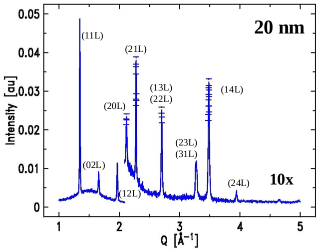
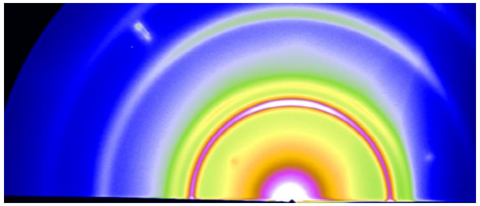
Introduction to Synchrotron X-ray Scattering Techniques

Mike Toney, SSRL Materials Sciences Division

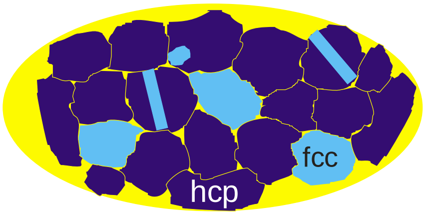
1. Why do x-ray scattering?
2. Basics of an x-ray scattering experiment
3. SSRL scattering beamlines
4. Some examples
   - SAXS: porous films
   - Powder: Pd nanoparticles
   - Textured films: ZnO nanostructures
5. Summary

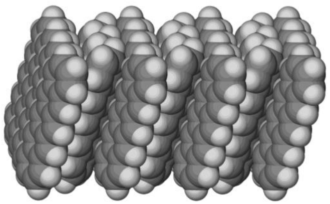




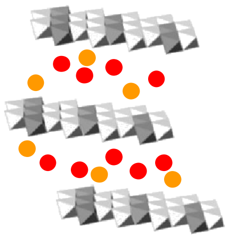
Why do SR X-ray scattering?

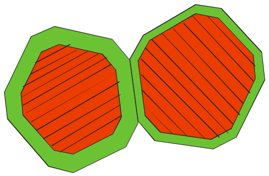
- ➢ Materials properties are caused or affected by their physical structure and morphology
- ➢ Improve your materials by understanding the structure.

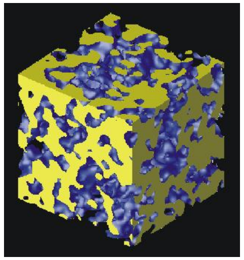


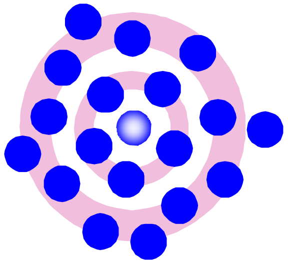


- Phase identification & quantify
- Where are the atoms: Atomic or molecular arrangement, crystal & surface structure
- Strain, lattice parameters (unit cell size)
- Grain/crystallite size (diffraction)
- Pore/particle size (SAXS)
- Other defects & disorder (faults, positional disorder)
- Crystallite orientation or texture

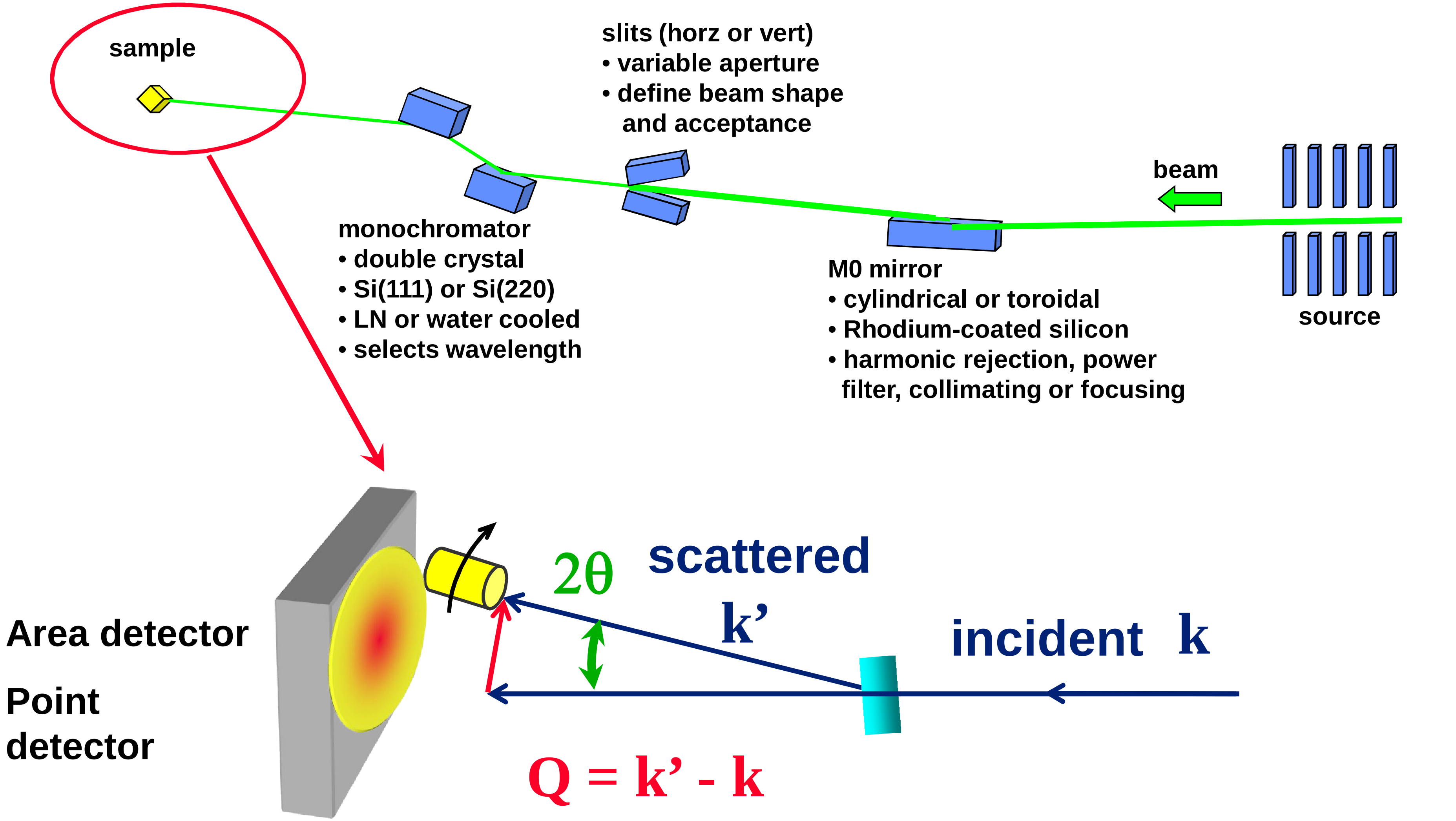








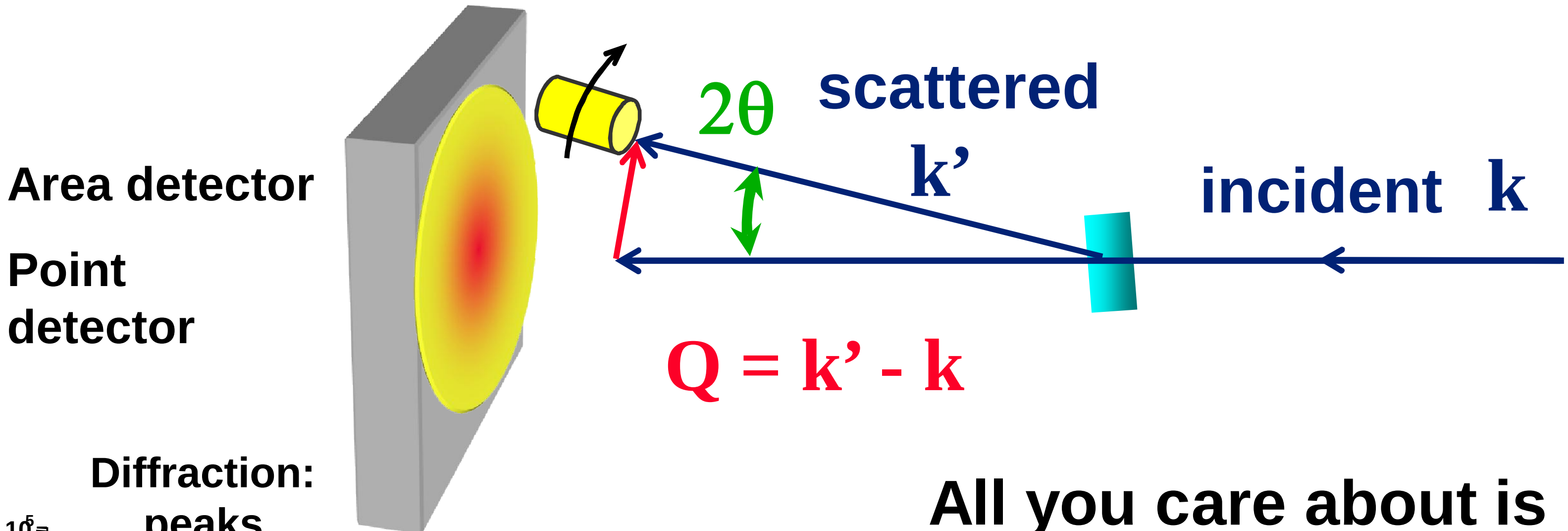
SR Scattering Experiment

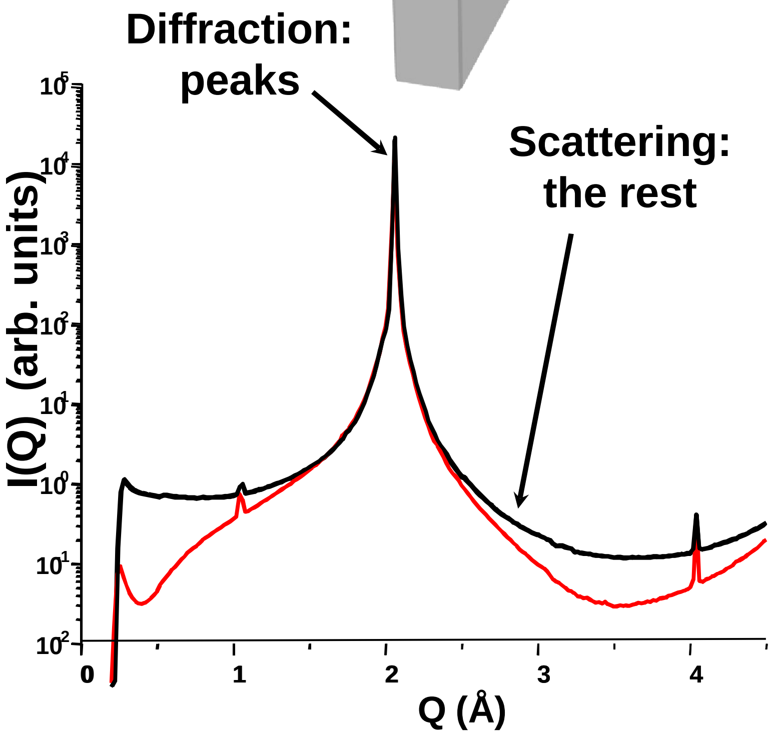


collect I(Q)

All you care about is Q

SR Scattering Experiment





All you care about is Q

At SSRL:

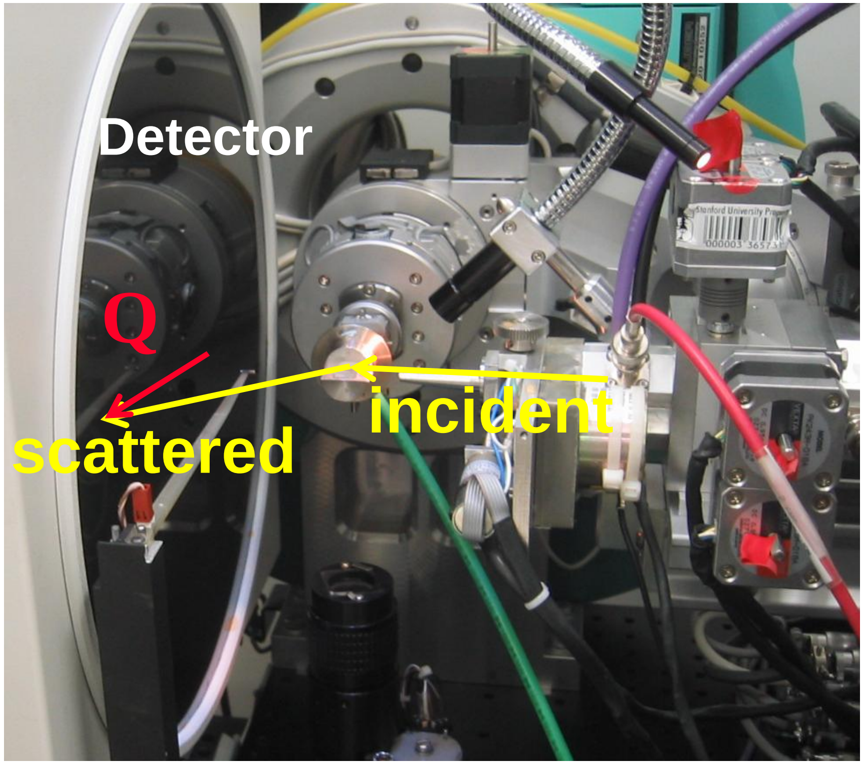
- Area detector: 11-3
- Point detectors: 2-1, 7-2, 10-2
- SAXS: 1-4

SR Scattering Experiment

Beamline	2-1	7-2 & 10-2	11-3 1-5
Detector	Point	(mostly) Point	Area
Advantages	High resolution Accurate peak position and shape Weak peaks Variable energy Reflectivity	High resolution Accurate peak position and shape Weak peaks Variable energy 4 degrees of motion	Fast measurement Collect (nearly) whole pattern
Dis-advantages	Slow Only 2 axes of motion	Slow Can be difficult to find textured peaks Complicated	Fixed wavelength Low resolution Peak shape and position inaccurate Weak peaks difficult
Used for	Powders Phase determination Reflectivity θ-2θ Anomalous diffraction	Single crystals Grazing-incidence Anomalous diffraction Surface studies Anomalous diffraction	Texture Real time experiments Polycrystalline, small grains Thin films

SR Scattering Experiment

Area detector (11-3)



2θ = scattering angle

Q = (4π/λ) sin θ

Advantages

- Fast measurement
- Collect whole pattern

Disadvantages

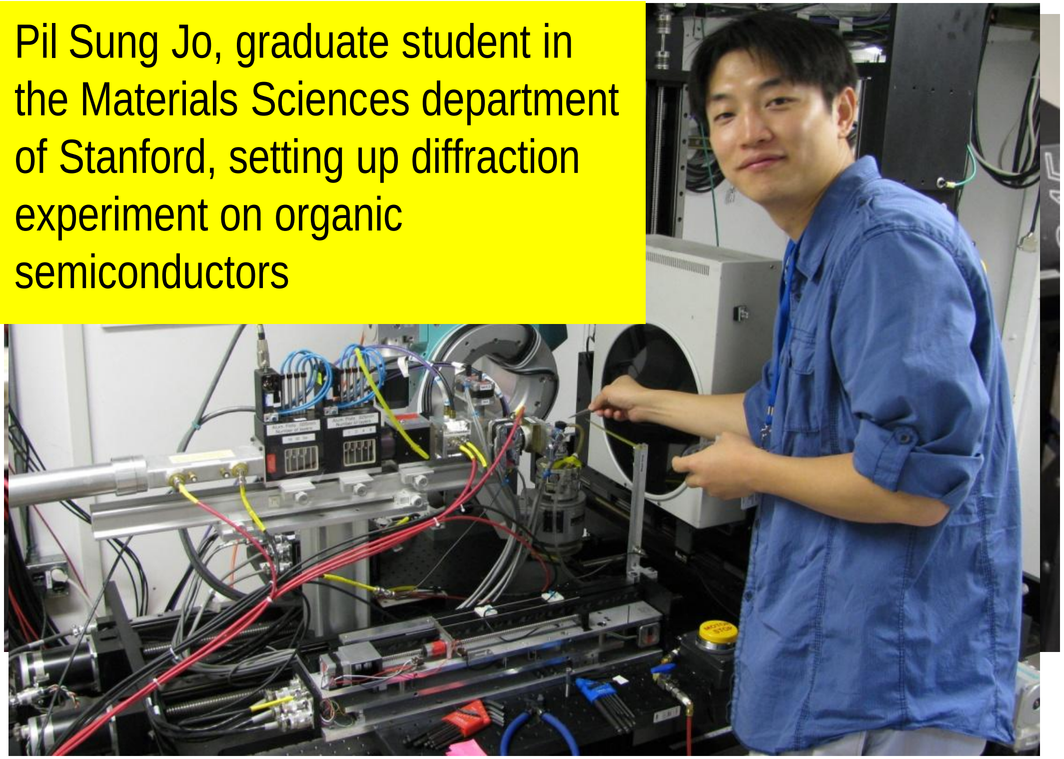
- Fixed wavelength
- Low resolution
- Peak shape & position inaccurate
- Weak peaks difficult

Used for

- Texture (crystallite orientation)
- Real time experiments (electrochemistry, stress-strain)
- Polycrystalline, small grains
- Thin films

SR Scattering Experiment

Area detector (1-5) - clone of 11-3



Pil Sung Jo, graduate student in the Materials Sciences department of Stanford, setting up diffraction experiment on organic semiconductors

Used for

- Texture (crystallite orientation)
- Thin films

Advantages

- Fast measurement
- Collect whole pattern

Disadvantages

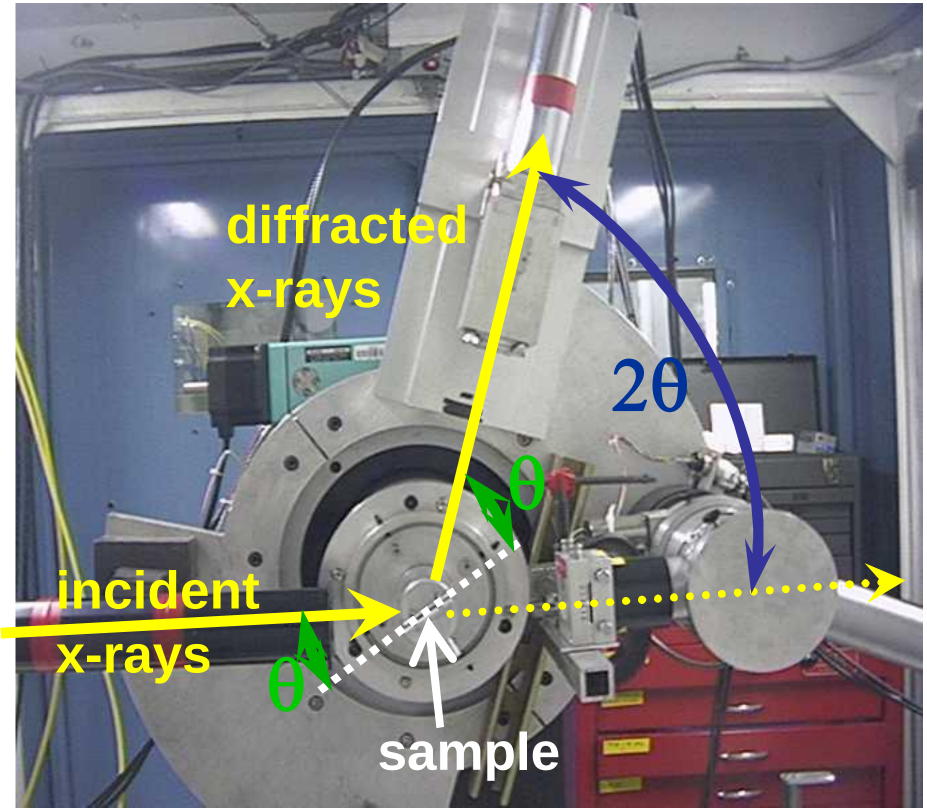
- Low resolution
- inaccurate peak shape /position
- Weak peaks difficult

Goal: Easy, seamless access for students from universities when research requires higher intensity & resolution than laboratory sources.

Phase I: Reconfigured bending magnet for thin film x-ray diffraction. Stanford Nanocharacterization Laboratory will pilot access

SR Scattering Experiment

Point detector (2-1)



2θ = scattering angle

Q = (4π/λ) sin θ

Advantages

- High resolution
- Accurate peak position & shape
- Weak peaks
- Variable energy
- Reflectivity

Disadvantages

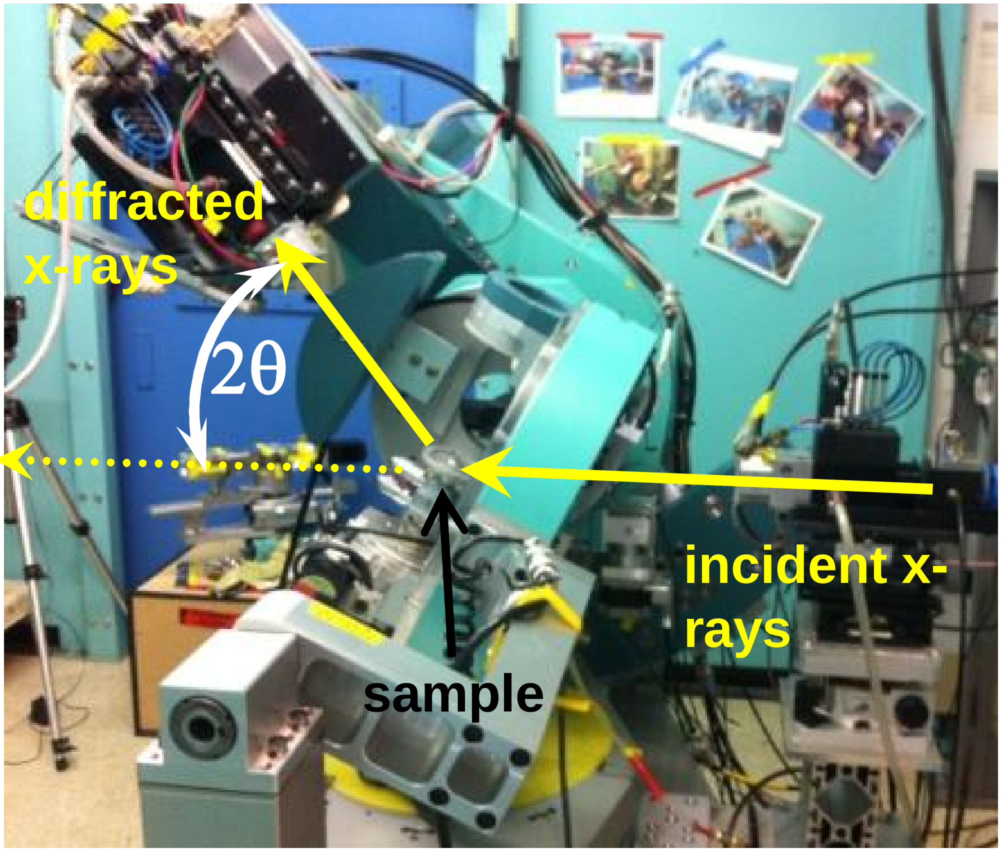
- Slow
- Only 2 degrees of motion (θ, 2θ)

Used for

- Powders
- Phase determination
- Reflectivity
- Anomalous diffraction
- θ-2θ measurements

SR Scattering Experiment

Point detector (7-2/ 10-2)



2θ = scattering angle

Q = (4π/λ) sin θ

Advantages

- High resolution
- Accurate peak position & shape
- Weak peaks
- Variable energy
- 4 degrees of motion (θ, 2θ, χ, φ)

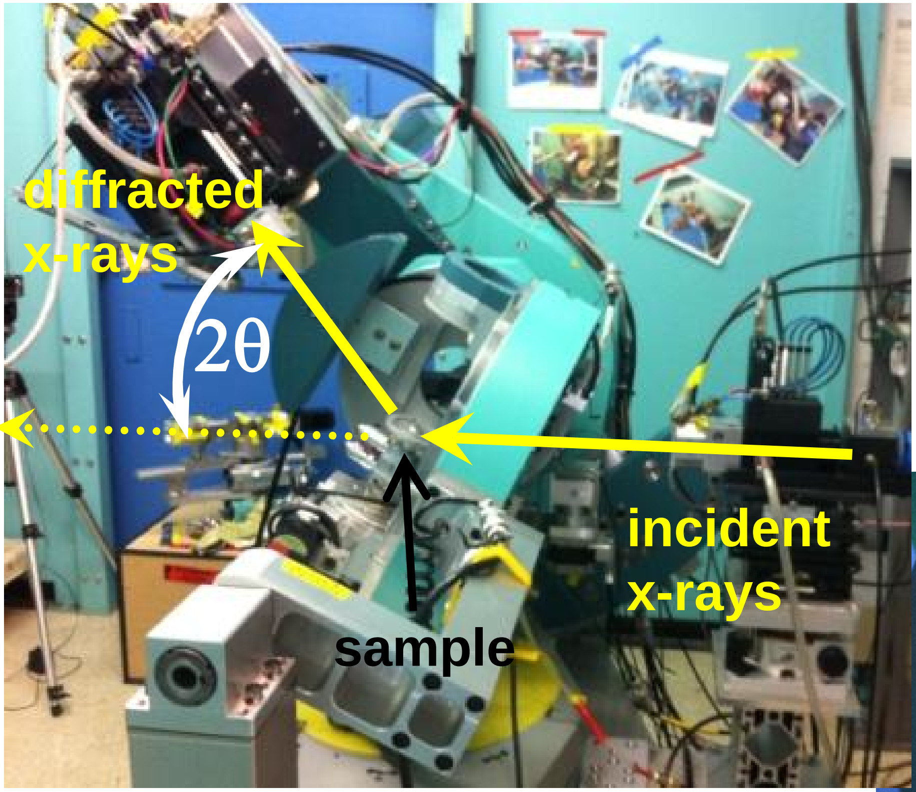
Disadvantages

- Slow
- Complicated
- Can be difficult to find peaks

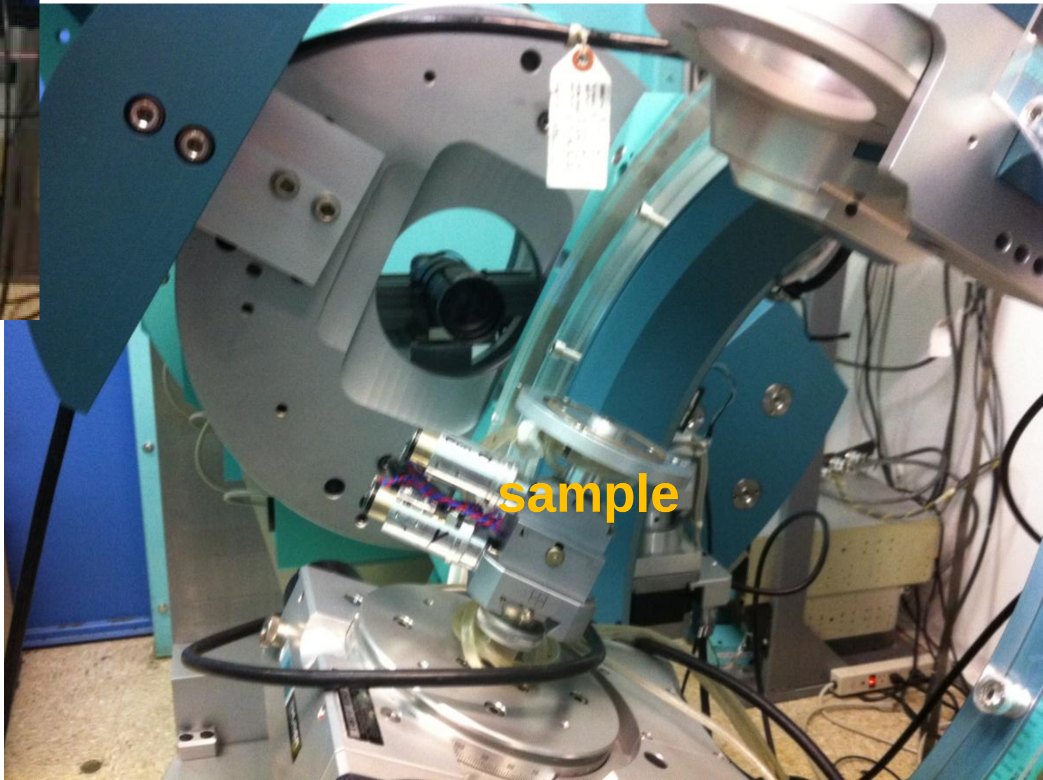
Used for

- Single crystals
- Grazing-incidence
- Anomalous diffraction
- Thin films
- Surface studies

SR Scattering Experiment

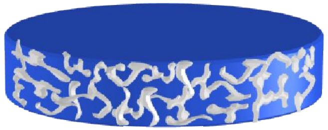


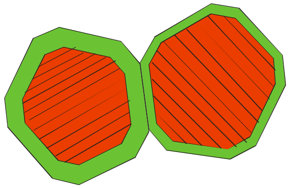
Point detector (7-2/ 10-2)

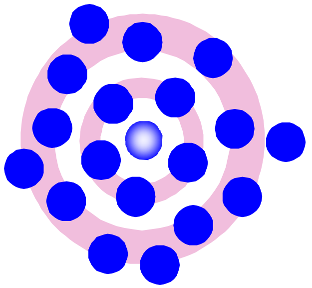


Types of scattering experiments

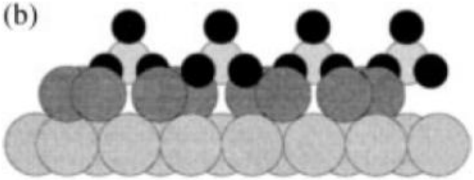
- Small Angle X-ray Scattering (SAXS)
  – probes structures 1-100 nm
- Powder Diffraction, including in-situ
  – random or isotropic; nanoparticles
  – poor crystalline order
- Thin Films: random, textured, epitaxial
  – wide variety
- Surface Scattering/monolayers
  – atomic structure at surface or interface



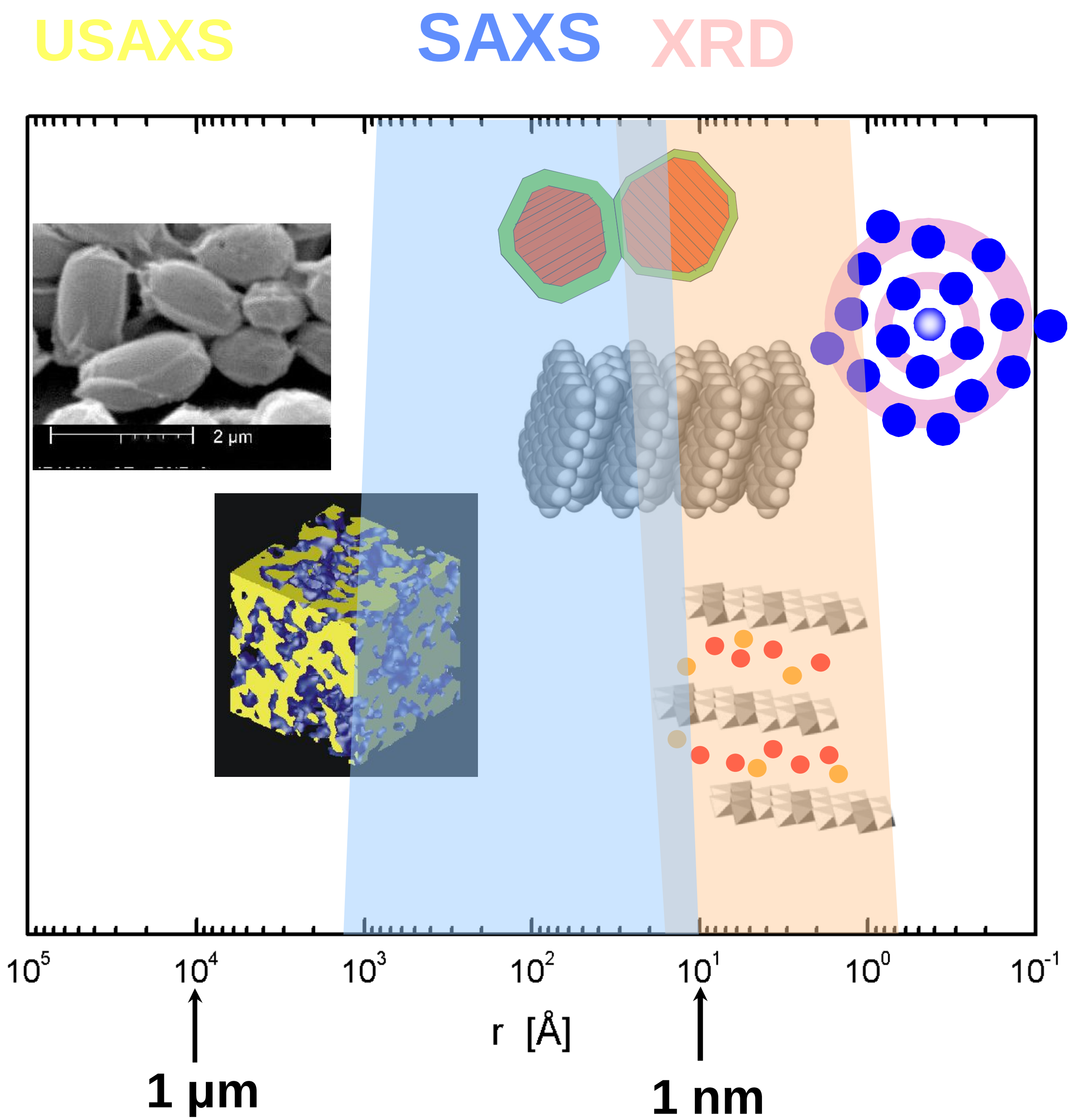




(b)



Lengths Accessed by Probes



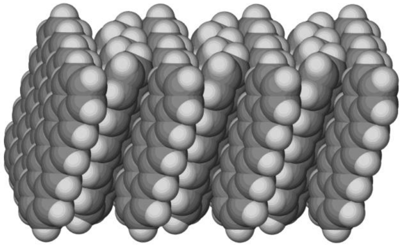
Summary: SR Scattering

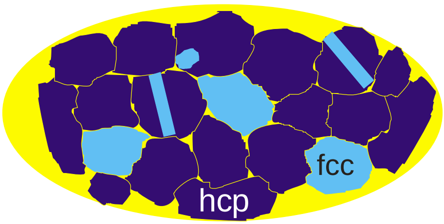
SR Scattering:

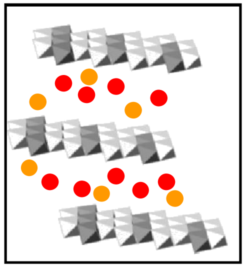
- **Q** is important variable: measure I(**Q**)
- choose **Q** to match length scale
- variety of materials

What can we learn:

- Phase identification & quantify
- Where are the atoms: crystal & surface structure
- Strain, lattice parameters
- Grain/crystallite size
- Pore/particle size
- Other defects & disorder
- Crystallite orientation or texture



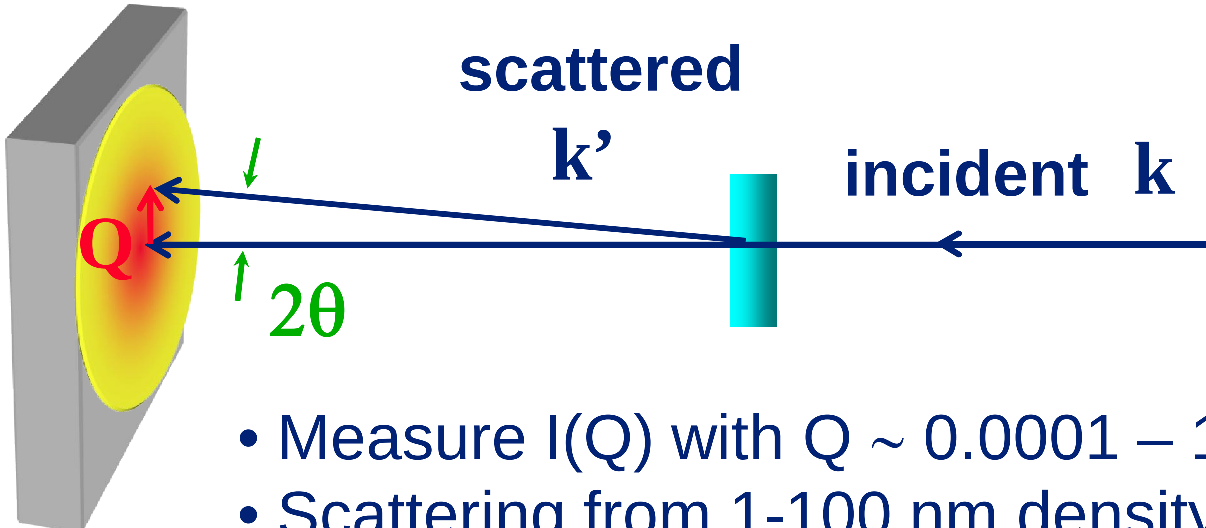




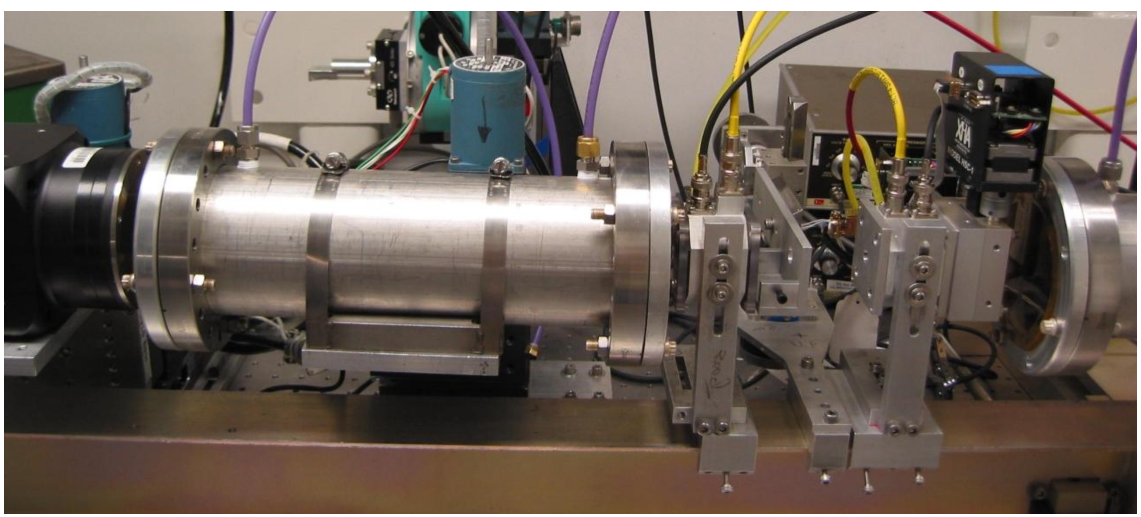
Small Angle Scattering

$\mathbf{Q = k' - k}$

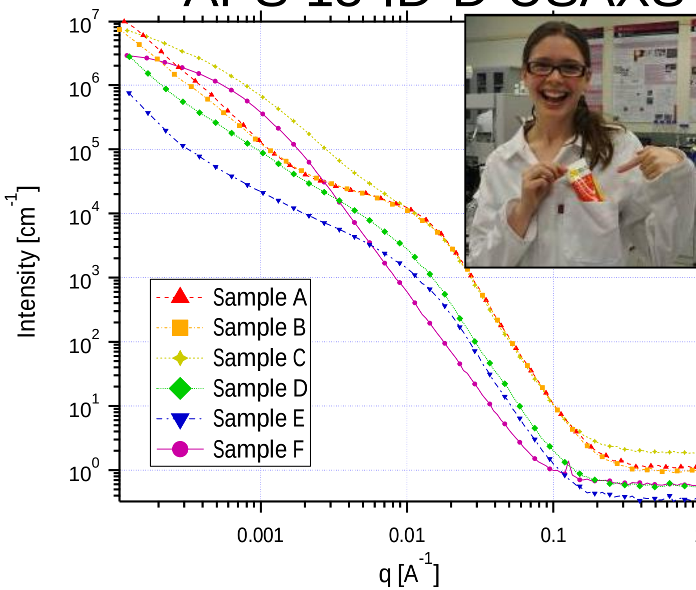
$|\mathbf{Q}| = (4\pi/\lambda)\sin\theta$



- Measure I(Q) with Q ~ 0.0001 – 1 Å^{-1}
- Scattering from 1-100 nm density inhomogeneities



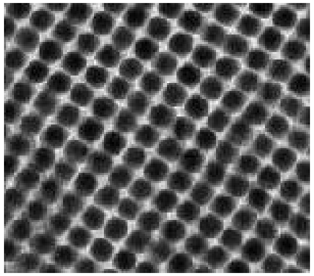
APS 15-ID-D USAXS

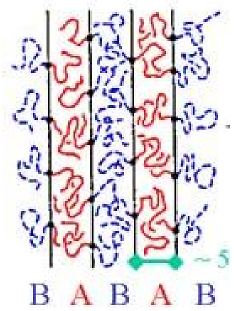


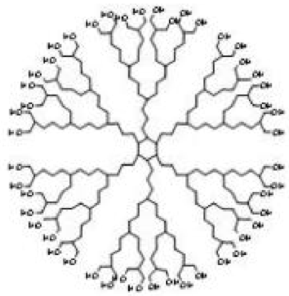
Small Angle Scattering

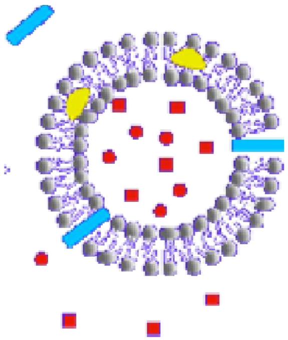
Scattering from density inhomogeneities with sizes 1-100 nm

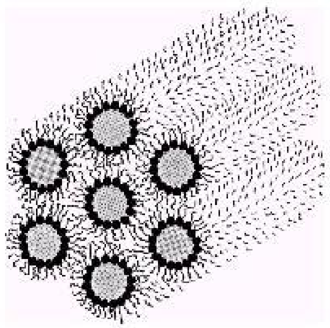
- nanoparticles (catalysts, bio-oxides, geo-oxides)
- nanoporous materials
- co-polymers
- dendimers
- supramolecular assemblies
- micelles
- colloids
- metallic glasses





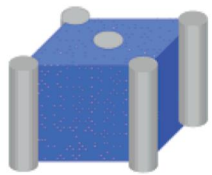


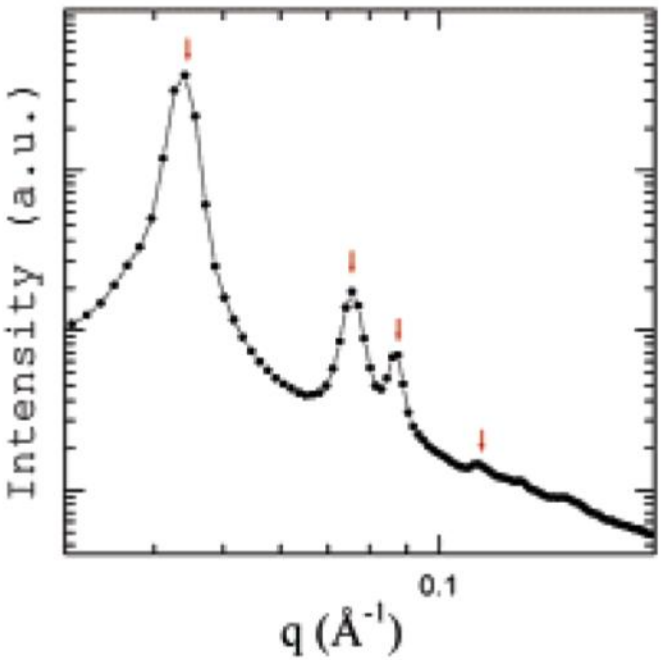




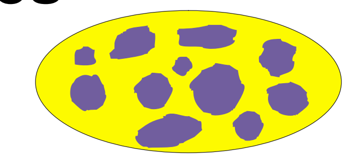
Small Angle Scattering

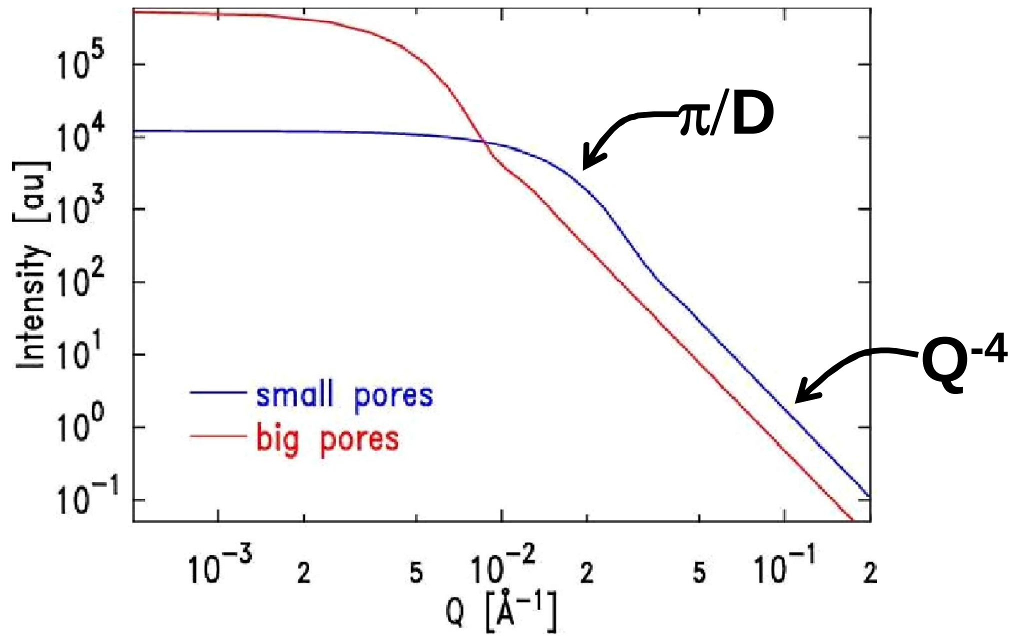
Hexagonal packed cylinders





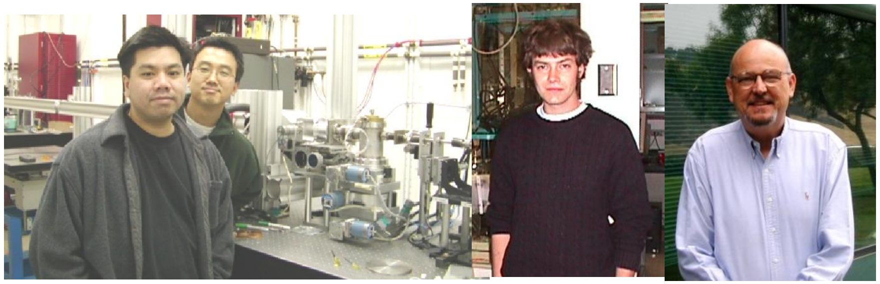
Isolated particles or pores with diameter D

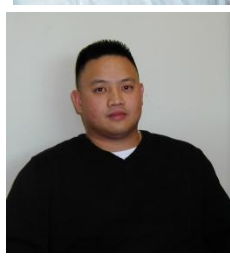




- Need large Q range:
  $1/D \lesssim Q \lesssim 10/D$

Example 1: Nanoporous Films

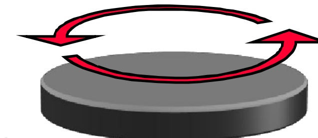




<u>IBM</u>
Elbert Huang
Jonathan Hedstrom
Ho-Cheol Kim
Teddie Magbitang
Robert Miller
Willi Volksen

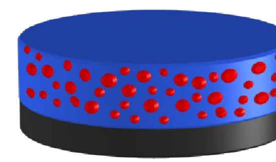
Matrix: Methyl Silsesquioxane (MSSQ), $CH_3SiO_{1.5}$

Porogen (thermally labile polymer): copolymer poly(methyl methacrylate-co-dimethylaminoethyl methacrylate) or P(MMA-co-DMAEMA)



1. **Spin coat MSSQ/Porogen solution**

Spin Coat

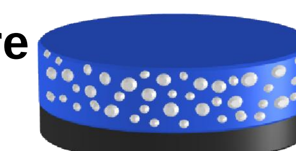


2. **Heat to 450°C, at 5°C/min under argon**

MSSQ crosslinks at 200°C
Poragen fully degrades at 400°C

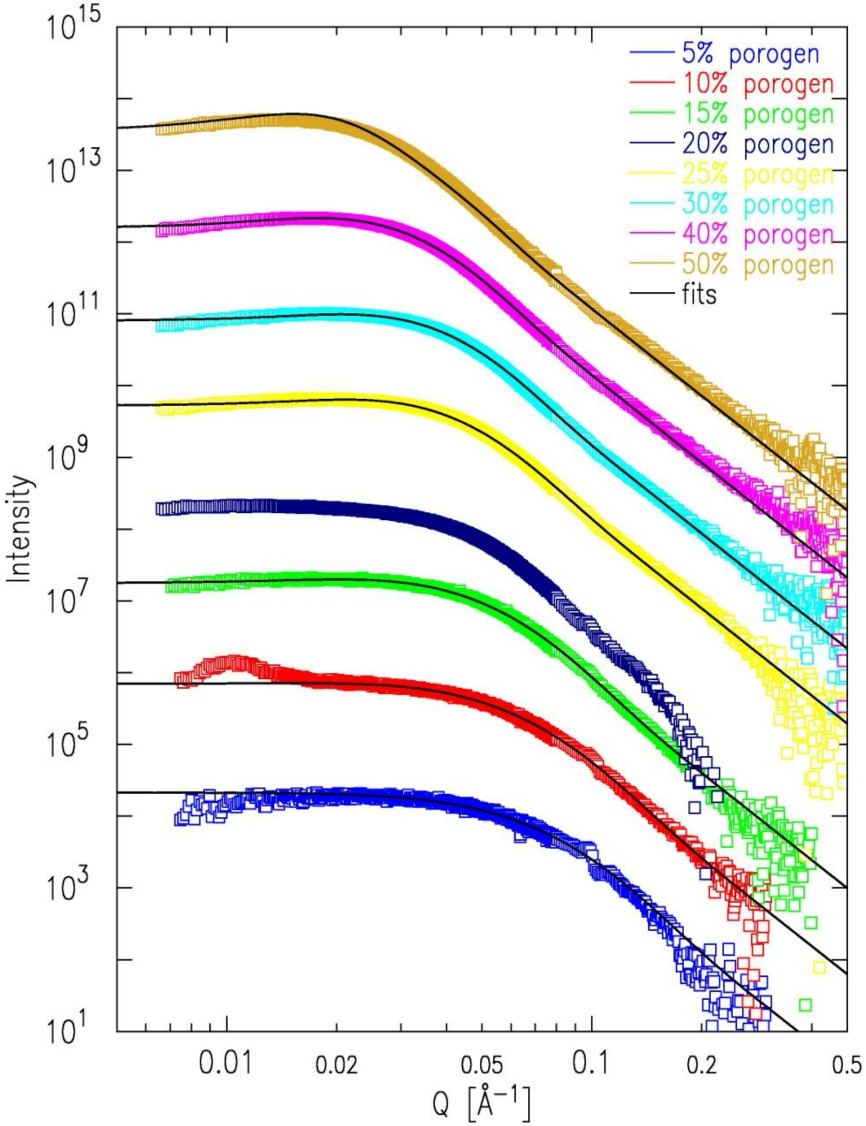
Δ Argon

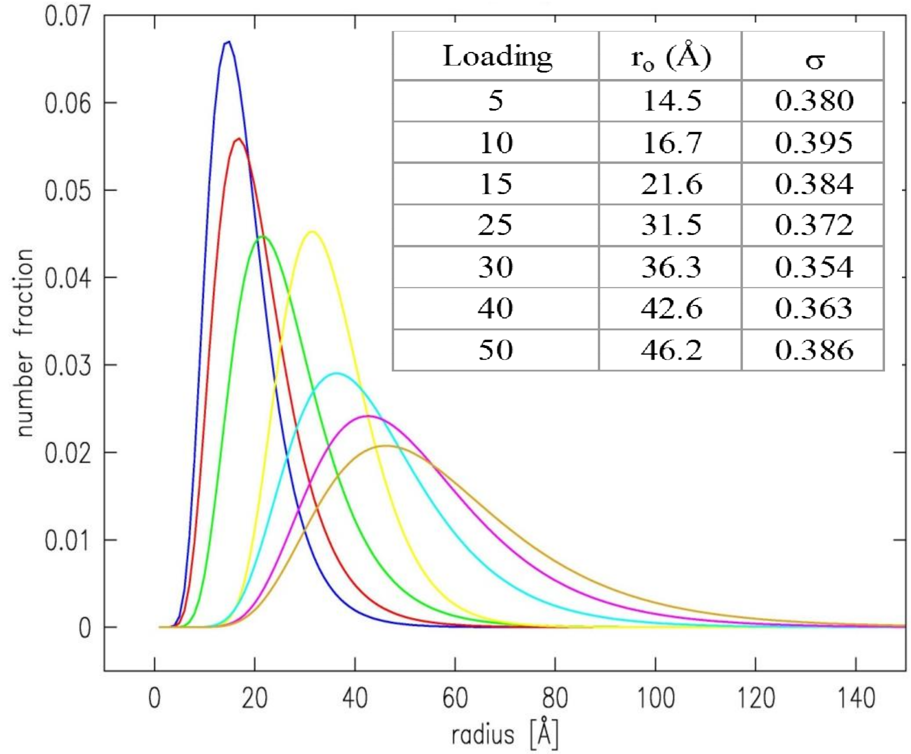
3. **Cool to room temperature**



- **Huang et al, Appl. Phys. Lett. 81, 2232 (2002)**
- **Huang et al., Chem. Mater. 14, 3676 (2002)**
- **Magbitang, Adv. Materials. 17, 1031 (2005)**

Nanoporous Films: SAXS Results





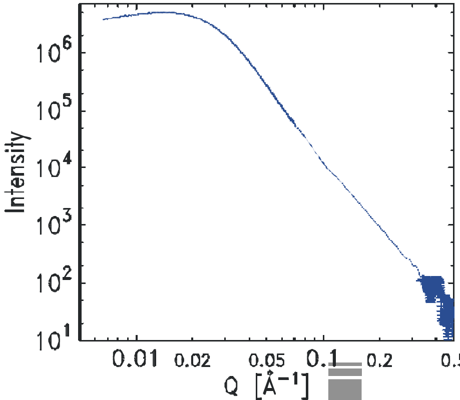
Loading	r_o (Å)	σ
5	14.5	0.380
10	16.7	0.395
15	21.6	0.384
25	31.5	0.372
30	36.3	0.354
40	42.6	0.363
50	46.2	0.386

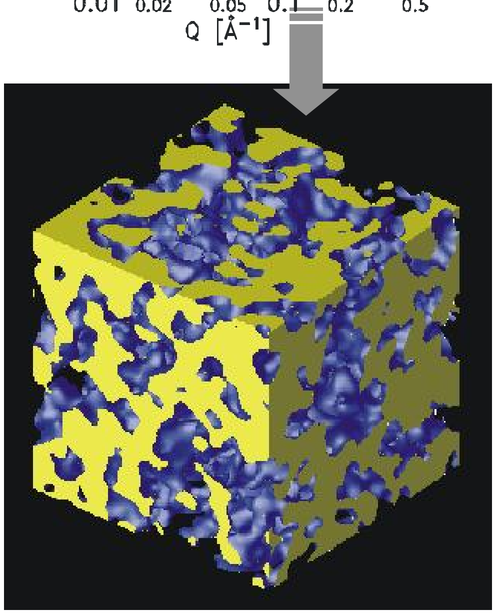
Find:
- reasonably small pores (good)
- broad distribution of pore sizes (bad)
- size increases with loading => agglomeration (bad)

Huang et al, Appl. Phys. Lett. 81, 2232 (2002)

Nanoporous Film Morphology

Goal: obtain representative real space picture (correct size scale and extent of interconnection)





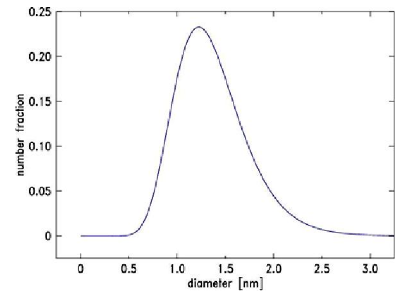
Approximations:

- morphology is "disordered" or random with no preferred direction
- morphology described by cosine waves:
  - with random phase and direction
  - non-random distribution of wavelengths (from SAXS)

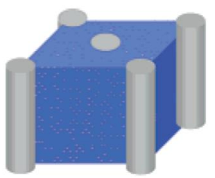
- Cahn, J.W., *J. Chem. Phys.* 42, 93 (1965).
- Berk, N.F. *Phys. Rev. Lett.* 58, 2718 (1987) & *Phys. Rev. A* 44, 5069 (1991).
- Jinnai, H., et al., *Phys. Rev. E* 61, 6773 (2000).
- Teubner, M., *Europhys. Lett.* 14, 403 (1991).
- Hedstrom et al., Langmuir 20, 1535 (2004)

Summary: SAXS

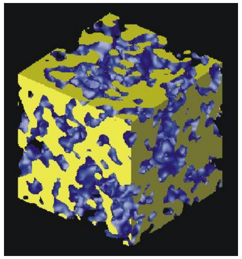
- Isolated Particles/Pores (not ordered)
  - ✓ Obtain average size & particle/pore size distribution (need large Q range)



- (More) Ordered Structures
  - ✓ particle/pore spacing and morphology



- Dense Network of Pores/Particles
  - ✓ Obtain representative morphology
  - ✓ Good for interconnected & bicontinuous morphologies

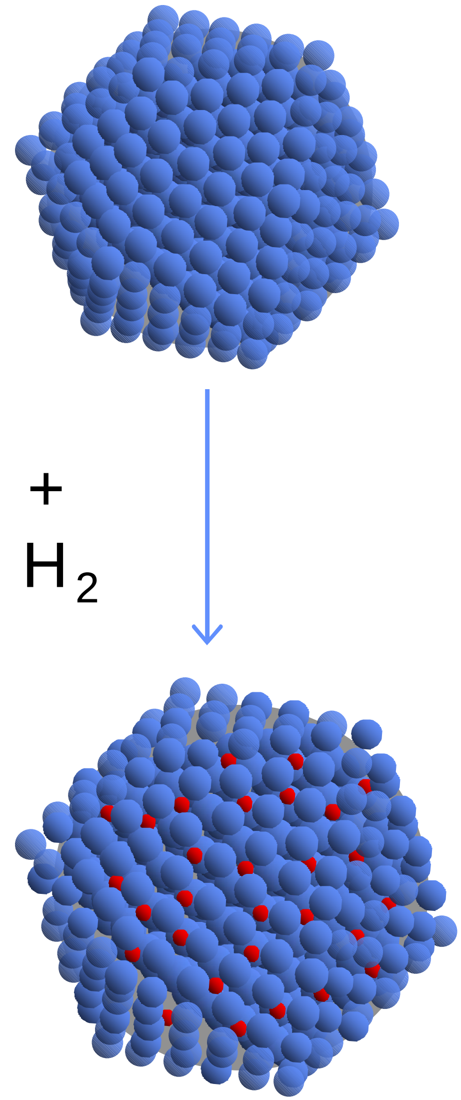


John Pople, up next!

Example 2: Nanoparticles

Motivation:

- Pd absorbs hydrogen at an atomic level
- Clusters behave differently to bulk
- Pd clusters:
  - size dependence
  - surface/volume ratio



TE WHARE WĀNANGA O WAITAHA
UNIVERSITY OF CANTERBURY
CHRISTCHURCH • NEW ZEALAND

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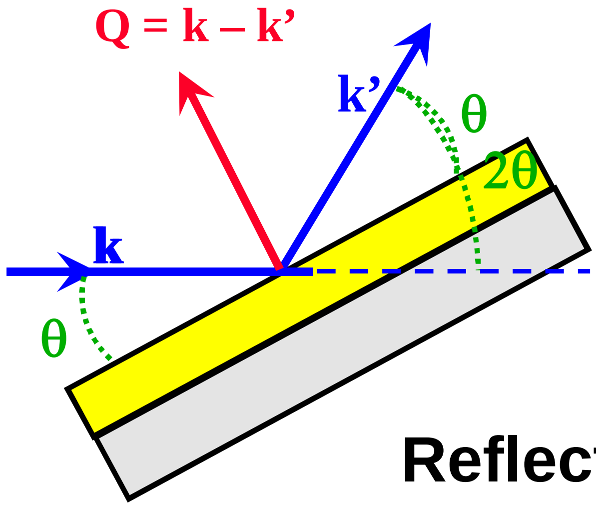
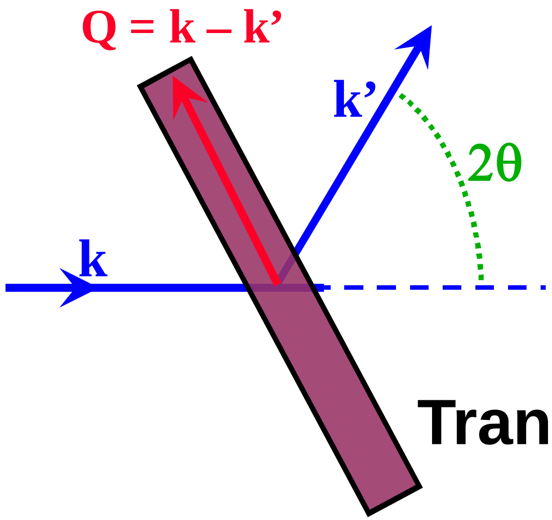
Nanoparticles: X-ray diffraction

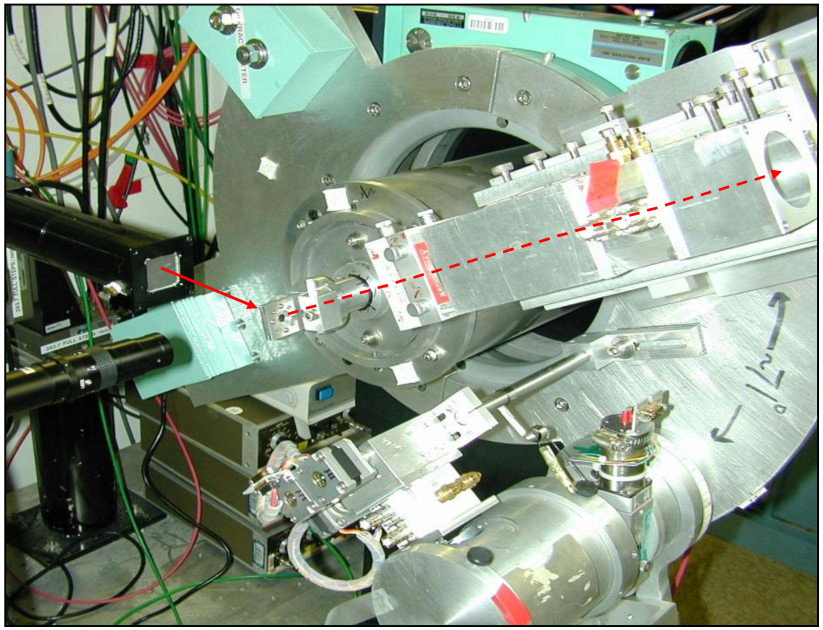


Reflection

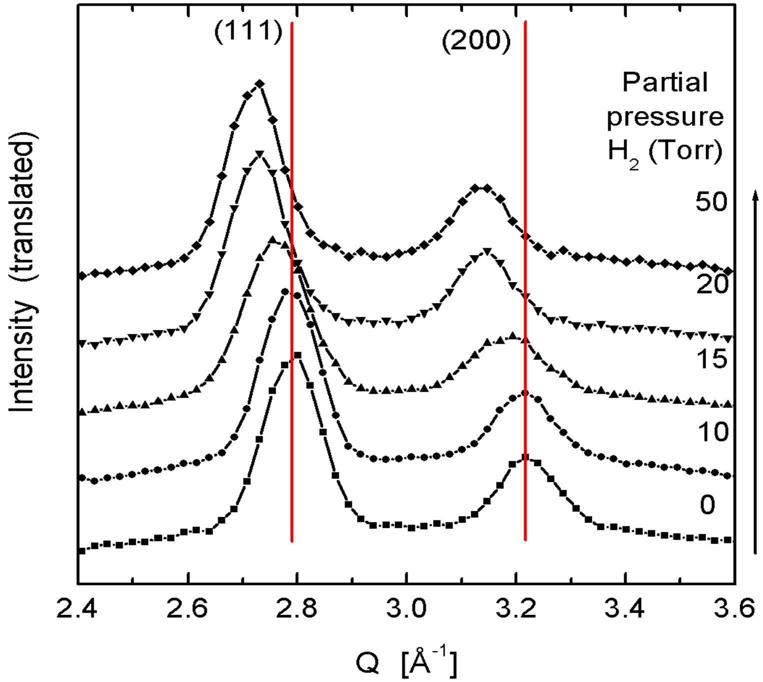


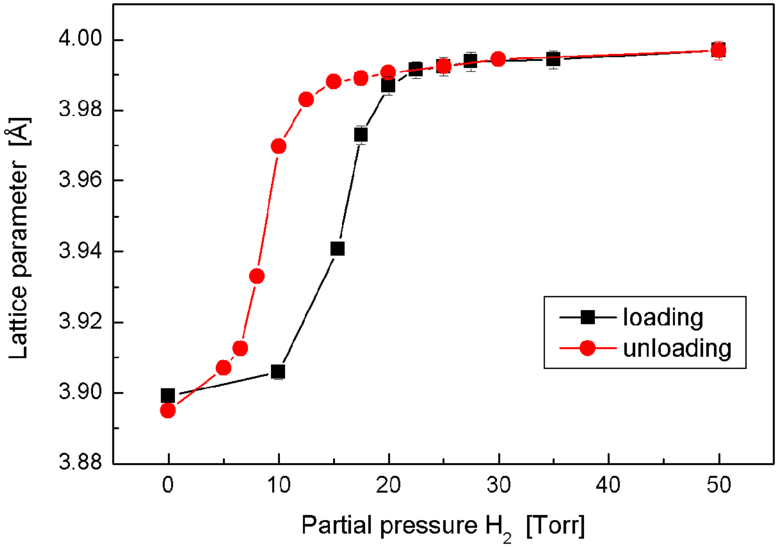
Transmission

Point detector (2-1, 7-2)



Nanoparticles: X-ray diffraction





In-situ Experiments – more later

APS sector 12

Ingham et al., Phys. Rev. B 78 245408 (2008).

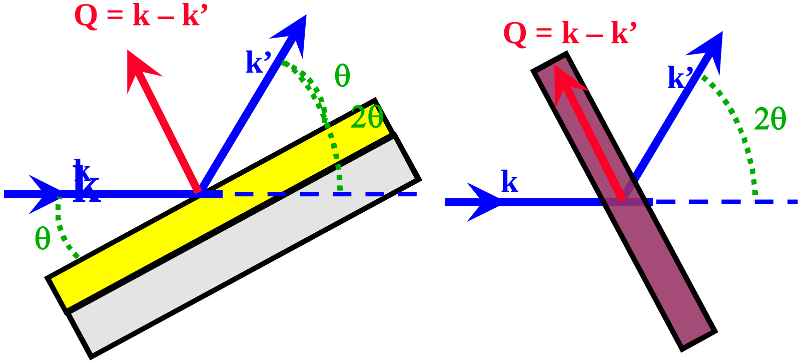
Summary: Nanoparticles

This work:

- Observe peaks corresponding to fcc Pd
- Lattice expansion upon addition of hydrogen
- Dependence on cluster size

Powder diffraction:

- Phase identification
- Structure determination
- Strain
- Crystallite size
- Defects
- *In situ* measurements
- Transmission and reflection geometries



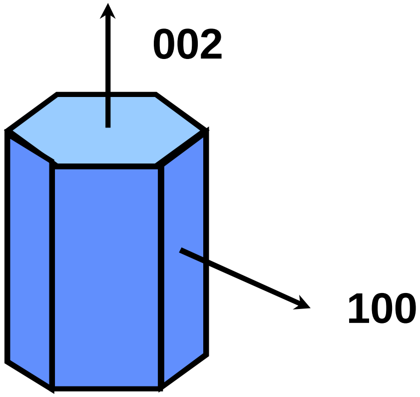
Apurva, Linda, Marc, Misra, Yezhou: this afternoon

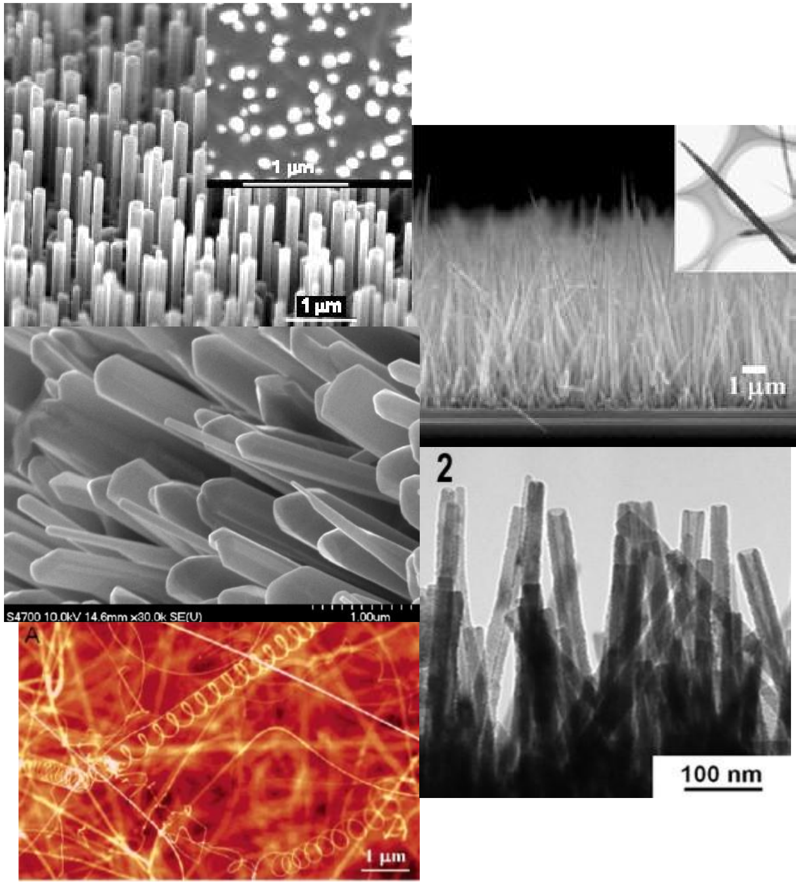
Example 3: ZnO

Motivation:

- ZnO exhibits a wide variety of nanostructures
- Electrochemical processing has many advantages
- Experimental parameters determine morphology

How does crystallography affect the growth of the nanostructures?





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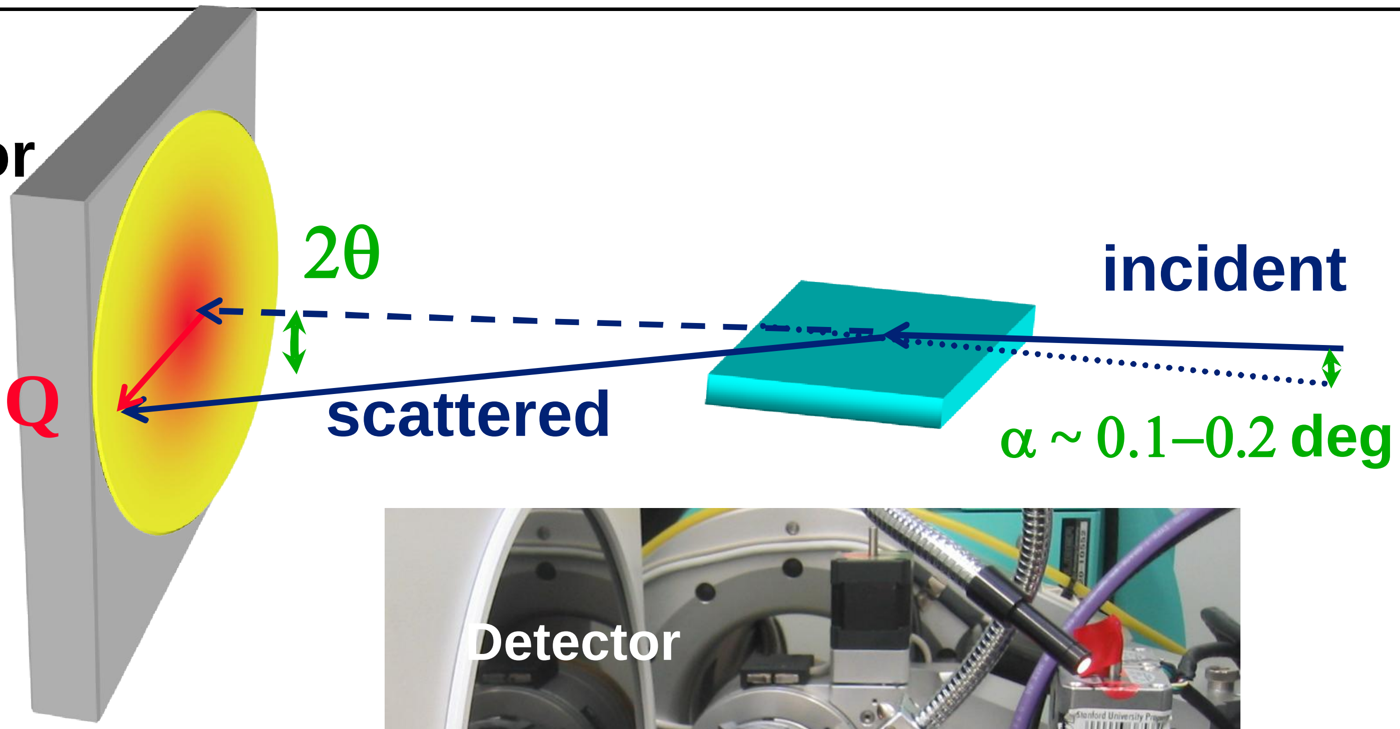
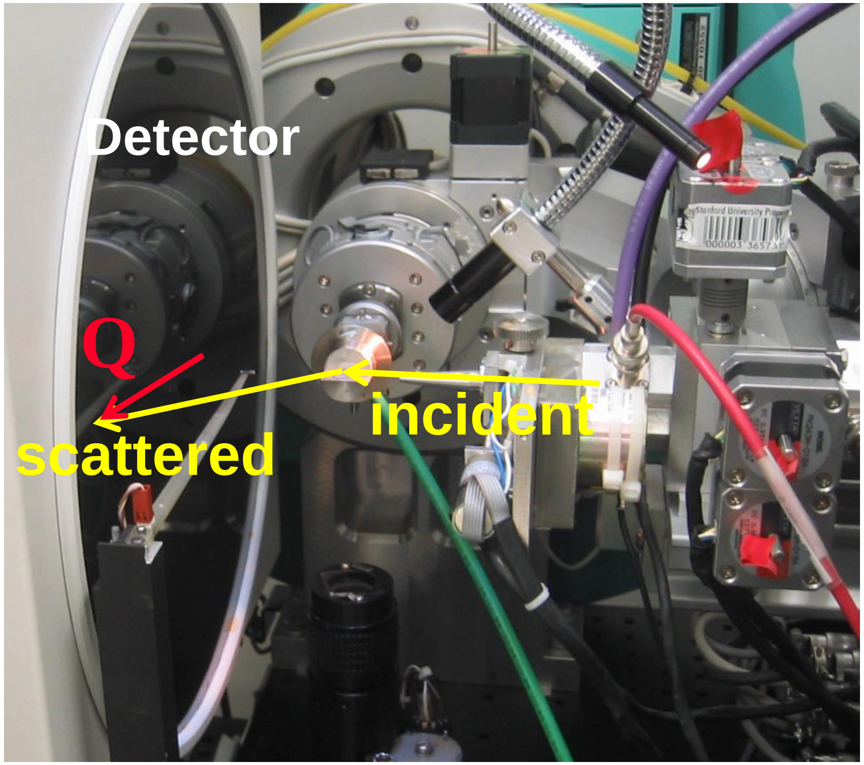
Thin Film Diffraction

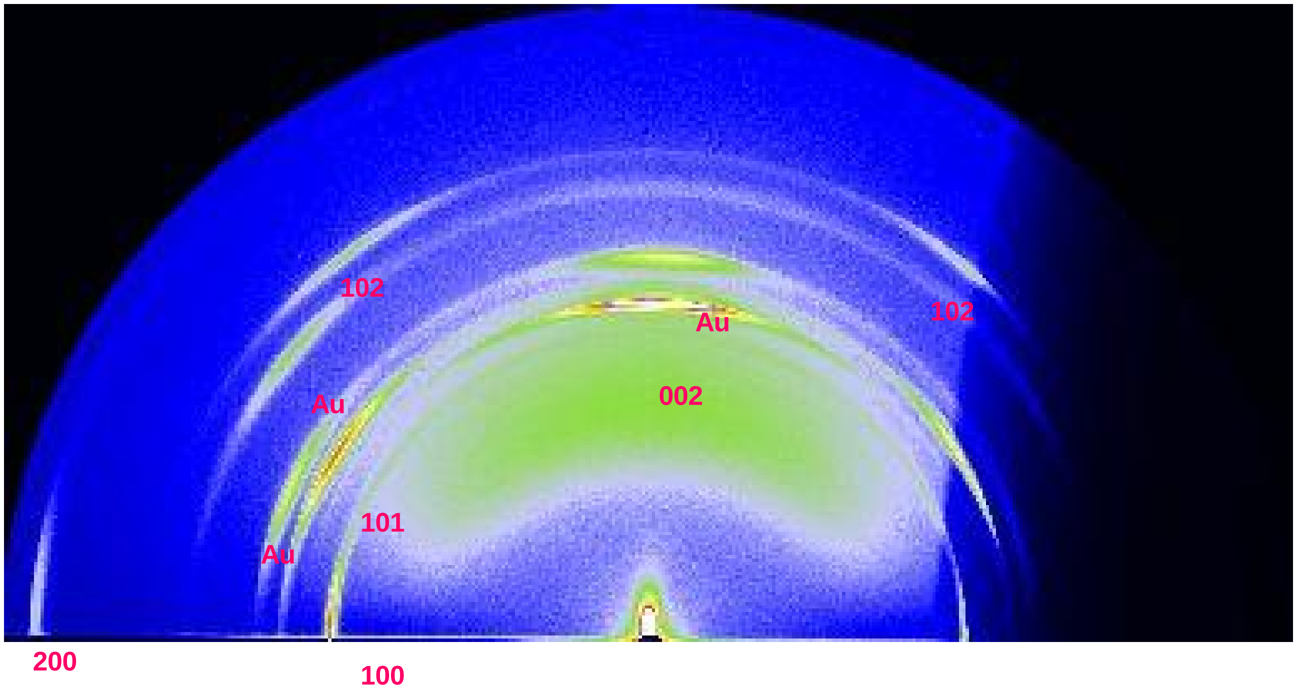


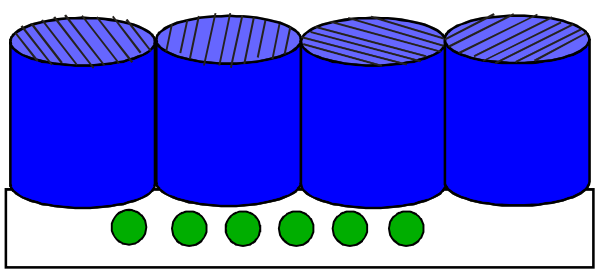


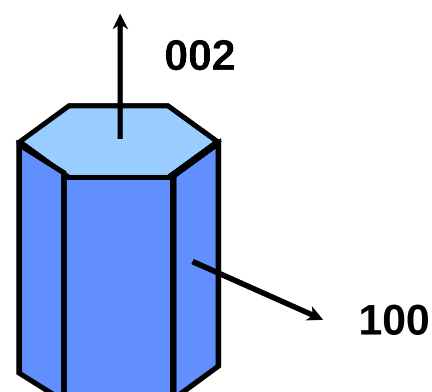
Beam line 11-3

ZnO: experiments

Ex situ:







ZnO: Summary

Summary:

•Texture increases with deposition time

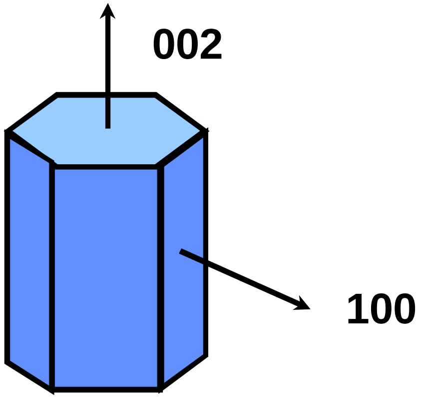
•Nanostructures are oriented along 002 direction

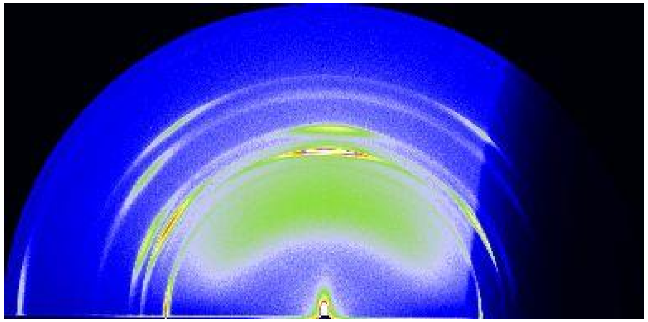
•Films deposited at less negative electrochemical potentials have poorer epitaxy

Thin films and texture:

- Surfaces, interfaces
- Structure, strain
- Orientation
- Crystallite size in-plane and out-of-plane

Arturas, Chad, Stefan, Chris, this afternoon



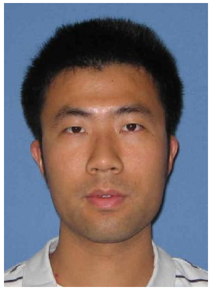


Summary

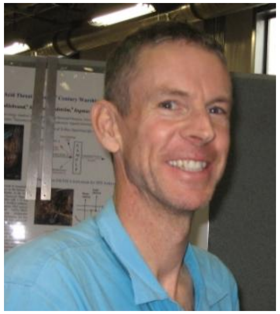
Speaker Mug Shots

- Typical SR x-ray scattering experiment & some examples: porous films, nanoparticles, textured films

- To be covered in this workshop:
  - Films: random, textured, epitaxial
  - SAXS
  - Powder
  - Poorly ordered
  - Surfaces













Bibliography

- B Warren, “X-ray Diffraction”, Dover (1990): $7.58 & eligible for FREE Super Saver Shipping on amazon.com

- BD Cullity & SR Stock, “X-ray Diffraction”, Prentice Hall (2001): $159.16.

- J Als-Nielsen & D McMorrow, “Elements of Modern X-ray Physics”, Wiley (2001): $92.89.

More Bibliography

- M. Tolan, “X-ray Scattering from Soft-Matter: Materials Science and Basic Research”, Springer (1998).
- RL Snyder, K. Fiala & HJ Bunge, Eds., “Defect and Microstructure Analysis by Diffraction”, Oxford (1999).
- V Holy, U Pietsch, T Baumbach, “High-Resolution X-Ray Scattering: From Thin Films to Lateral Nanostructures”, Springer-Verlag, (2004)
- O Glatter, “Small Angle X-Ray Scattering”, Academic (1982).
- “Modern Aspects of Small Angle X-Ray Scattering”, H. Brumberger (Editor), Springer (1994).
- Int. Union of Crystallography: Links to everything crystallographic. www.iucr.org . See : www.iucr.org/cww-top/edu.index.html and also Teaching and Education in Crystallography: www.minerals.csiro.au/mirror/w3vlc/edu.index.html.
- Structural data for thousands of minerals: database.iem.ac.ru/mincryst/
- Lawrence Berkeley: X-ray interactions with matter, data & calculations www-cxro.lbl.gov/optical_constants/
- International Centre for Diffraction Data - purveyors of the Powder Diffraction File (PDF) www.icdd.com