X-ray and Neutron Microdiffraction

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Two words

Spatial Resolution
Materials characterization begins 3 questions

- What is the elemental composition?
- What is the crystal/local structure?
- What are the defects?

X-rays and neutrons probe structure and defects through scattering (diffraction)
Spatial resolution essential!

- **Most materials** *polycrystalline*(0.1-50 μm)
  - Anisotropic
  - Heterogeneous
  - Plastic/elastic deformation/ diffusion/ oxidation/

- **Even within** single and “perfect” crystal:
  - Strain
  - Defects
  - Spontaneously organize to reduce energy
Spatial resolution essential for most advanced energy systems
New X-ray/ Neutron Sources Changing the Possible

- Brilliance figure-of-merit for spatially-resolved exp.
- X-ray brilliance doubling faster than Moore’s law
- SNS with 10x brilliance 100x more efficient detectors

TOPAZ/ SNS
Spatial Resolving Optics Improving Rapidly

- X-ray focal spot size routinely below 100 nm
- Neutron focusing optics below 100 μm

Neutron optics with <70 μm Focus
X-ray micro/nanofocusing optics rapidly evolving

- CRL-50 nm
- FZP<30 nm
- Kinoform <70 nm
- MLL <15 nm
- KB <7 nm
- NMM<80 nm
Diffraction mapping emerging area in electron and x-ray microscopy

- EBSD-transformed study of polycrystals
  - Surface phase
  - Surface orientation
  - FiB-3D mesoscale structure

- 4D X-ray microscopy Lienert et al.
  - Time resolved
  - Deep penetration

- Coherent X-ray Diffraction (Robinson et al.)
  - Simple structures

- Polychromatic X-ray microdiffraction
  - Phase/texture/strain/
  - Nondestructive
  - Submicron
X-ray Micro/nanoprobe beams map chemistry and structure
Monochromatic micro crystallography probes simple crystal systems

Fresnel Zone Plate

Wide-range of focusing choices

Ferroelectrics ideal samples

BaTiO$_3$

Al

30 um diameter Mesa: Aluminum pad on top of Barium Titanate. Substrate base is (001) Silicon.
Thompson et al. study dimensionality of ferroelectricity

- Thickness
- Ribbons
- Dynamics

Diffraction from a ferroelectric stripe

Ferroelectricity found with few unit cells
Cai et al. and others study ultra-small nanocrystalline volumes with existing microbeams

• 150 nm beam resolves crystalline substructure in individual Sn₂O₃ nanobelts
APS Nanoprobe opens new opportunities for spatially resolved

- Diffraction proposals compelling
- Physics of small
- Integrated circuit materials

~30 nm now
<10 nm possible in future
NSLSII ~1 nm!
4DXRD Microscope emerging tool for studying mesoscale dynamics - single rotations

- Singly focused monobeam illuminates numerous grains
  - Bragg condition satisfied by single rotation
  - *Time resolution! (4D)*

- Grain outline determined
  - Ray tracing
  - conical slit
  - Back-projection tomography

- $E > 50$ keV allows deep measurements

*Best with high-energy beams/Beamline 1 at APS*
4DXRD Microscope powerful dynamics probe

• Recrystallization growth individual grains-deep

• Rotations/texture evolution individual grains during deformation
  – Tests deformation models
4DXRD Microscope provides additional powerful capabilities

- Grain boundary mapping in coarse grained materials-5\(\mu\)m

- Single crystal refinement for polycrystals

- Macro/microstrain

*Ideal for neutrons! But needs high-resolution detectors!*

Strain tensor elements in torsion sample
Polychromatic simplifies microdiffraction

Solves intrinsic problem with conventional microdiffraction - Sample does not need to be rotated!

Special software required - Can index polycrystalline samples

3D nondestructive probe of stress/strain/crystal structure!
3-D X-ray Crystal Microscope has specialized elements

<0.25 x 0.25 x 0.5 μm³
strain~10⁻⁴-10⁻⁵
Provides Submicron 3D Maps With New Information

- Phase boundaries
- Grain boundaries (3D)
- Elastic strain
- Deformation / Nye tensor

Nondestructive!
Laue methods essential for some samples

Glass capillary with sample

X-rays

sample

Laue pattern
Differential aperture microscopy resolves submicron along incident beam!

- Simplifies data interpretation
- Submicron Z resolution
- Isolates weak diffraction from strong
- First demonstration by Larson et al. on deformed Cu -
As wire moves its edge cuts through Laue spots

- Near-surface fluorescence provides moving shadow
- Long scans needed for deep penetration
Measurements of elastic strain tensor *inside* bent single crystal Si illustrate power of DAXM

Orientations to 0.001°

Maps crystal properties in 3D

- Phase
- Texture (orientation)
- Elastic strain tensor
- Nye tensor (deformation)

T. Bieler et al.
Experimental Hutch 34ID-E at UNICAT, Advance Photon Source

- Differential aperture
  - (wire scan, ~ 200 μm above sample surface)
- Mirror box
- Amorphous Si Area detector
Ongoing research too extensive to cover

- Fracture/stress localization in thin films
- Residual stresses/ deformation/ grain boundary network near welds
- Complex phase patterned materials
- Extreme environmental chambers
Ongoing too extensive continued..

- Domain wall structure measurements
- Sn whisker growth
- High-performance alloys
- Nanomaterials
Energy scans allow structure determination

- Generalization of orientation software can identify phases
- Energy scans provide integrated reflectivities.
- Identified two minor crystal phases tetragonal/hexagonal

Cannot be found by powder
Grain-growth/ Budai et al. characterized epitaxial growth RABiTS

Optical: ~50μm grains

CeO₂ Observation:
Exact epitaxy for growth at low T; lattice tilts at high T
Relative CeO$_2$ orientation depends on deposition temperature

**Step edge growth - good:**
- Crystallographic tilt towards $\perp$
- Tilt increases monotonically with miscut

**Island growth - bad:**
In-situ observations of 3D Grain Growth

Hot-rolled (200° C 1xxx Al(~1%Fe,Si) Alcoa Polycrystal
Thermal Grain Growth in Hot-Rolled Aluminum

1 µm pixels, Boundaries: 5° & 20°

- Anneal 250°C, 1 hr
- Anneal 350°C, 1 hr
- Anneal 355°C, 1 hr
- Anneal 360°C, 1 hr

• GB motions include both high-angle and low-angle boundaries
• Complete and detailed 3D evolution needed for validation of theories.
Thermal Grain-Growth And Microstructure Refinement in Polycrystalline Al

Orientation Maps

GND Density

250°C  350°C  355°C  360°C

• 3D X-ray Microscopy Measurements of Dislocation Density Finds Microstructure Refinement to Be Important
Deformation mediated by “dislocations”

- Individual dislocations can be seen with TEM—but…

  X-ray people complain thin electron samples
  Fundamentally different

  Neutron people complain thin X-ray samples
  Fundamentally different

What is “thin” and “bulk”?
Local orientation and plastic/elastic deformation mapped in pendeoepitaxially grown GaN

- Reduced dislocations
- Direct confirmation of tilted wing structures
- New information on local plastic/elastic strain
Deformation typically larger near surfaces/grain boundaries
Deformation in polycrystals illustrates grain boundary behavior

Ni
0.6mm thick

Step size: 25 µm
4000 µm

Indexation

<110> <111> <001>
Deformation induced rotations across grain boundaries sensitive to boundary type

![Graph showing the relationship between misorientation and grain boundary angle for Ni with points representing different boundary types. The graph indicates that normal high-angle grain boundaries and coincidence site lattice boundaries have distinct distributions.](image-url)
Submicron spatially-resolved crystallography opens new opportunities
Do neural networks provide a path forward?

- Visualization of 3D tensor data unsolved problem

- Human mind well adapted to 3D visualization based on binocular 3D data.

- Neural network not “limited” by streamlined processing of human brain
Coherent diffraction offers promise for atomic resolution with focused beams

• Focusing
  – Better spatial resolution
  – Poorer field-of-view

• 2 nm with 3rd generation source and 1 μm focal spot

• 2 Å with 10 nm spot- or 4th generation source
Neutron microdiffraction additional opportunities

Magnetism

Atomic motions

Low Z materials

Nobel prize to Shull and Brockhouse
Focused beams extend neutron science

- Inhomogeneous samples
- Small samples in environmental chambers
- Spatial resolved distributions deep in samples
Even the most intense neutron source must be used efficiently

Neutron sources $10^{12}$ lower brilliance than advanced x-ray

Neutrons expensive $10^{13}$ more expensive!

$10^{-16} \$/x-ray

$10^{-3} \$/neutron

Increase divergence/bandpass

$10^{-9} \$/ neutron
Neutron microfocusing optics evolving

- Sagittal focusing optics < 300 μm
- Lobster eye optics ?
- NMM < 100 μm
- Wolter optics < 200 μm
“Deflected” KB™ can collect larger divergence

- Basic element elliptical mirror
- Increase divergence with multiple reflections
- Optics within state-of-art

2D Focusing complicated but possible
Gravity complicates polychromatic neutron microbeams

Tricks to reduce dispersion

- $M \sim 1$
- $M$ small
- $F_1$ small
- Reflections

\[ \Delta y_{total} \sim \frac{gF_1^2}{2v^2} M(1 - M) \]

\[ m = \frac{1 - \sqrt{2}}{\sqrt{2}} \]
Spallation neutron science intrinsically polychromatic

- Analogous to polychromatic X-ray microdiffraction but includes energy
- Allows for structure determination
- Absolute strain measurements
SNAP experiments diffraction high pressure cells

- Focusing optics work near theoretical limit
- Minor improvements should enable 25 micron measurements
Neutron mirrors produce microbeams

- Better signal-to-noise
- Resolve inhomogeneities
- Map crystal distributions

Useable 25 µm beams?
Conclusion: Microdiffraction

- Addresses long-standing issues in materials physics
- Techniques and instrumentation are rapidly evolving
- Answers specific questions about materials systems (Energy materials)
- Extend x-ray and neutron characterization to new classes of samples.
  - Dangerous
  - Inhomogeneous
  - Samples in extreme environments
Materials structure tiny- intrinsically 3D
And spatial resolution- is needed urgently
The frontiers moving quickly now-excitements in the air
Though ask the average person- they really couldn’t care

CHORUS

Nondispersive - optics change what we can see
Mesostructure- resolved by crystallography
Atomic defects quantified - so that we can surmise
Emergent structures origins- at the mesoscopic size

New optics and new methods- extend what we can do
With spatial resolution- time resolution too
Nondestructive lets us watch- materials deep inside
Chambers or complex system - where once they could hide

Emerging applications- I've tried to show a few
Energy materials- have challenges quite new
With x-ray and neutron beams- we now are freed
To study these materials- on the scale that we need