Introduction to Synchrotron X-ray Scattering Techniques

Mike Toney, SSRL

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

sample

monochromator
  • double crystal
  • Si(111) or Si(220)
  • LN or water cooled
  • selects wavelength

slits (horz or vert)
  • variable aperture
  • define beam shape and acceptance

M0 mirror
  • cylindrical or toroidal
  • Rhodium-coated silicon
  • harmonic rejection, power filter, collimating or focusing

beam

source

Area detector

Point detector

incident \( k \)

\( Q = k' - k \)

scattered \( 2\theta \)

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

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SR Scattering Experiment

Area detector (11-3)

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 (e.g. soils)
- Thin films

\[ 2\theta = \text{scattering angle} \]
\[ Q = \left(\frac{4\pi}{\lambda}\right) \sin \theta \]
SR Scattering Experiment

Point detector (2-1)

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

\[ Q = \left(\frac{4\pi}{\lambda}\right) \sin \theta \]

\[ 2\theta = \text{scattering angle} \]
SR Scattering Experiment

Point detector (7-2/10-2)

Advantages
- High resolution
- Accurate peak position & shape
- Weak peaks
- Variable energy
- 4 degrees of motion ($\theta$, $2\theta$, $\chi$, $\phi$)

Disadvantages
- Slow
- Complicated
- Can be difficult to find peaks

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

$2\theta = \text{scattering angle}$

$Q = (4\pi/\lambda) \sin \theta$
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
Lengths Accessed by Probes

USAXS  SAXS  XRD  EXAFS

1 nm  μm
Summary: SR Scattering

SR Scattering:

- $Q$ is an 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

Iron metal
Fe oxide
Small Angle Scattering

\[ Q = k' - k \]

\[ |Q| = \frac{4\pi}{\lambda}\sin \theta \]

- Measure \( I(Q) \) with \( Q \sim 0.0001 - 1 \text{ Å}^{-1} \)
- Scattering from 1-100 nm density inhomogeneities
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: \( \frac{1}{D} \leq Q \leq \frac{10}{D} \)
Example 1: Nanoporous Films

Matrix: Methyl Silsesquioxane (MSSQ), CH$_3$SiO$_{1.5}$

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

1. Spin coat MSSQ/Porogen solution

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

3. Cool to room temperature


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Argon

MSSQ crosslinks at 200°C
Porogen fully degrades at 400°C
Nanoporous Films: SAXS Results

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

**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)

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

\[ \text{Example 2: Nanoparticles} \]
Nanoparticles: X-ray diffraction

\[ Q = k - k' \]

Reflection

Transmission

Point detector (2-1, 7-2)
Nanoparticles: X-ray diffraction

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 Mehta, etc: 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?
Thin Film Diffraction

Area Detector

$\theta$

$\alpha \sim 0.1-0.2$ deg

Beam line 11-3

incident

scattered

Detector
ZnO: experiments

Ex situ:
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

MFT, Arturas Vailionis, this afternoon
Summary

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

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


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