upgrade – high-energy interface diffraction/scattering
- 20ID Upgrade – UHV surface XAFS, surface resonant scattering/reflectivity

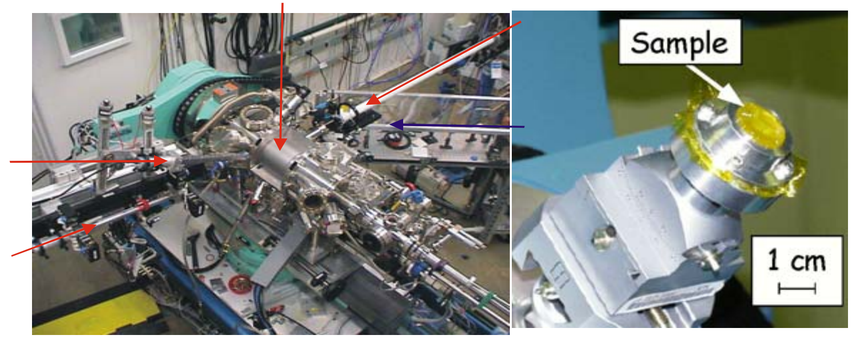
Dedicated Sector for In-Situ X-Ray Interface Science (XIS)

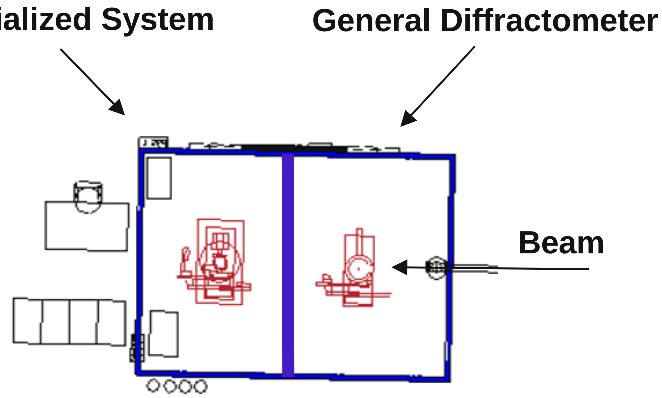
Primary Science Programs:

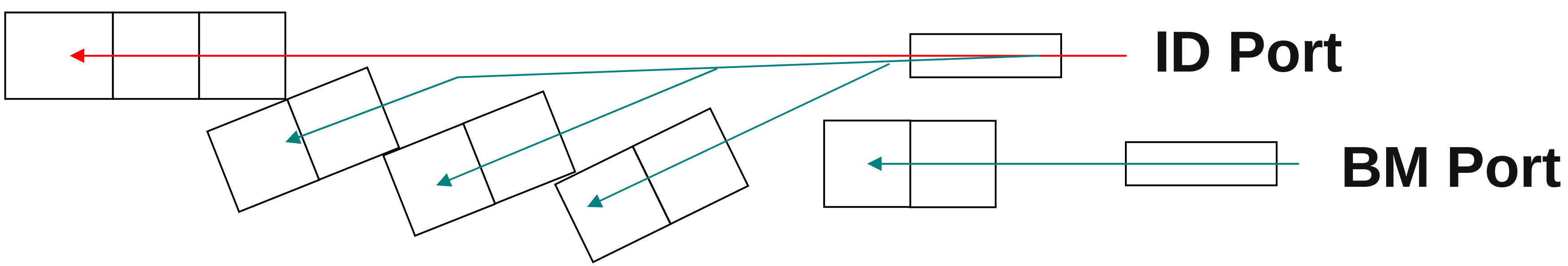
- Materials Growth & Processing
- Interfacial Chemistry
- Control of Interfacial Properties

Facilities:

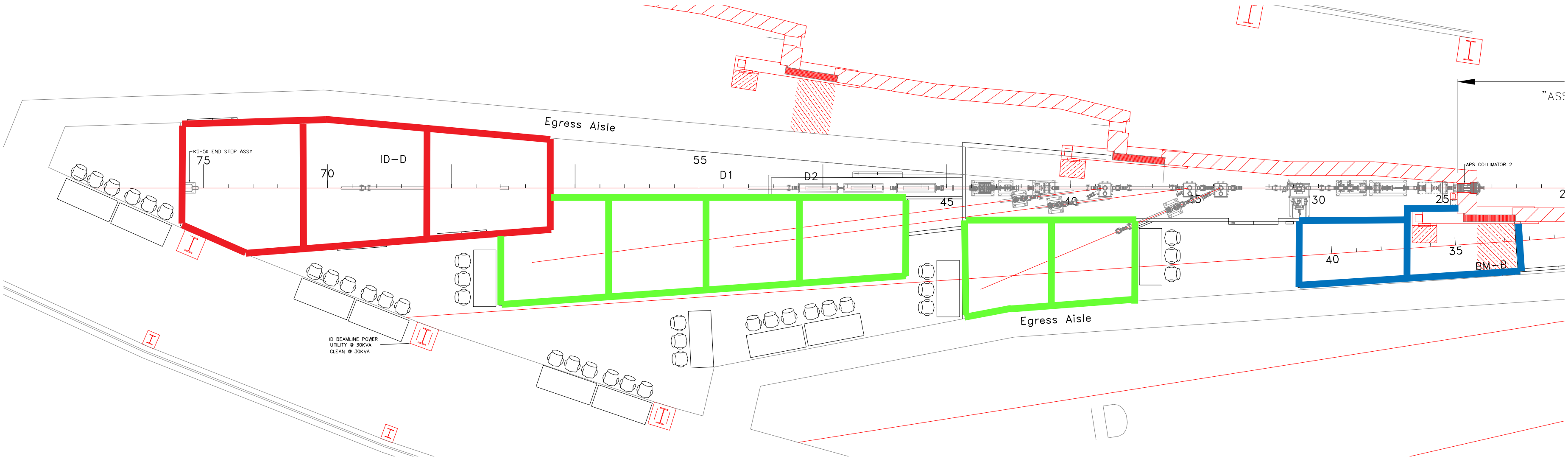
- Dual-canted Undulator ID Beam Line
    - One fully tunable branch Beam Line
    - One fixed-energy branch
- One BM line (diffraction)
- 11 experimental stations with 5 simultaneous x-ray experiments
- Specialized end-stations available off-line
- Environmental Cells attach to General Diffractometers
- Lab Facilities & Infrastructure supporting Interface Science
- Partner Groups desirable for end-station development





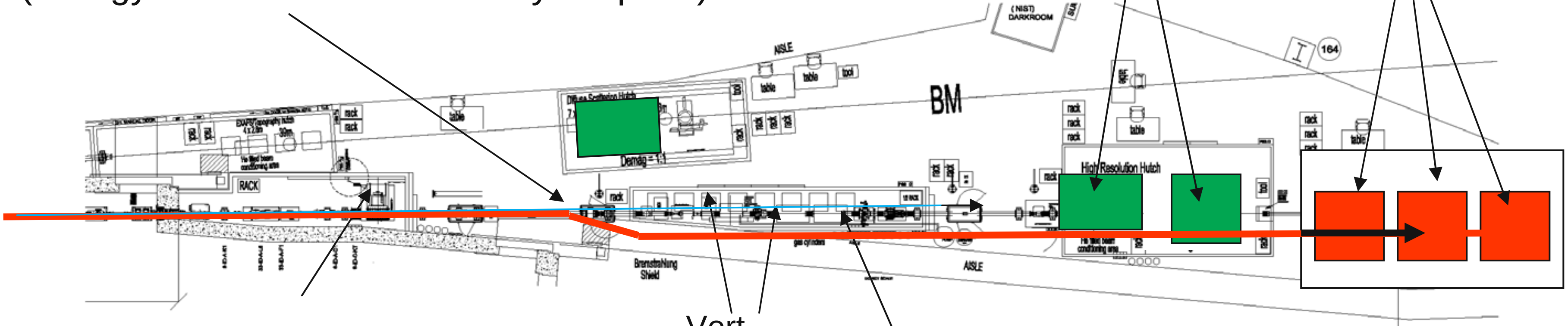


XIS Conceptual Design – Phase 1



- Dual-canted Undulator ID Beam Line
  - Tunable branch Beam Line: 4 – 40 keV
  - Fixed-energy branches: 10 keV, 30 keV, 30 keV with Si(111)
- One BM line (diffraction)
- New instruments in phase 1:
  - XRIM
  - Surface diffraction with XPS/XSW
- Once operational, this will be the premier interface science facility worldwide

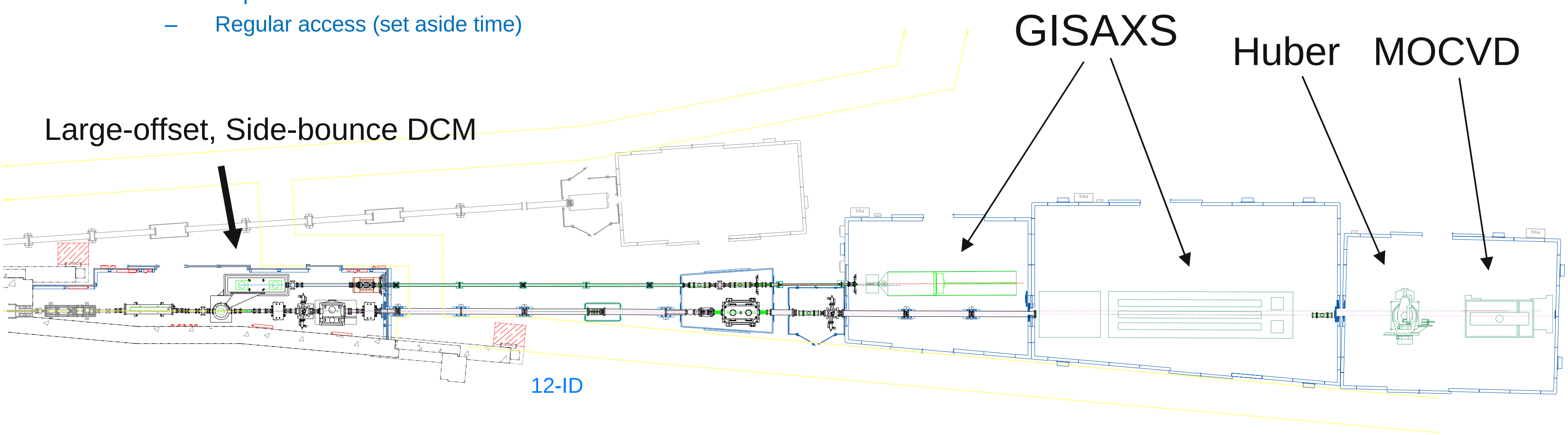
Sector 33 Canted Undulator Proposal



- Canted undulator source, large-offset monochromator, expanded hutch
- BM beam line optics & diffractometer upgrades
- Instrument upgrades (AFM, SEM, STM, new sources, LEEM, PEEM, stages, XPS, RHEED, new laser, UHV-GISAXS, …)
- Permanent location of the sector 33 instruments (Newport, XSW, MBE, PLD, Huber, XSW chamber)

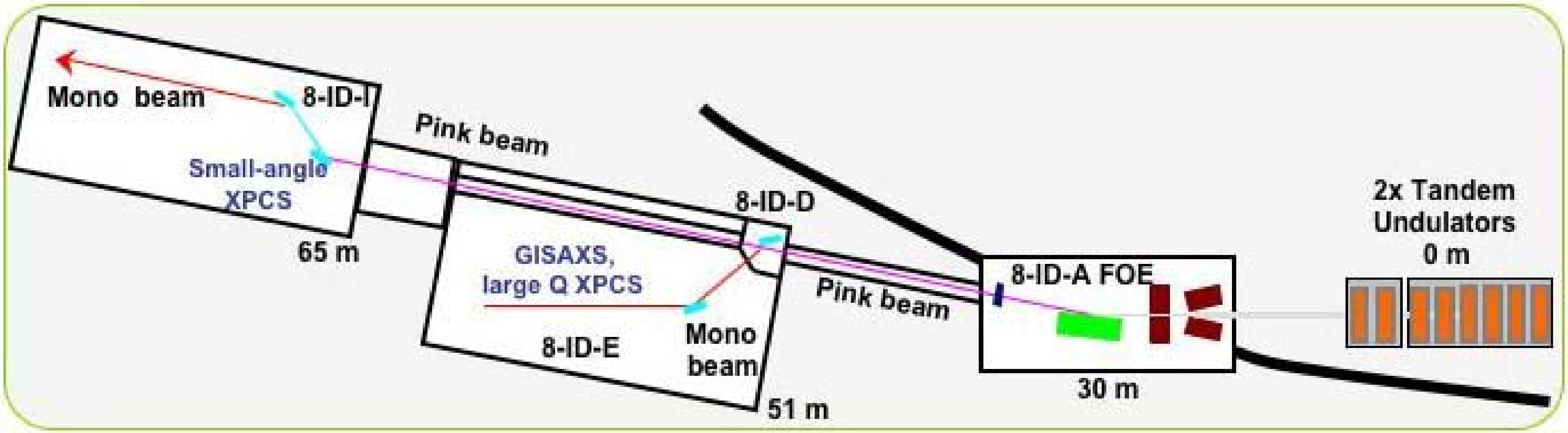
12 - ID Upgrade to Two Beamlines with Canted Undulators

- Versatile Anomalous and time resolved SAXS/WAXS/GISAXS/USAXS beamline [12-ID-C]
  - Technically complicated experiments which takes full advantage of insertion device capabilities
  - Pink beam – high flux for fast experiments
  - Wide Q range 0.001 – 5.0
  - Wide energy range 4.5 – 36 Kev
  - Combined experiments – XANES, MS, DSC
- Surface Scattering [12-ID-D]
  - MOCVD
  - Diffractometer (from 12-ID-B)
  - Wide energy range 4.5 – 36 Kev
  - 60 cm mirror in 12-ID-C
- Dedicated (7.4 – 13.9 Kev) SAXS/WAXS/GISAXS beamline [12-ID-B]
  - Easily adjustable Q range (0.006 – 2.0)
  - Rapid access
  - Regular access (set aside time)



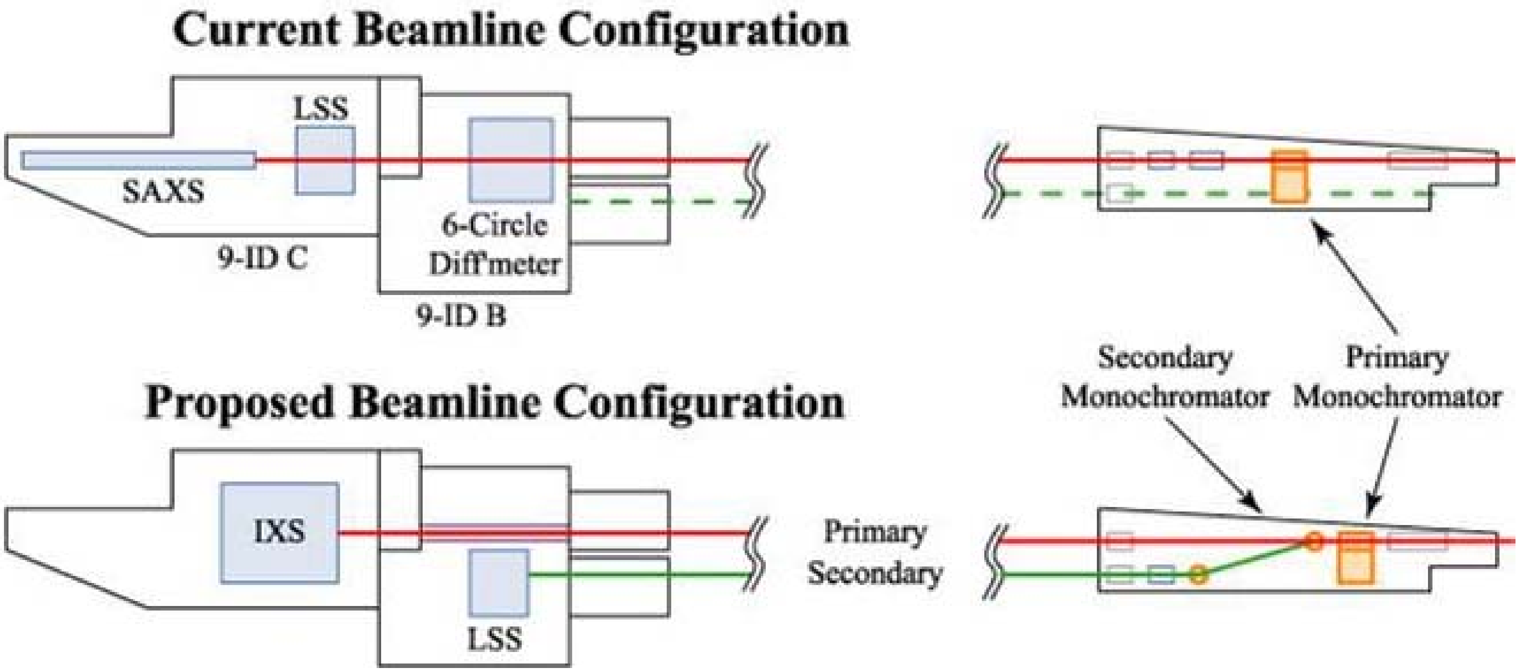
8ID Upgrade (to maintain GISAXS Leadership Position)

- Long straight-section to accommodate long and two undulators (Tandem Design)
  - Long, small period undulator: Maximizes brilliance for XPCS
  - Shorter length, longer period undulator : Energy tunability for GISAXS
- Large-Offset Double Bounce Monochromator for 8-ID-E : Continuous Energy Tunability
- Simultaneous and independent photon energy operation of 8-ID-I and 8-ID-E
- With higher q-resolution, GISAXS may cross the boundary to small-angle coherent diffraction imaging, which may share the setup with GISAXS.
- 1M / 2M-pixel PILATUS detector to achieve ms-time resolution
- Results: GISAXS with energy tunability and XPCS with much higher brilliance (Sandy/Attenkofer)



9ID Upgrade – Liquid surface scattering

- Branch beam line dedicated for Liquid Surface Scattering (4-30 keV)
  - Implement canted undulator source
  - Develop large offset monochromator

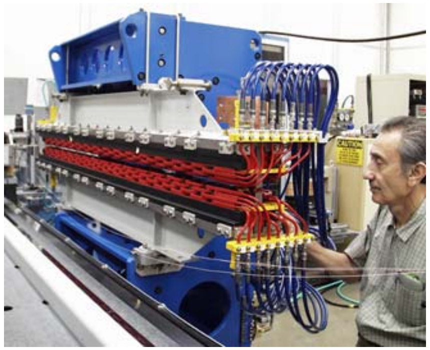


Interfacial magnetism: Future Needs

UHV magnet/goniometer higher-resolution XPS, X-PEEM, and scanning probe microscopies (X-STM, AFM)

- New optimized insertion devices - Polarization modulation at the source

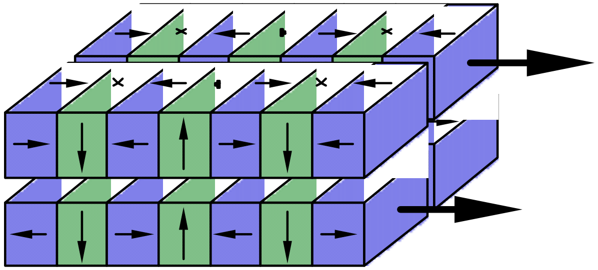
Soft X-rays



Electromagnetic CPU

- Current design limits polarization reversal to ~1Hz
- New design (laminated pole pieces) could enable reversal at >30Hz (lock-in detection).
- $>10^3$ increase in sensitivity when coupled with improvements to beamline optics

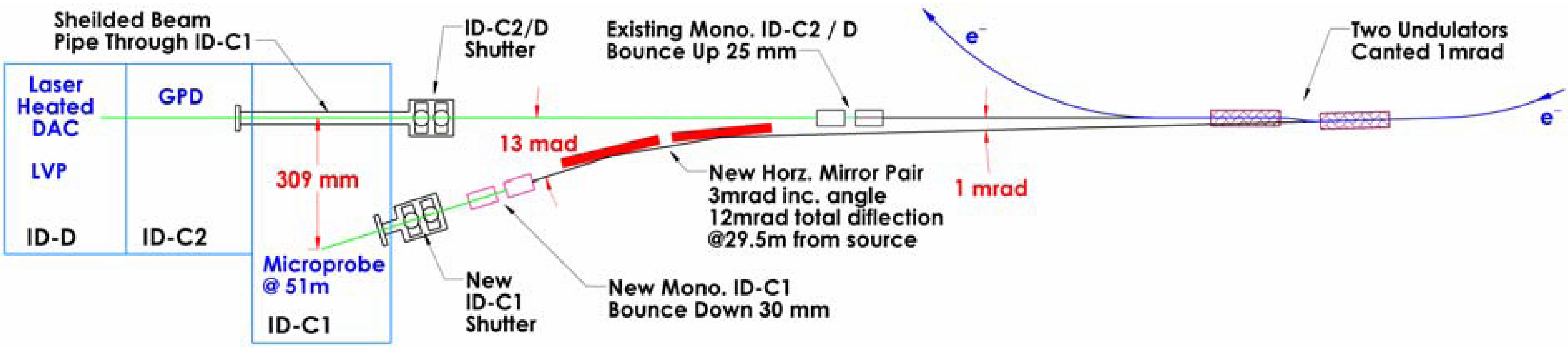
Hard X-rays



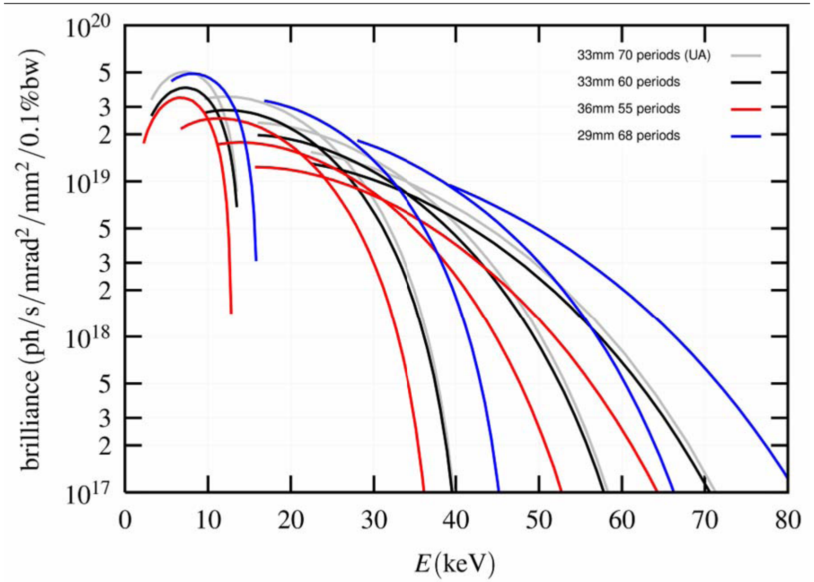
Apple-II device

- Accesses new energy ranges 2.4 – 3.5 keV & > 10 keV
- ~10-20x increase in flux over current scheme using phase retarders
- Phase retarders still used for fast switching (lock-in detection)

Sector 13 Canted Undulator Upgrade

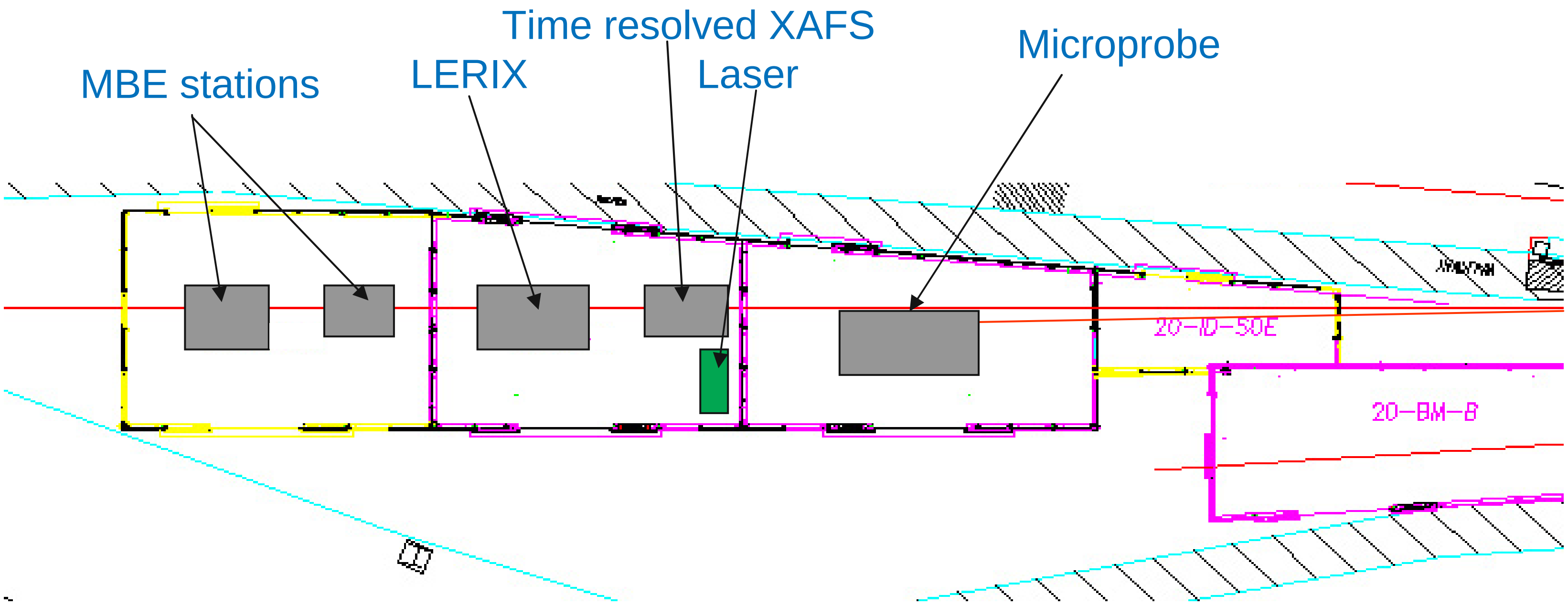


- Canted undulator front end
- 5-100 keV branch beam line
  - High-pressure science
  - Mineral/water interface science
- Highly penetrating for in-situ studies



Sector 20 Canted Undulator Upgrade

- Dedicated x-ray microprobe
  - ➢Improved optics, better detectors, improved stability
- More access to and permanent locations for existing experiments
  - ➢Time-resolved XAFS
  - ➢LERIX spectrometer
  - ➢MBE surface science – surface XAFS, surface resonant scattering



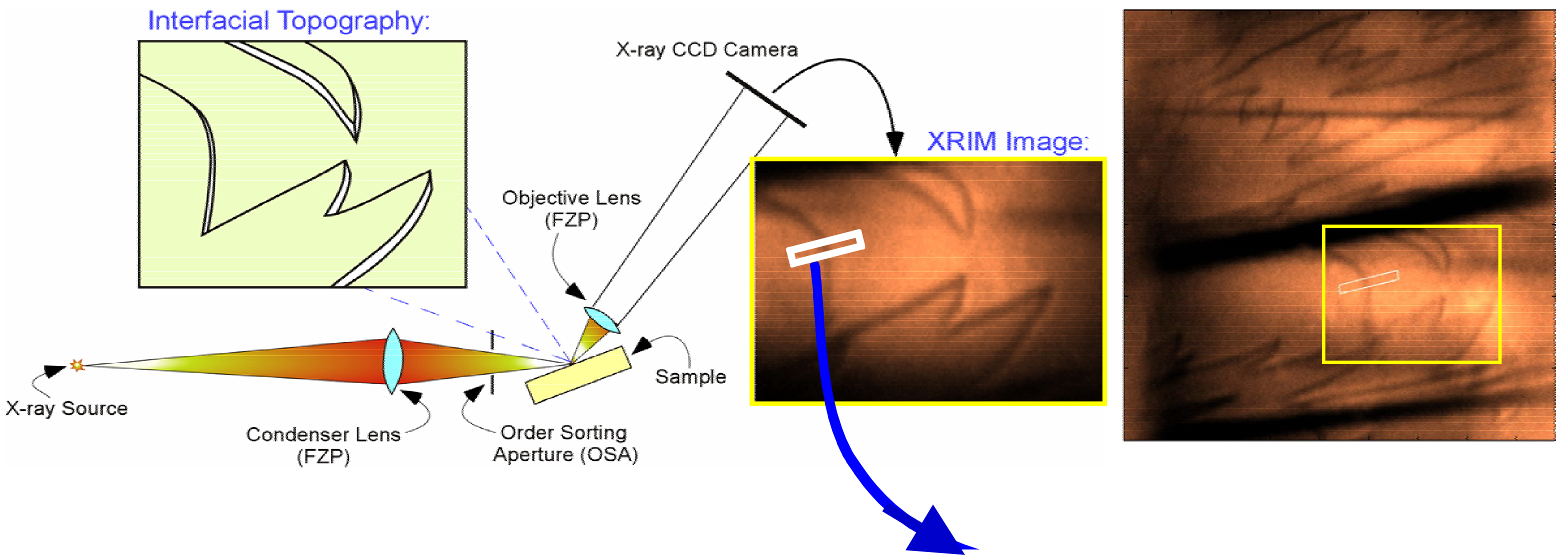
Requirements for New Imaging Capabilities

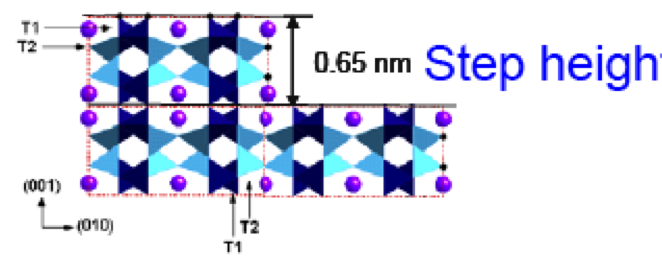
- Coherent Diffraction & Scattering
  - CDI applied to GISAXS
  - Surface XPCS
  - CDI from surfaces & interfaces

- X-Ray Interface Microscopy (XRIM) applied to many/all interface science instruments

X-Ray Interface Microscopy

Imaging: Full field X-ray microscopy



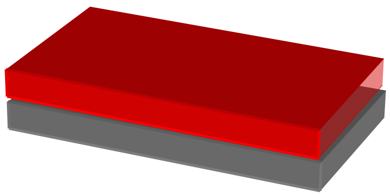


→ Implement as a general capability

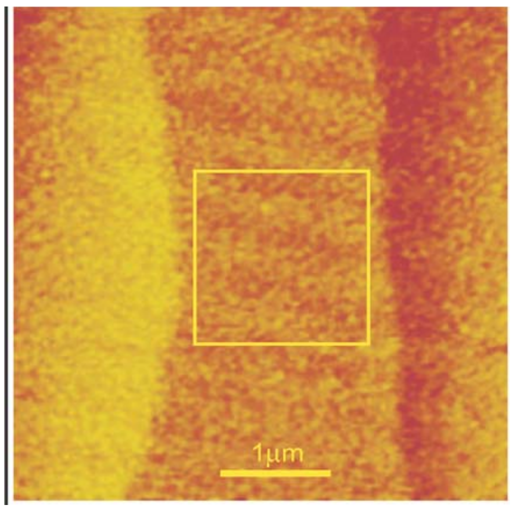
→ Significant improvements possible with new optics/detectors:

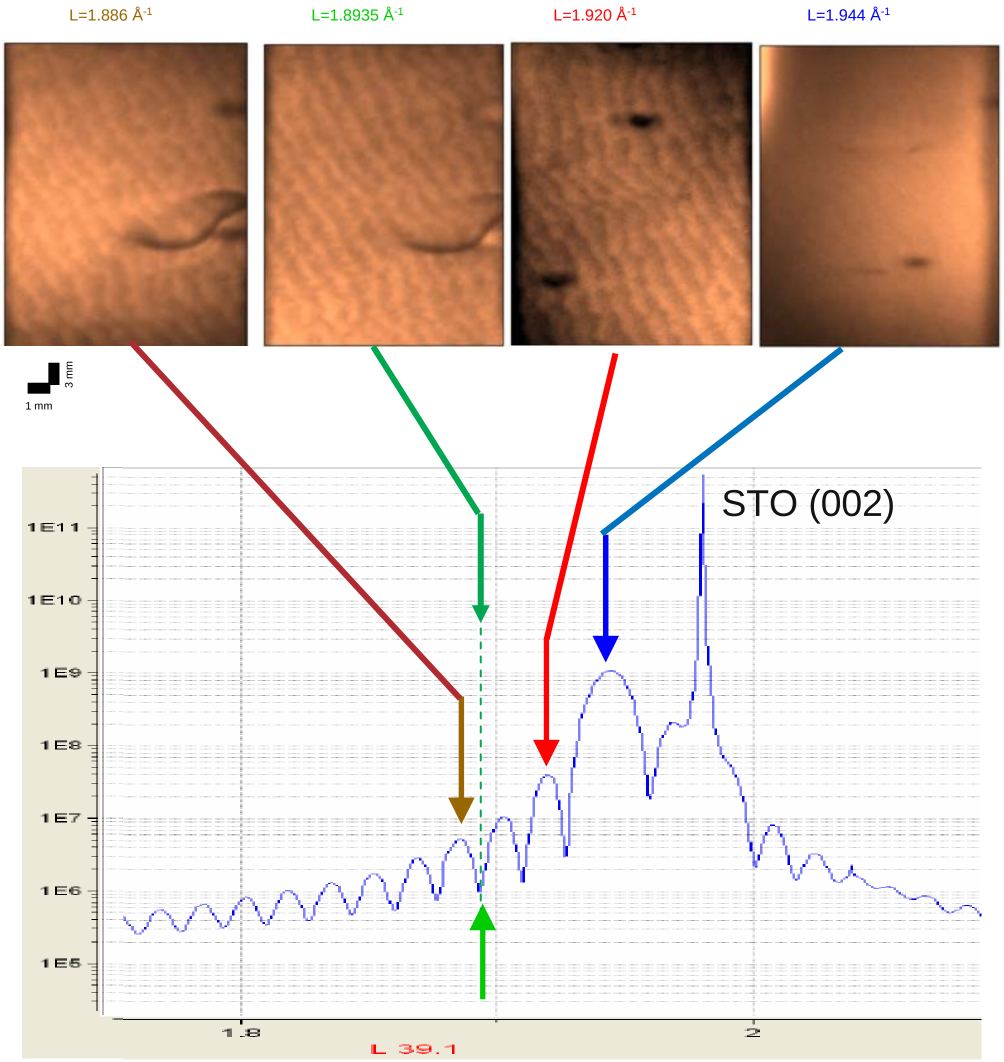
- resolution (~5x better to ~ 30nm)
- image rate (>100x better to < 1 sec)

X-Ray Interface Microscopy of $SrRuO_3$ on $SrTiO_3$



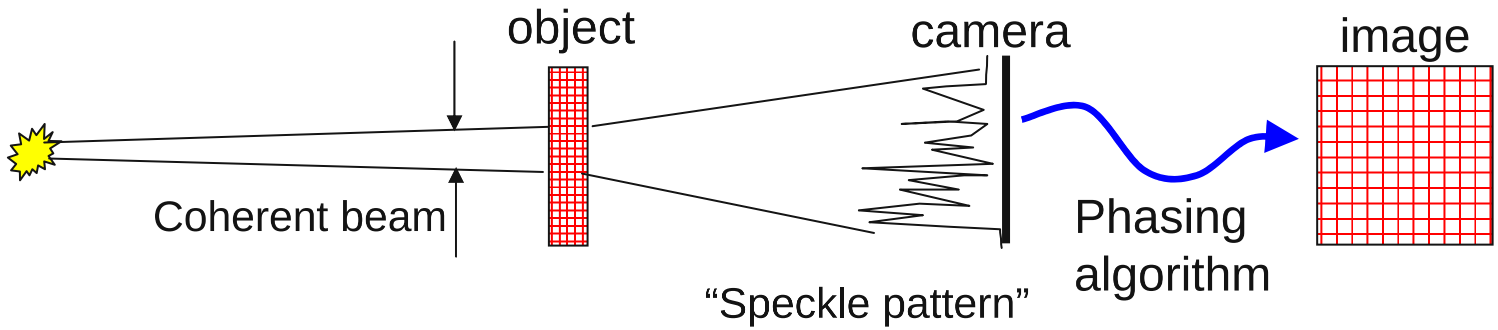
Pulsed Laser Deposition used to grow 100 layer film





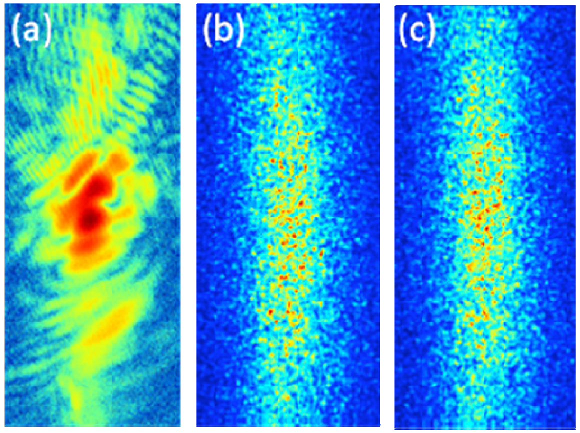
Requirement for New Capabilities (beam coherence)

Coherent Diffraction Imaging:

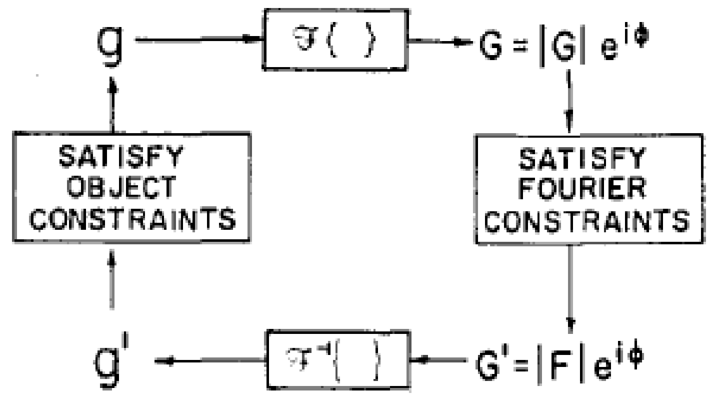


- photon correlation spectroscopy
- coherent diffraction imaging

-robust phasing transforms scattering data to microscopic images

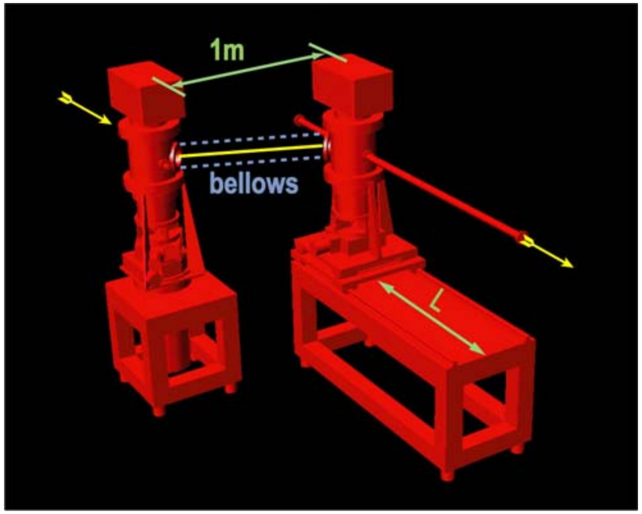


Au(001) Hexagonal reconstruction peak:
Pierce et al., unpublished results (2008)



Fienup, Opt. Lett. 3, 27 (1978)

Specific Development Opportunities



- Canted front ends with new undulators
- Wide-offset side-diffracting monochromators
- New Beam Line Optics & focusing
- New Undulator designs
- New Detectors & support
- Data analysis support
  - Improved dynamics scattering theory for simulating the structures from the measurements.
  - Real-time data reduction and visualizations
  - Algorithms and data manipulation for GISAXS CDI, CoBRA & other phase extension/correction methods
- Fully equipped laboratories with limited wet-chemistry and surface analytical capabilities to support interface science needs
  - where users can work on & prepare their samples
  - Preliminary and ancillary surface characterization tools
- Improved temporal resolution (GISAXS, growth, surface dynamics…)

Specific Requests: Partnerships

- CATs such as DND & CARS
- Argonne Divisions (CNM, MSD, Chemistry, etc…)
- Instrumentation & Community Partnerships (CMMP 2010)
  - Support from NSF instrumentation grant (by external university users)
  - DoE BES (by external university users)
- Specialized endstation partnerships
  - Future development of XIS
  - Current: Simon Fraser University

- X-Ray Optics Vendors/suppliers

Examples that support the overarching Renewal themes

- *Mastering Hierarchical Structures Through X-ray Imaging*
  - X-Ray Interface Microscopy

- *Real Materials in Real Conditions in Real Time*

  GISAXS (energy-related)
  - Organic photovoltaic materials and catalysts at surfaces and interfaces

  Surface Diffraction
  - Time-resolved in-situ materials growth studies such as PLD and MOCVD

  Reflectivity
  - Ordering of interfacial “hydration layers” for a wide range of mineral – water interfacial systems

Summary

- Proposed initiatives for interface science dedicated facilities (Reflectivity, Standing Waves, GISAXS, Surface & Interface Scattering, Liquid Surface Scattering) directly address requirements established by the Science Case Reports.

- There are many direct connections between the proposed scientific capabilities and the two major scientific themes for the Renewal: *Mastering Hierarchical Structures Through X-ray Imaging* and *Real Materials in Real Conditions in Real Time.*

- New capabilities proposed for Interface Science at APS will enable transformational discovery in diverse scientific areas ranging from medicine and environmental science to new materials creation and interfacial property control.

- New and upgraded instruments will keep the APS at the forefront of interface science research (experiment and scattering theory).

- There are significant opportunities to exploit emerging novel x-ray methods such as coherent diffraction imaging or XRIM to study Spatio-temporal dynamics at interfaces and surfaces in complex environments.