X-ray and Neutron Microdiffraction

Gene E. Ice

Materials Science and Technology Division

Oak Ridge National Laboratory

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10µm

ZnO(22-40)

Si (00L)
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
Optics improving rapidly

- Both chromatic and achromatic <20 nm
- New choices
  - Mirrors
  - Zone plates
  - Laue zone plates
  - Compound refractive optics

Graphs showing size vs. position with markers indicating Osaka mirrors and KB mirrors.
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
Monochromatic micro crystallography probes simple crystal systems

Wide-range of focusing choices

Ferroelectrics ideal samples

Thompson et al. Study domain growth/switching etc.
Cai et al. and others study ultra-small nanocrystalline volumes with existing microbeams

- 150 nm beam resolves crystalline substructure in individual Sn₂O₃ nanobelts
Short-range chemical order heterogeneity magnetically annealed crystal now accessible

- 6 orders of magnitude weaker than Bragg scattering
- Area detector integrates over plane in reciprocal space

7.092 keV
APS Nanoprobe opens new opportunities for spatially resolved

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

~30 nm target/ <10 nm possible in near 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-5µm

- Single crystal refinement for polycrystals

- Macro/microstrain

*Ideal for neutrons! But needs high-resolution detectors!*
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 6 key Elements

<0.3 x 0.3 x 0.5 μm³
strain~10⁻⁴-10⁻⁵
MicroLaue patterns depend on internal structure/orientation

- Phase/phase boundaries

- Texture (0.01°)/grain boundaries

- Elastic strain tensor ($1 \times 10^{-4}$)

- Dislocation Tensor
Laue methods essential for some samples

Glass capillary with sample

X-rays

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)

Sample stage

K-B Focusing mirrors

CCD

telescope

shutter

slit
- 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

![Image of domain wall structure measurements with measurements at +700 nm, 0 nm, and -400 nm.](image)

![Image of Sn whisker growth and nanomaterials with a scale of 10 µm.](image)
Energy scans allow structure determination

- Generalization of orientation software can identify phases

- Energy scans provide integrated reflectivities.

- Identified two minor crystal phases: tetragonal/hexagonal

\[ \text{BAM braze } \text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20} \]

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

Optical: ~50µm grains

CeO$_2$ 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

• 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

<table>
<thead>
<tr>
<th>0.6mm thick Ni</th>
<th>10.0 mm</th>
<th>0.7 mm</th>
</tr>
</thead>
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Step size: 25 μm

4000 μm

Indexation

250 μm
Deformation induced rotations across grain boundaries sensitive to boundary type

![Graph showing misorientation vs. grain boundary angle for Ni. The graph indicates that normal high-angle grain boundaries and coincidence site lattice are sensitive to deformation induced rotations across grain boundaries.]
New information about deformation

- Near surfaces and interfaces
- In single and polycrystals
- Organization dynamics of defects (Krivoglaz defects of 2nd kind)

Lattice Rotation Map
Deformation found during electromigration

- Device reliability linked to electromigration-MA/cm²

- Theories assume stress development opposes mass transport

- Need to measure stress drove development of polychromatic microdiffraction

Al (Cu) interconnects studied

- Deformation big grains.
- Small grains rotate.
- Deformation preceded Cu diffusion.
- Unpaired dislocations develop parallel to the electrical field.
- Little dislocation activity near the anode end of the wire (Cu enhanced).
Neutron analog additional opportunities

Magnetism

Atomic motions

Low Z materials

Nobel prize to Shull and Brockhouse
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 mirrors produce microbeams

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

Useable 25 μm beams?
Spallation neutron science intrinsically polychromatic

- Analogous to polychromatic X-ray microdiffraction *but includes* energy
- Allows for structure determination
- Absolute strain measurements
Will extend neutron science

- Inhomogeneous samples
- Small samples in environmental chambers
- Spatial resolved distributions deep in samples
SNAP experiments diffraction high pressure cells

- Focusing optics work near theoretical limit
- Minor improvements should enable 25 micron measurements
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
Advanced materials structures- intrinsically 3D
And spatial resolution- is needed urgently
X-ray and neutron beams- can penetrate to see
Materials crystal structures- and heterogeneity

**CHORUS**

_Nondispersive - optics change what we can see_
_Mesostructure- resolved by crystallography_
_Atom 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