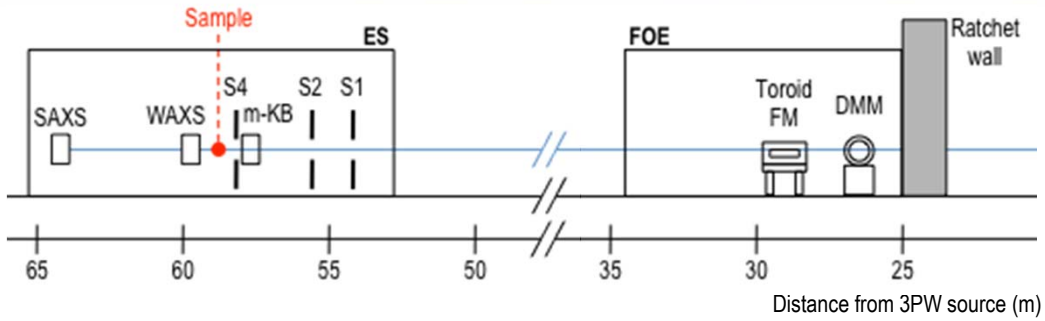
Complex Materials Scattering (CMS) beamline update

First Light: August 26, 2016
First General User: June 16, 2017
First Paper: May 24, 2017

NSLS-II SAC Meeting, September 20th, 2017

CMS beamline at a glance

SAXS/WAXS beamline to facilitate rational design and discovery of new functional materials, by unraveling the relations between constituents, processing, structure, and properties



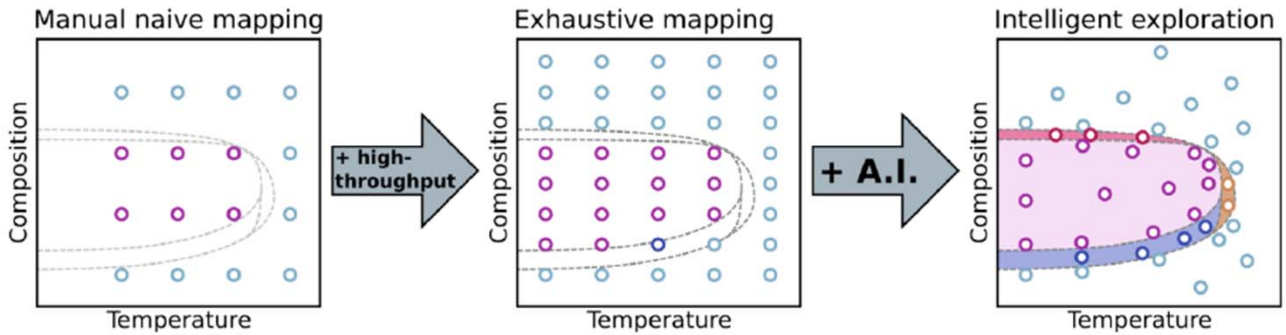
- Transmission & grazing-incidence SAXS/WAXS with broad q range to probe structural order at multiple length scales.
- High throughput to explore large parameter space for variety of materials and processing conditions.
- In situ and time-dependent measurements under non-equilibrium, processing conditions.

Parameter	Specifications achieved
Operating E:	10-17 keV
$\Delta E/E$:	0.7% with Double Multilayer Monochromator
Flux (@500 mA):	Up to 3×10^{12} photons/s
Beam size (FWHM):	Routine size of 200 μm (H) x 100 μm (V) Tunable down to 50 μm (H) x 25 μm (V)
Beam div. (FWHM):	< 0.1 to 1.4 mrad (H); ≤ 0.1 mrad (V)
Accessible q range:	0.003 to 5.0 $Å^{-1}$ (d-spacing of 0.1 to 200 nm)

Long-term scope

Goal: Autonomous experiments to *intelligently* explore materials structure in large parameter space, where

- automatable tasks are ceded to machine control
- researchers are liberated to focus on science



Need: Automated work flow at beamline that integrates:

- robotic sample handling
- efficient data collection
- real-time data reduction and analysis pipelines
- tagging and visualization of structural features in multi-dimensional parameter space
- decision making algorithms to guide subsequent measurements

Collaborations with BNL/CFN Partner User group, BNL/CSI, and Berkeley Lab ALS & CAMERA

Short-term (2-year) goals and capabilities being developed

1. Versatility to accommodate a large majority of users' needs for scattering measurements on new material systems.

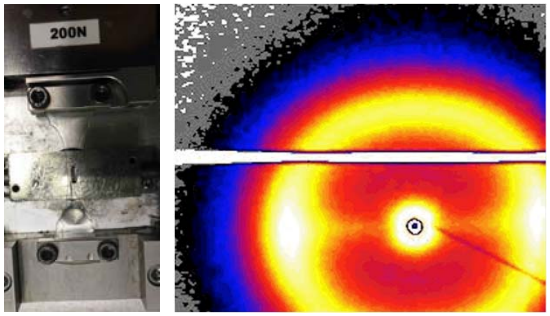
2. Expand accessible sample parameter space

- High throughput for common ex-situ samples: capillaries, thin films, …
- In situ environments: thermal/solvent annealing, tensile strain, …
- Efficient experimental control via software developments, including data acquisition, processing, analysis pipelines → partnership with CFN

Sample exchanger (L) and garage (R) inside air- & vacuum-compatible sample chamber

Versatility and efficiency, a prerequisite to the long-term scope, also provides infrastructure and time to explore new capabilities for sophisticated/challenging experiments:

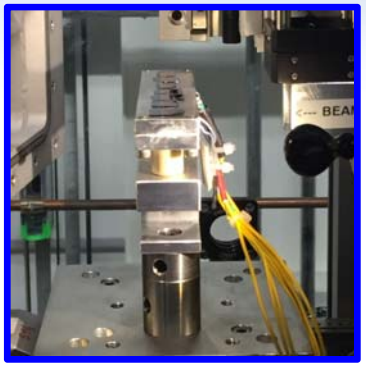
- Ongoing: "Critical-Dimension" CD-SAXS, CD-GISAXS, GISAXS tomography
- Near future: scanning-probe SAXS/WAXS, x-ray reflectivity, …



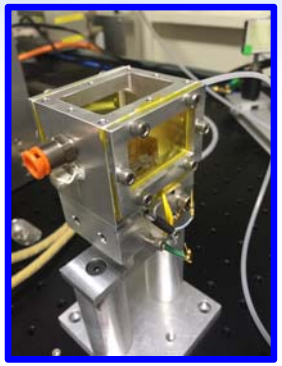
In-situ SAXS from a nano-structured hydrogel film under tensile strain [Vogt group, U. Akron]

Examples of sample setups used by users so far

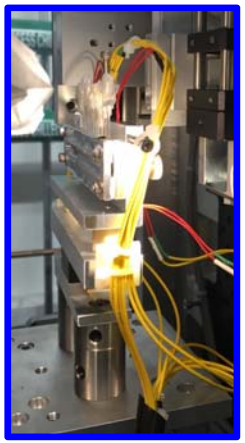
Beamline-supplied



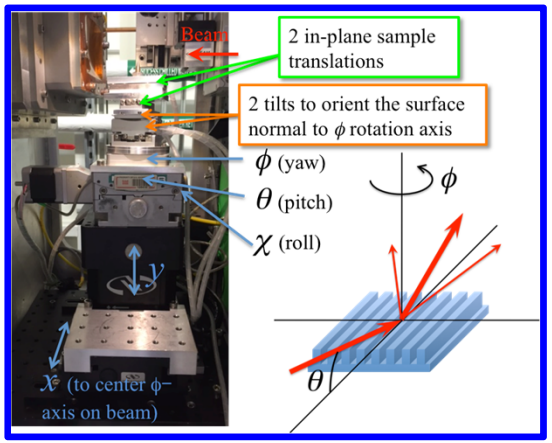
Ex-situ & in-situ T-annealing thin-film bar



Solvent annealing cell



Ex-situ & in-situ T-annealing capillary holder

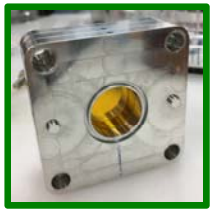


Setup for CD-GISAXS & GISAXS tomography

User-supplied

Linkam heat & tensile stages [Vogt group, U. Akron]

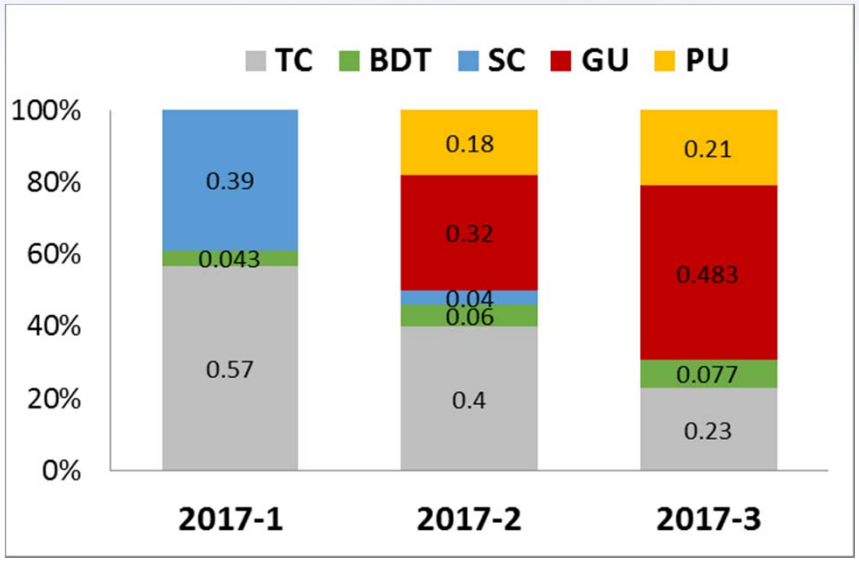
Electro-spray deposition cell for block copolymers [Osuji group, Yale U.]



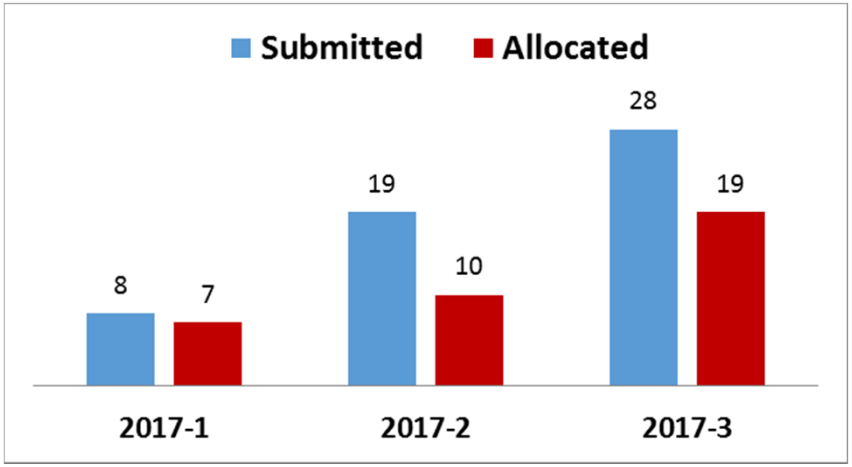
Cell for liquid-surface NP assembly [Herman group, Columbia U.]

User stats

Fractional Beam Time Usage



Proposals



Publications to date (1 published, 1 accepted, 2 submitted):

- J. Liu, J. Lhermitte, Y. Tian, Z. Zhang, D. Yu and K. G. Yager,* "Healing X-ray Scattering Images," *IUCrJ* 4, 455-465 (2017).
- C. Ye, C. Wang, J. Wang, C. G. Wiener, X. Xia, S. Z. D. Cheng, R. Li, K. G. Yager, M. Fukuto, and B. D. Vogt,* "Rapid Assessment of Crystal Orientation in Semi-Crystalline Polymer Films using Rotational Zone Annealing and Impact of Orientation on Mechanical Properties," *Soft Matter* (accepted August 17, 2017): DOI: 10.1039/C7SM01366C

Partner-User agreement with CFN

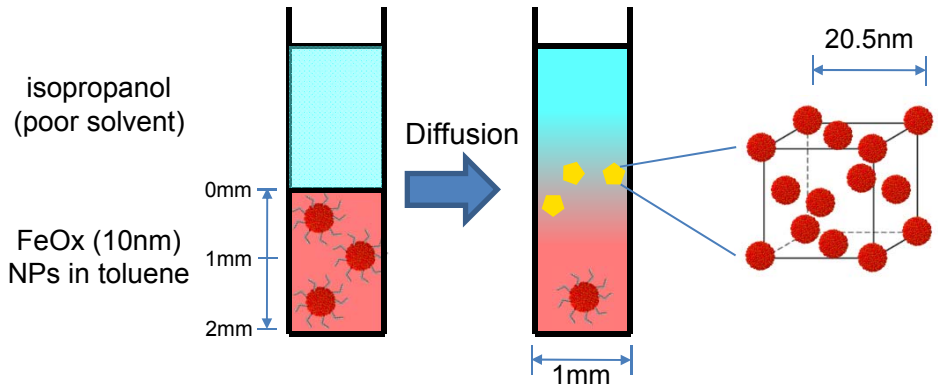
- PU Lead PI: Kevin Yager, BNL/CFN
- Duration: 3 years after the start of GU operation at CMS
- PU beamtime to be allocated:
  - 30% of available user time before the start of GU operation at SMI; 10% after
  - At least 75% of PU beamtime to be devoted to "CFN general users highly rated by a peer-review process that includes review by the NSLS-II PRP"
- PU contributions:
  - CFN-owned endstation equipment that was moved from NSLS X9 to CMS, including sample/WAXS vacuum chamber, WAXS detector, SAXS flight tubes, optical tables and stands.
  - $150K (with burden) toward hardware needed to enhance beamline throughput
  - 2.0 FTE before the start of GU operation at SMI; 0.7 FTE after
  - Full user support during PU beamtime
  - Participate in: development of long-term vision and plans for CMS, beamline operation and scheduling, beamline R&D efforts (e.g., software developments)

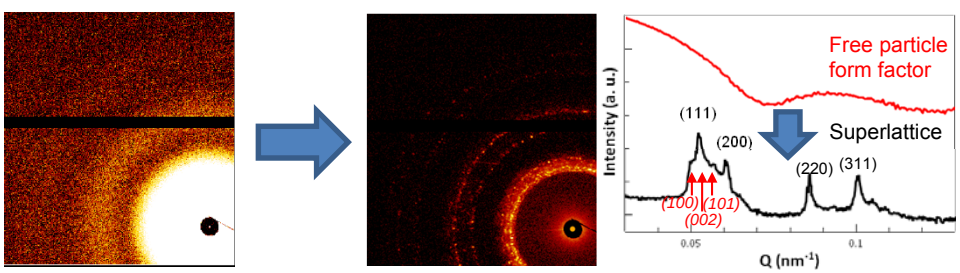
Science highlight 1: Internal research

In-situ Monitoring of Nanoparticle Superlattice Formation in Solution

Ruipeng Li, M. Fukuto (BNL/NSLS II), and I. Herman (Columbia U.) (work in progress)

Aim: Kinetic control of NP self-assembly via good/poor solvent gradient

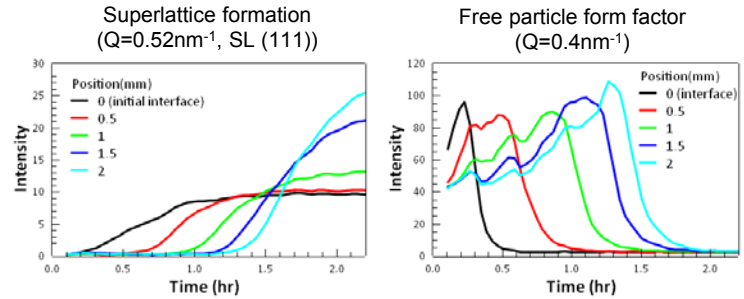




Form factor of free particles

Superlattice : FCC + HCP (new phase)

From SAXS at different positions from interface



- Solvent gradient method facilitates rapid superlattice formation with large grain size (~10 μm), only in hours (days to weeks for evaporation of pure solvent).
- A new HCP phase has been observed, unlike the pure FCC phase observed for assembly from good solvents only via slow evaporation or spin-coating.

Future plans:

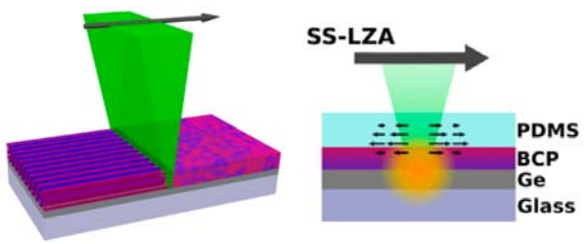
1. Develop microfluidic cell to better control the solvent boundary and convert time into spatial coordinate.
2. Explore solutions with various polarity and viscosity.
3. Explore NPs with non-spherical shapes, binary mixtures of different sizes

Science highlight 2: Partner-User group

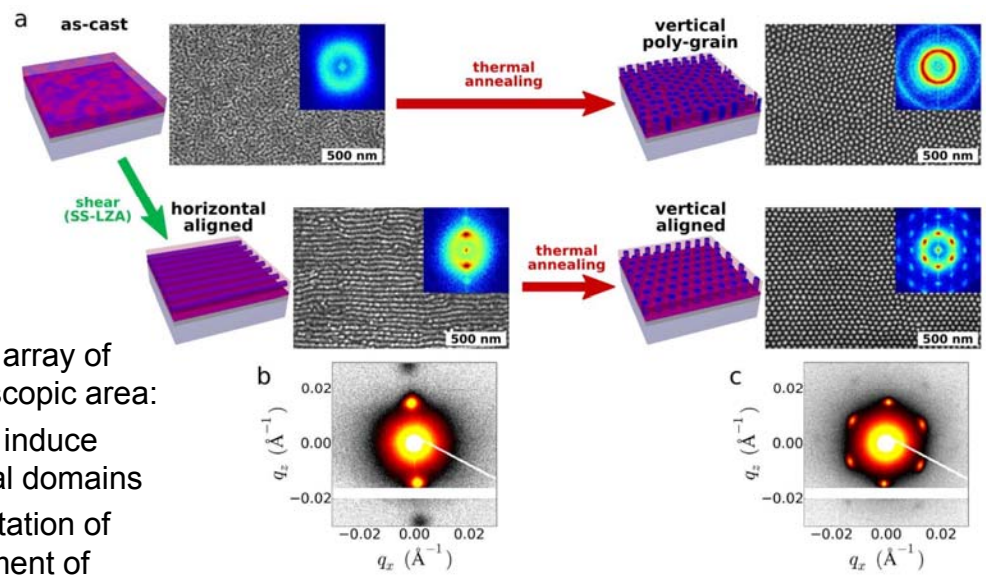
Pathway-Engineering for Highly-Aligned Block Copolymer Arrays

Y. Choo, P. W. Majewski, M. Fukuto, C. O. Osuji (Yale U.), and K. G. Yager (BNL/CFN) (submitted)

Aim: Control processing steps to achieve target block-copolymer (BCP) morphologies normally inaccessible to single-step processing.



- Single-step thermal annealing yields poly-grains of hexagonally packed, vertically oriented cylindrical BCP domains.



- Two-step processing to induce a highly aligned array of hexagonally packed BCP domains over macroscopic area:
  1. Soft-shear laser zone annealing (SS-LZA) to induce horizontally aligned, surface-parallel cylindrical domains
  2. Thermal annealing to induce vertical re-orientation of cylindrical domains, promoting in-plane alignment of hexagonal array orientation along the shear direction

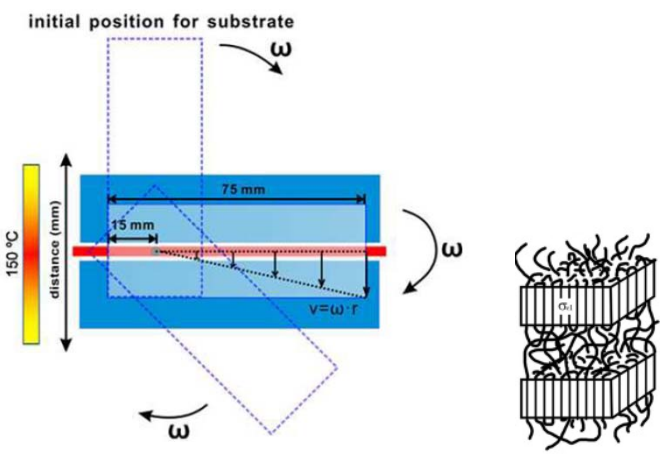
Significance: macroscopic alignment of nanostructures without an external template or external field.

Science highlight 3: External group

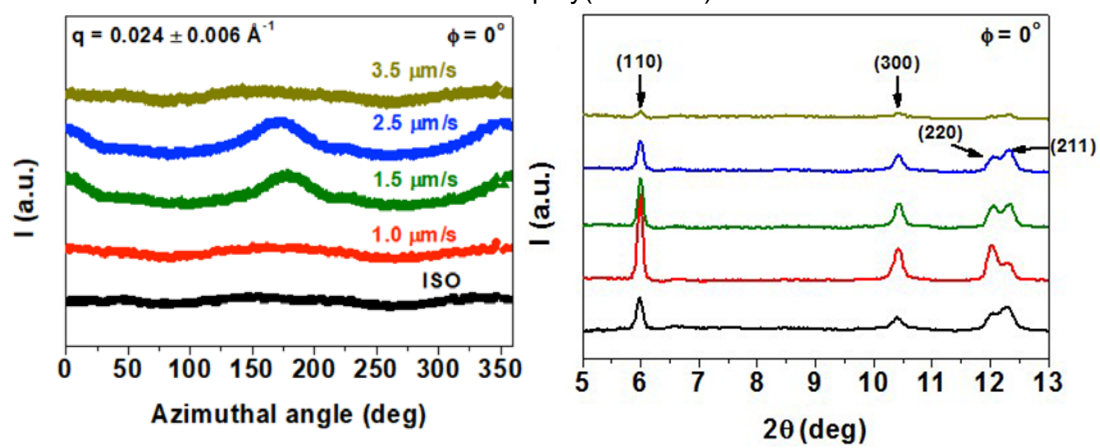
Rapid Assessment of Crystal Orientation in Semi-Crystalline Polymer Films using Rotational Zone Annealing and Impact of Orientation on Mechanical Properties

C. Ye, C. Wang, J. Wang, C. G. Wiener, X. Xia, S. Z. D. Cheng, R. Li, K. G. Yager, M. Fukuto, and B. D. Vogt (U. Akron), *Soft Matter* 2017 (accepted): DOI: 10.1039/C7SM01366C

Aim: Probe the effects of zone-annealing (ZA) sweep rate on lamellar orientation anisotropy (SAXS), chain-packing crystallinity (WAXS), and mechanical properties



From transmission SAXS/WAXS on poly(1-butene) films at normal incidence



Results: Combinatorial approach based on Rotational Zone Annealing (RZA) reveals an optimal ZA sweep rate (distance from rotation center) for maximizing crystallinity and lamemllar orientation anisotropy, also consistent with the ZA sweep rate at which the film's elastic moduli are maximized.

Future plans

Near-term (2-year) development priorities

- Continue commissioning of high-throughput capabilities, toward Rapid and Mail-In Access
- Continue to expand in-situ capabilities available to users
- Integrate data analysis pipelines and scattering-image classification algorithms being developed by CFN Partner User group.
- Technique developments: CD-SAXS/CD-GISAXS, GISAXS-tomography, scanning-probe SAXS/WAXS for heterogeneous materials, specular reflectivity

350 μm line containing ~25 nm Au islands

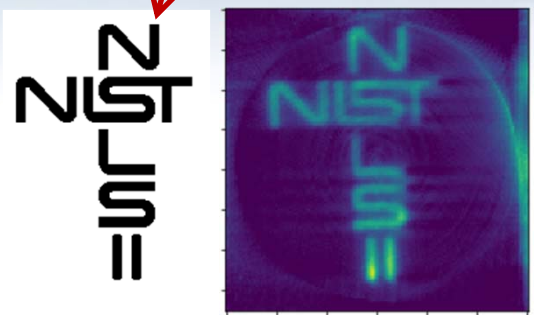
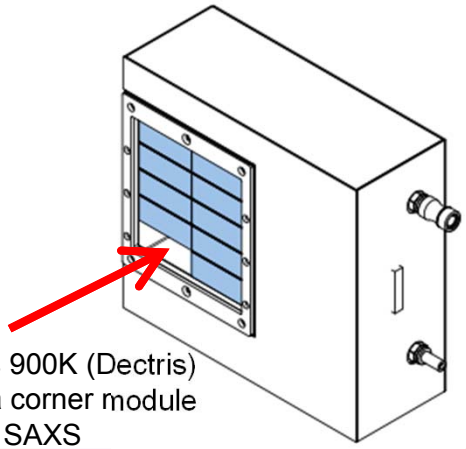


Image (right) reconstructed from **GISAXS tomography** scans at CMS [L. Richter et al., NIST]

Upgrade priorities (funds yet to be secured)

- Large SAXS vacuum flightpath (~$500K) for the new vacuum-compatible Pilatus 2M.
- New in-vacuum, photon-counting area detector for WAXS (~$300K).



Proposed Pilatus 900K (Dectris) for **WAXS**, with a corner module removed to pass SAXS

Summary

- Versatile SAXS/WAXS beamline targeting diverse materials-science user communities
- Focus on high-throughput, in-situ, and efficient experiments and analysis, toward enabling intelligent exploration of materials structure in large parameter space
- Strong, successful partnership with CFN
- Good progress with technical and science commissioning since First Light
- User operation commenced, with steady increase in user beamtime, user proposals submitted and allocated, and user publications.

END

Appendix (back up material, not expected to be shown)

List of pubs

J. Liu, J. Lhermitte, Y. Tian, Z. Zhang, D. Yu and K. G. Yager,* “Healing X-ray Scattering Images,” *IUCrJ* **4**, 455-465 (2017).

C. Ye, C. Wang, J. Wang, C. G. Wiener, X. Xia, S. Z. D. Cheng, R. Li, K. G. Yager, M. Fukuto, and B. D. Vogt,* “Rapid Assessment of Crystal Orientation in Semi-Crystalline Polymer Films using Rotational Zone Annealing and Impact of Orientation on Mechanical Properties,” *Soft Matter* (accepted August 17, 2017): DOI: 10.1039/C7SM01366C

List of invited talks

M. Fukuto, “11-BM Complex Materials Scattering (CMS): A New SAXS/WAXS Beamline at NSLS II,” ACS POLY Symposium: Federally Funded Polymer Research, 254th ACS National Meeting, Washington DC, August 20, 2017.

CMS capabilities

Focus areas:

- Transmission & grazing-incidence SAXS/WAXS with broad q range to probe order at multiple length scales.
- High throughput to explore large parameter space for variety of materials and processing conditions.
- In situ and time-dependent measurements under non-equilibrium, processing conditions.

Strengths:

- Focus on high-throughput and efficient parameter-space exploration
  → complementarities with more specialized capabilities at SMI and CHX
- Strong partnership with CFN
- Simultaneous SAXS/WAXS
- In-air and in-vacuum sample environment; vacuum important for reducing background for weakly scattering systems (e.g., polymers)
- Robotic sample exchanger for common ex-situ samples, also air- and vacuum-compatible
- Variety of in-situ environment setups
- Multiple sample stage stack for scanning-probe SAXS/WAXS, CD-SAXS/CD-GISAXS, GISAXS tomography
- Secondary microfocusing option; 2x increase in flux for GISAXS/GIWAXS, downward beam deflection for liquid-surface GIXS
- Relatively large hutch to facilitate future upgrades/expansion of endstaiton capabilities

Weaknesses:

- Old WAXS detector form NSLS: CCD with long read-out time, mismatch with new SAXS detector (Pilatus 2M)
- Old SAXS pipes from NSLS: changing sample-SAXS detector distance requires manual exchange of pipes
- Relatively confined sample space

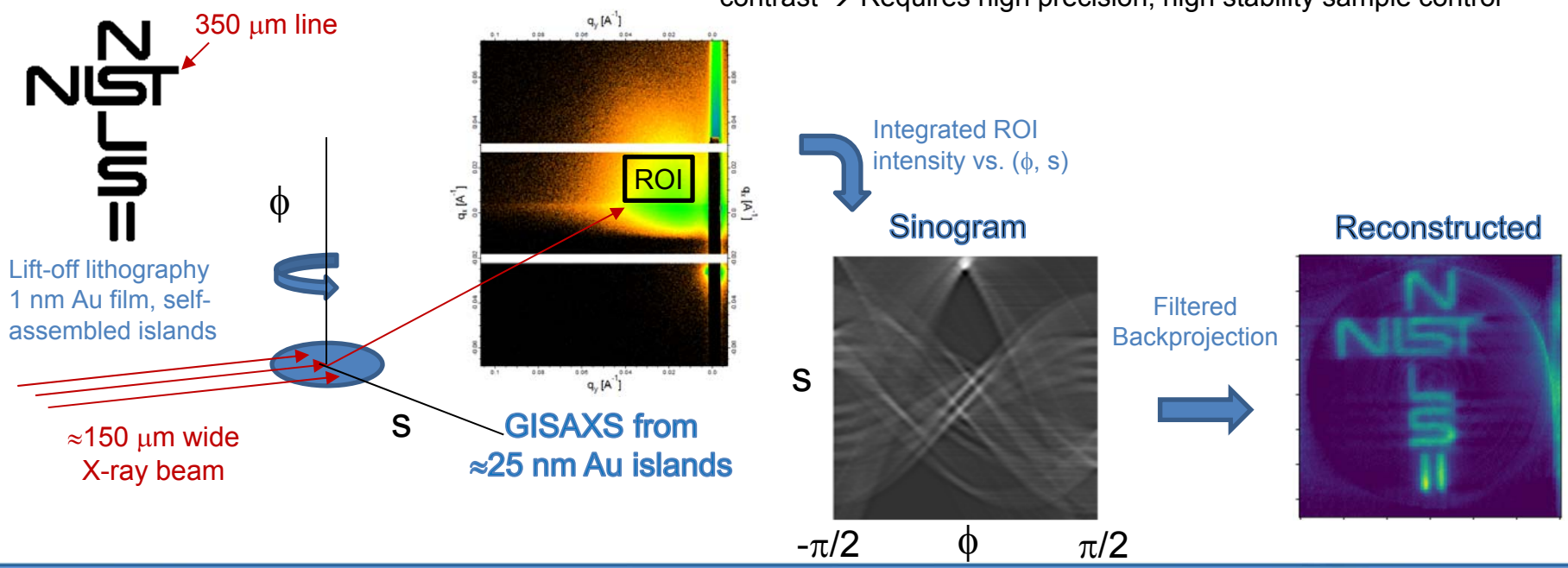
Science highlight 3': External group

GISAXS tomography

L. Richter, E. Gann, S. Engmann, D. DeLongchamp (NIST), R. Li, M. Fukuto (BNL/NSLS II) (in progress)

Nanostructure of thin (≤ 100 nm) films critical to diverse technologies

- Selective membranes, Smart coatings
- Sensors, Optoelectronics

GISAXS/GIWAXS gold standard for nanoscale measurements

- GI techniques have compromised meso- and micro-scale resolution due to foot print projection
- 2D Tomography can reconstruct micro-scale images with nanoscale contrast → Requires high precision, high stability sample control