Challenges for X-Ray Characterization of Nanoscale Soft Matter Assemblies

Ron Pindak

Brookhaven National Laboratory

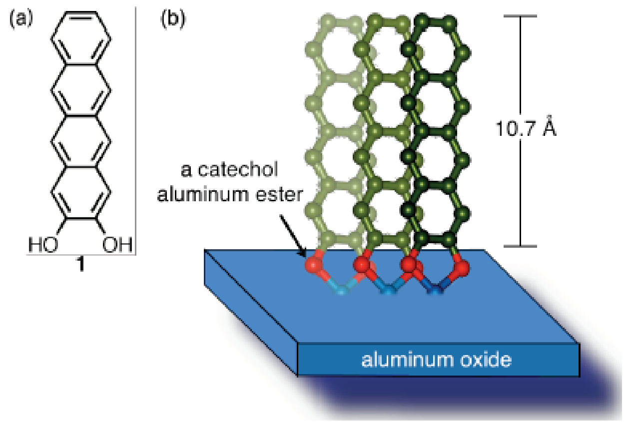
Focus Remarks on two systems:

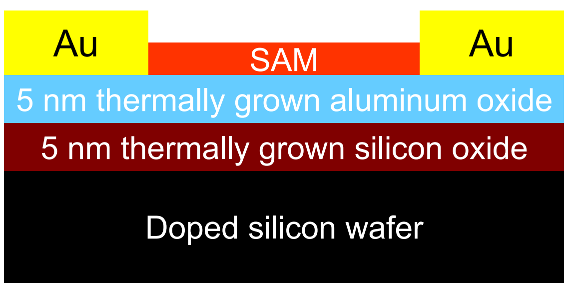
- Epitaxial organic - inorganic assemblies
- Organic assemblies on mechanically or chemically nanopatterned surfaces

Technique development done on 'general-purpose' diffraction beamlines at the NSLS and the APS

Epitaxial organic - inorganic assemblies

Properties of functionalized organic self-assembled monolayers (SAMs) can often be optimized if the SAMs are ordered. Ordering can be induced by chemical fine-tuning of the interactions with an organic or inorganic substrate.





Open questions:

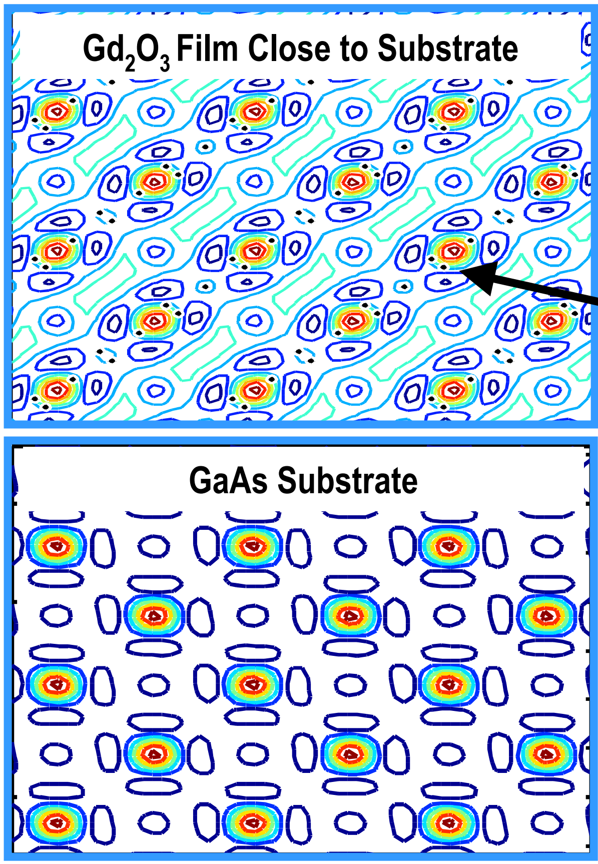
- **How is the SAM ordering affected by substrate surface structure? Oxidation?**
- **How does the ordering of the SAM impact charge mobility?**
- **If a metallic electrode is applied to an organic, what is the nature of the interface?**
- **How stable is the structure of the SAM to humidity? temperature? UV-radiation?**

Atomic resolution imaging of interfacial structures is needed !

Electron Density Maps (EDMs) of Buried Interfaces in Inorganic Epilayers

Semiconductor Passivation

Gd_2O_3 on GaAs

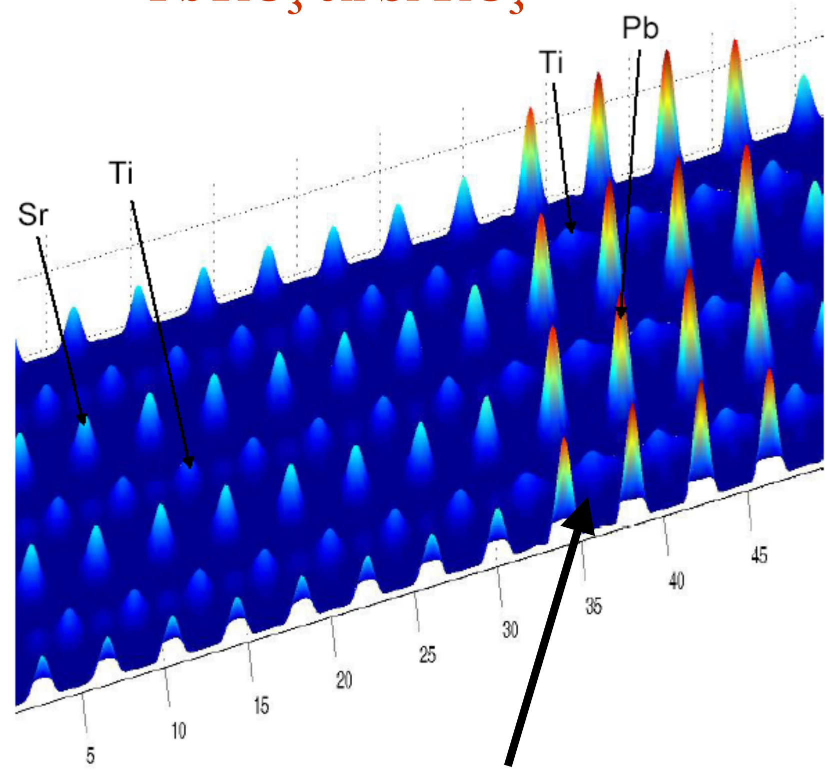


Layer sequence differs than that of bulk Gd_2O_3

EDMs parallel to substrate

Thin Film Ferroelectrics

$PbTiO_3$ on $SrTiO_3$

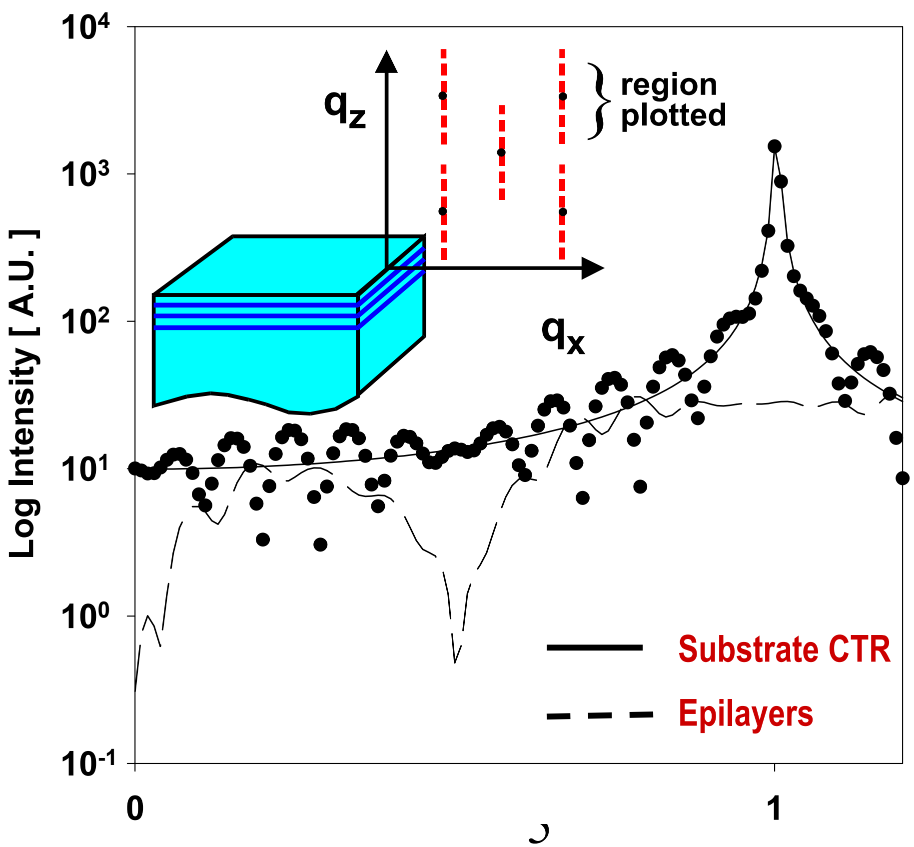


0.1 Angstrom Ti displacements deep inside the interface

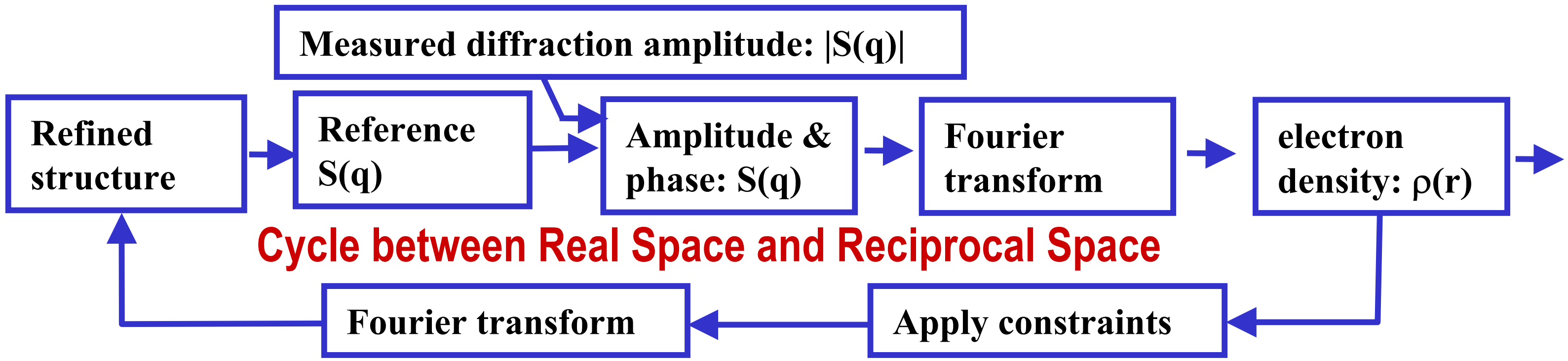
EDM perpendicular to substrate

Crystal Truncation Rods Contain Amplitude and Phase Information

- For conventional modeling approaches, incorrect structural guesses are unlikely to converge on actual structure ⇒ need *model-independent* approach.
- The measurement of continuous scattering amplitudes along crystal truncation rods (a coherent interference between bulk and epilayers) 'oversamples' at a frequency greater than the lattice wavevector so contains *phase* information.



Iterative Procedures: Crystal Truncation Rod Data → Electron Density Maps



Demonstrated Iterative Procedures:

- COBRA begins with a conventional fit to a model to determine a refined model or reference structure factor; phases determined from reference structure factor and measured amplitude differences along CTRs. Method used to produce the Gd_2O_3 on GaAs and $PbTiO_3$ on $SrTiO_3$ electron density maps - converged in < 6 iterations.

  M. Sowwan, Y. Yacoby, R. Pindak, J. Pitney, R. McHarrie, M. Hong, J. Cross, D. Walko, R. Pindak, R. Clark, E. Stern, Phys. Rev. B 66, 205311 (2002).

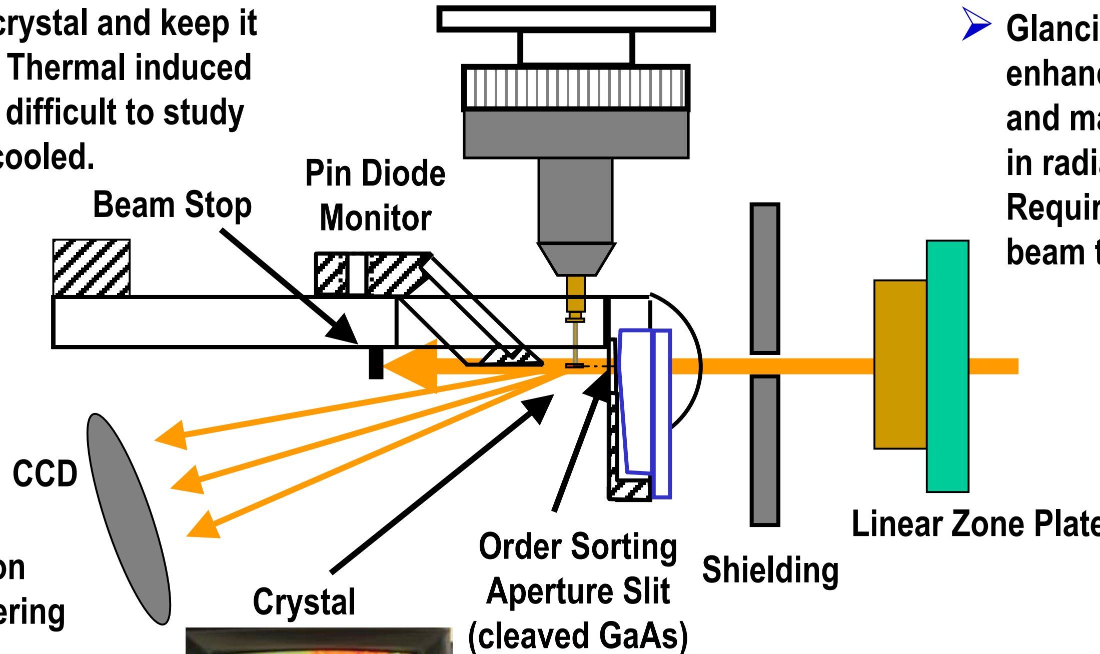
- Random Phase Technique starts with a random phase assignment. Iterate using algorithm derived from maximum entropy theory. Applied to analyze Au(110)-(2x1) surface reconstruction - converged in < 40 iterations.

  P.F. Lyman, V.L. Shneerson, R. Fung, R.J. Harder, E.D. Lu, S.S. Parihar, and D.K. Saldin, *Phys. Rev. B - Rapid Comm.* 71, 081420 (2005).

Crystal Truncation Rod Analysis Extended to Organics

Challenge: large unit cells result in high density of diffraction features and weak scattering since fewer unit cells in scattering volume. For atomic resolution need to analyze 500-1000 CTRs compared to 10-20 CTRs for inorganics and use long (30 sec.) exposures.

- Need to put beam on crystal and keep it there while scanning. Thermal induced reorientation makes it difficult to study proteins unless cryo-cooled.
- Glancing incidence geometry enhances surface / scattering and may result in a reduction in radiation damage. Requires focusing the input beam to 0.2 microns.



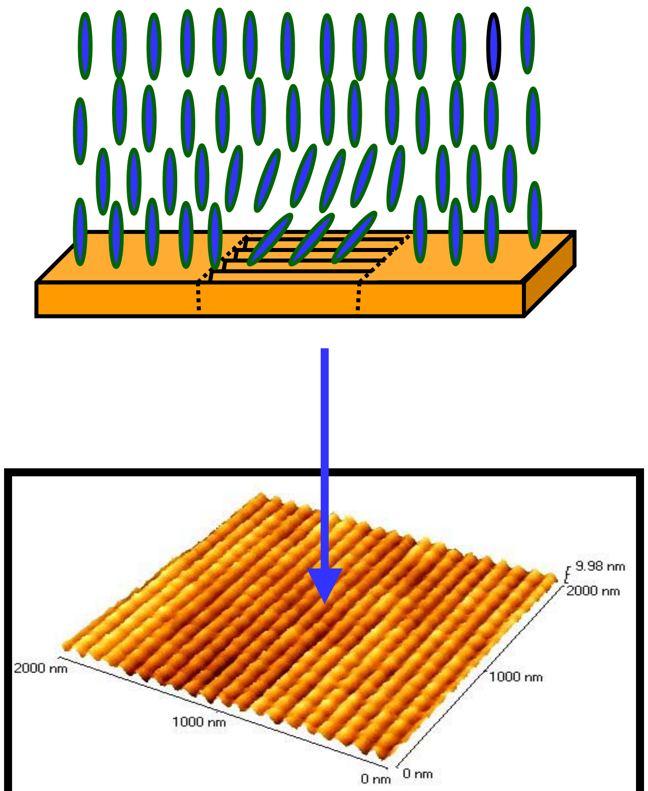
- High density of diffraction features and weak scattering require a low-noise area detector. ALSO, need software to collect data from multiple crystal truncation rods.

- Radiation damage will require multiple samples for a complete data set. Need softwareand robotic sample changer to conveniently orient crystals.

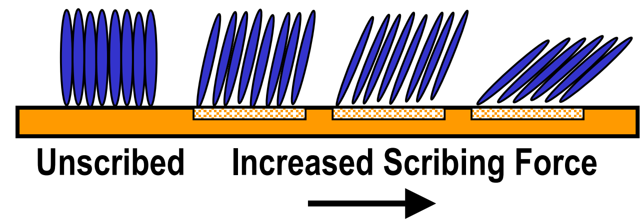
… with B. Chapman (*BNL*), Y. Yacoby (*Hebrew U.*), J. Cross (*APS*), E. Stern (*U. Wash.*)

Organics on Nanoscale Mechanically or Chemically Patterned Surfaces

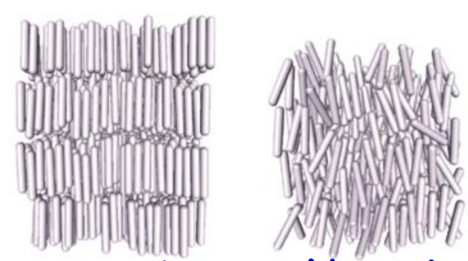
Example: effect of a AFM-scribed polymer alignment coating on liquid crystal ordering



AFM Patterned Substrate
20 nm features
100 µm x 100 µm area



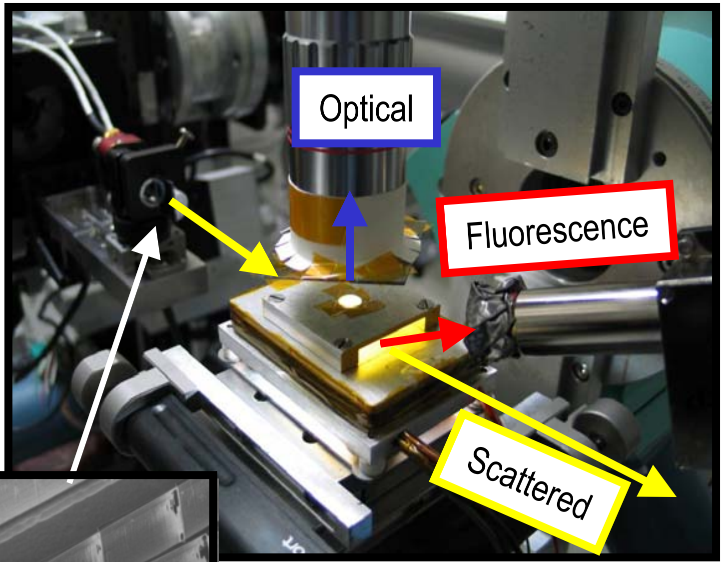
- Polymer alignment coating induces nematic liquid crystal molecules to orient perpendicular to surface.
- Scribing parallel lines induces a tilt of the molecules with the tilt angle dependent on scribing strength.

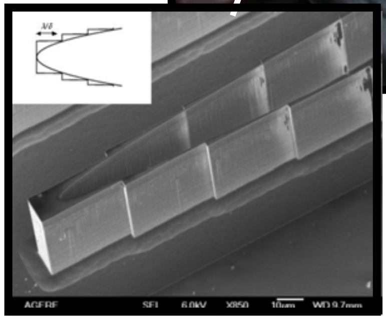


- Smectic layer align parallel to surface.
- How does tilt affect smectic ordering?

X-Ray Microprobe Diffraction from Patterned Areas

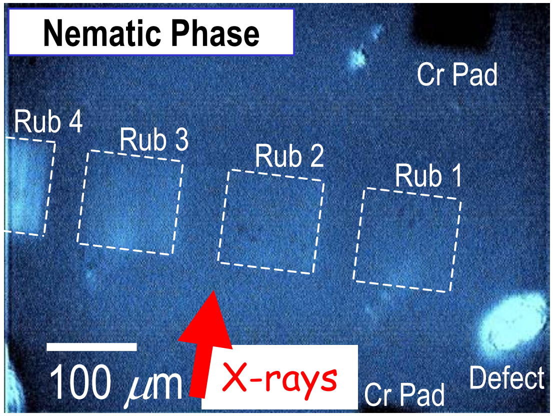
- In-situ high resolution optical observation is essential. Here used to determine temperaure of nematic - smectic transition. More challenging when working in a transmission geometry since x-ray and optical probes are collinear.



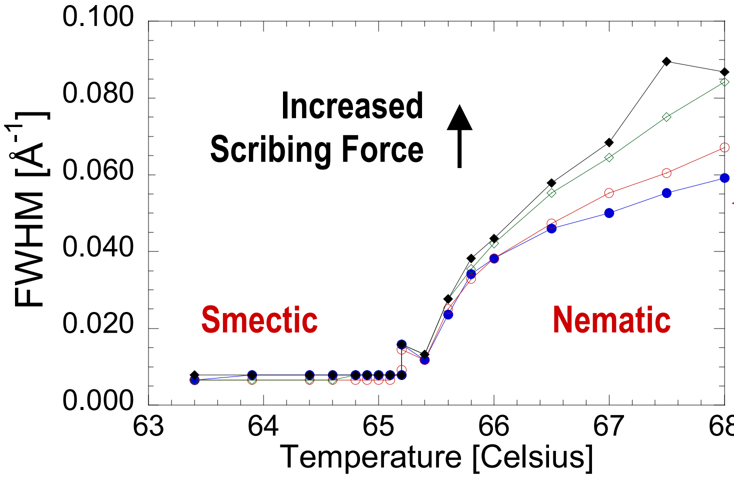


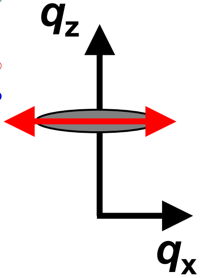
- Sub-micron focused beam needed to keep beam footprint within scribed area for the small diffraction angles typical in organics.

… with B. Chapman, K. Evans-Lutterodt (*BNL*), I. Syed, G. Carbone, C. Rosenblatt (*CWRU*)



- Use x-ray fluorescence from 4 surrounding Cr alignment pads to position x-ray beam on each scribed area - 1μm vertical misalignment moves beam 57 μm laterally.





- Surface-induced smectic order within nematic exhibits broader transverse mosaic with increased scribing strength. Scribing has no effect on ordering within smectic phase.

Summary

Structural characterization of nanoscale organic - inorganic assemblies with atomic-level resolution will require:

- **Investment in detector and software development.**
- **Incorporating in-situ complementary techniques such as high-resolution optical microscopies.**
- **Availability of well-supported and well-instrumented 'general purpose' beamlines for technique innovation.**
- **Need process for reviewing 'high risk' technique development projects.**