X-ray analysis:
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AMC2019
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X-ray interactions with matter

- **Coherent scattering**
- **Incoherent scattering**
- **Fluorescence**
- **Photoelectron**
- **Auger electron**

**Incident x-ray photons** $h\nu_0$

**Interaction volume**
- $2 \text{ nm} \sim 30 \, \mu\text{m}$
- $10 \, \mu\text{m} - 5 \text{ cm}$

**Sample**

**X-ray radiation mostly used in lab instruments:**
- **Cu radiation**
  - $\text{Cu K}\alpha$: $\lambda = 0.15418 \, \text{nm}$
    (8.05 keV, conventional resolution)
  - $\text{Cu K}\alpha 1$: $\lambda = 0.15056 \, \text{nm}$ (high resolution)
X-ray interactions with matter

Coherent scattering
(Diffraction, Thompson or Rayleigh scattering)

1. Incoming photon
2. Oscillating electron
3. Scattered photon
No loss of energy.

Incoherent scattering
(Compton scattering)

1. Incoming photon
2. Energy is partially transferred to electron

Fluorescence

1. Incoming photon
2. Expelled electron (photoelectron)
3. Hole is created in the shell
4. Outer shell electron moves to the inner shell hole
5. Energy excess emitted as characteristic photon.

Auger electron

1-4 Hole created (3) after photoelectron emission (2) is occupied by outer electron (4).
5. Excitation energy is transferred to electron
6. Electron ejected from atom (Auger electron)
Fundamentals of diffraction

“Real” space

Set of planes

Reciprocal space

Point

$F$

$(h k l)$

$\frac{2\pi}{d}$

origin

M. von Laue 1879-1960
X-rays from crystals, 1912.
Fundaments of diffraction

“Real” space $\xrightarrow{\mathcal{F}}$ Reciprocal space

\[ \frac{2\pi}{d} \]

origin
Fundamentals of diffraction

“Real” space \[ \mathcal{F} \] Reciprocal space

(hkl) (hkl) origin
Fundaments of diffraction

“Real” space \( \mathcal{F} \) Reciprocal space

\[
d
\]

\[
\frac{1}{d}
\]

Phase loss problem to reconstruct electron density

Measure \( I \sim |f|^2 \)
Fundaments of diffraction

“Real” space \( \mathcal{F} \) Reciprocal space

\[
\frac{1}{d}
\]

Intensity (Counts)

Two-Theta (deg)
Bragg’s law and Ewald’s sphere

**Bragg’s law**

\[ 2d \sin \theta = n \lambda \]

**Elastic (Thompson’s) scattering**

\[ q = k_1 - k_0 \]

**Ewald’s sphere**

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

Detector → **Diffracted beam** → Incident beam → X-ray source

---

Paul P. Ewald 1888–1985

1862–1942 1890–1971

**“Real” space** → **Reciprocal space** → \( \mathcal{F} \)
Continuous intensity distribution along diffraction ring, no distortion

Intensity varies along the ring

Distortion / shift of the diffraction ring

Spotty features in the diffraction ring

<table>
<thead>
<tr>
<th>No texture. Homogenous grain size distribution.</th>
<th>Texture</th>
<th>Residual stress</th>
<th>Non homogenous distribution of grain sizes; spots due to large grains</th>
</tr>
</thead>
</table>

X-ray tube

Detector

2θ/ω scan

ω

k₀

q

k₁

2θ

d

ω

(rocking curve)
2θ–ω scan:
Probes $d$-spacing variation
Along $q$
Phases id, composition, lattice constants
Grain sizes, texture, strain/stress

ω scan:
Probes in-plane variations
Normal to $q$
Mosaicity, texture and texture strength

2θ/ω scan

$q$

$k_0$

$k_1$

$d$

$\omega$

$2\theta$

Omega scan
(rocking curve)
X-ray tube

Detector

2theta/omega scan

$2\theta$

$k_0$

$q$

$k_1$

$d$

X-ray scattering pattern with peaks indicating crystallographic planes.
X-ray tube

Detector

2theta/omega scan

Peak position:
identification, structure, lattice parameter

Peak width:
crystallite size, strain, defects

Peak area or height ratio:
preferred orientation

Peak tails:
Diffuse scattering, point defects

Background:
amorphous contents
1
What type of radiation?
- Cu, Cr, Mo, Ag, W...
- Penetration depth
- $2\theta$ peak positions
Line or point focus?
- Peak resolution and shape
- Sample irradiated area
What type of monochromator?
• Filter, x-ray mirror, crystal monochromator
• White radiation, $K\alpha_1 + K\alpha_2$, $K\alpha_1$
4
X-ray beam footprint on the sample?
• Shape, size
• Depth
Horizontal, vertical goniometer?
Sample stage? 3,4 circle?
What type of detector?

- Resolution
- Point, Line, Area
Bragg-Brentano focusing configuration

- X-ray source
- Focus
- Divergence slit
- Receiving slit
- Detector
- Single crystal monochromator ($\lambda$)
- Secondary Optics:
  - Scatter and soller slits
- Detector rotation ($2\theta$)
- Divergent beam not good for grazing incidence analysis
- Specimen
- Diffractometer circle (fixed during measurement)

Sample height positioning is critical
XRD powder analysis walkthrough

Crystalline phases

Amorphous (zero background holder)

20 30 40 50 60 70 80 90 100 110

2-theta (degrees), Cu K-alpha radiation

Intensity (sqrt counts)
XRD powder pattern

~ 20 w% amorphous added

No amorphous added
Peak fit and shape analysis

Peak fit: Data + Peak shape + Instrument resolution

FWHM = f (2θ)

Crystallinity = \( \frac{\sum \text{Peak areas}}{\text{Total area}} \) = 81.7%

Amorphous contents = 1 – (crystallinity) = 18.3%
Calcite
CaCO₃
FOM 1.1
PDF 04-012-0489
RIR 3.45
Space group R-3c(167)

Dolomite
Ca₁₀₇Mg₀₉₃(CO₃)₂
FOM 15.0
PDF 04-011-9830
RIR 2.51
Space group R-3(148)
**Search / match**

- Peak position + intensity ratio
- Search against...
- ICDD PDF4 database ICSD, etc.
- Match! Fingerprinting identification of phases

<table>
<thead>
<tr>
<th>Hits</th>
<th>Formula</th>
<th>FOM</th>
<th>PDF</th>
<th>RIR</th>
<th>Space group</th>
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<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>1.1</td>
<td>04-012-0489</td>
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<td>R-3c(167)</td>
</tr>
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<td>Dolomite</td>
<td>Ca₁₀₇Mg₉₃(CO₃)₂</td>
<td>15.0</td>
<td>04-011-9830</td>
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Search / match

Second round
Focus on unmatched peaks

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Second round

Focus on unmatched peaks

Search / Match

Identify additional phases (~ > 1 w%)

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<tr>
<td>√</td>
<td>Calcite  ( \text{CaCO}_3 )</td>
<td>1.1</td>
<td>04-012-0489</td>
<td>3.45</td>
<td>R-3c(167)</td>
</tr>
<tr>
<td>√</td>
<td>Dolomite ( \text{Ca}<em>{1.07}\text{Mg}</em>{0.93}(\text{CO}_3)_2 )</td>
<td>15.0</td>
<td>04-011-9830</td>
<td>2.51</td>
<td>R-3(148)</td>
</tr>
</tbody>
</table>
Quant: RIR reference intensity ratio

\[
\text{Ratio of crystalline phases} \sim \left( \text{Ratio of peak areas corrected by RIR of each phase} \right)
\]

\[\text{RIR} \sim \frac{I}{I_{\text{corundum}}}\]

Ratio of crystalline phases:
- Calcite: 79.2 w%
- Dolomite: 20.8 w%

(no amorphous included)
Rietveld refinement

Non-linear least square minimization

For each data point \( i \):

Minimize this function:

\[
\Phi = \sum_{i=1}^{n} w_i (Y_i^{obs} - Y_i^{calc})^2
\]

Sum over \( n \) data points

\( n \) data points
\( p \) phases
\( m \) Bragg reflections for each data \( i \)

\( w_i, b_i, K_i, Y_{ij} \) weight, background, scale factor and peak shape function

Refinement of parameters:

Background
Sample displacement, transparency and zero-shift correction
Peak shape function
Unit cell dimensions
Preferred orientation
Scale factors
Atom positions in the structure
Atomic displacement parameters

Minimize and converge figures of merit/quality:

\( R \)
Rietveld refinement

Calcite: 80.7 w%
Dolomite: 22.2 w%
Amorphous: 17.1 w%

Crystallite size:
Calcite: 56.8 nm
Dolomite: 35.6 nm
Rietveld refinement

Calcite, CaCO₃, hexagonal, R̅₃c (167)
0.499 nm/ 0.499 nm / 1.705 nm <90.0/90.0/120.0>
Rietveld refinement

Dolomite, $\text{Ca}_{1.07}\text{Mg}_{0.93}(\text{CO}_3)_2$, hexagonal, R3 ($\bar{1}48$)
0.481 nm/ 0.4819 nm / 1.602 nm <90.0/90.0/120.0>
Crystallite size $\leq$ Grain size $\leq$ Particle size

Domain of coherent diffraction

$\sim$ XRD, TEM

$\sim$ SEM

$\sim$ SEM (number average)
SAXS (volume average), DLS (volume$^2$ average), ...
Crystallite size analysis

Scherrer’s equation:

\[
\frac{k \ast \lambda}{\cos(\theta) \ast (\text{FWHM})}
\]

Size =

- \( k \): shape factor (0.8-1.2)
- \( \lambda \): x-ray wavelength
- \( \text{FWHM} \): full width at half maximum (in radians)

Simplistic approximation!
Not accounting for peak broadening from strain and defects

Directional measurement!
Measured along the specific direction normal to the (hkl) lattice plane given by the 2\( \theta \) peak position

Peak width
(FWHM or integral breadth)

Measurement

Fit

Peak position 2\( \theta \)
Crystallite size analysis

2 nm Fe$_3$O$_4$ nanoparticle

20 nm (111) grains in Cu foil

145 nm Si powder
Peak shape analysis

Peak fit functions:
- Gaussian
- Lorentzian
- Pearson-VII (sharp peaks)
- Pseudo-Voigt (round peaks)

Information from fit:
- Position
- Width (FWHM)
- Area
- Deconvolution
- Skewness
Correction for instrument resolution

Use FWHM curve as a function of 2θ from standard sample (NIST LaB₆): specific for each diffractometer.

\[ \beta^D = (\beta_{\text{meas}})^D - (\beta_{\text{instr}})^D \]

\( D : \) deconvolution parameter

- \( D : 1 \) (~ Lorentzian)
  \[ \beta = (\beta_{\text{meas}}) - (\beta_{\text{instr}}) \]

- \( D : 2 \) (~ Gaussian)
  \[ \beta^2 = (\beta_{\text{meas}})^2 - (\beta_{\text{instr}})^2 \]

- \( D : 1.5 \)
  \[ \beta^{1.5} = (\beta_{\text{meas}})^{1.5} - (\beta_{\text{instr}})^{1.5} \]
### Potential artifacts in size determination

For this calculation assume:
- Instrument resolution ~ 0.15°
- Cu radiation

<table>
<thead>
<tr>
<th>2θ = 40° Measured peak width</th>
<th>Size, nm $D = 1$ (Lorentzian)</th>
<th>Size, nm $D = 1.5$</th>
<th>Size, nm $D = 2$ (Gaussian)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\beta = \beta_{\text{meas}} - \beta_{\text{instr}}$</td>
<td>$\beta^{1.5} = (\beta_{\text{meas}})^{1.5} - (\beta_{\text{instr}})^{1.5}$</td>
<td>$\beta^2 = (\beta_{\text{meas}})^2 - (\beta_{\text{instr}})^2$</td>
</tr>
<tr>
<td>0.30°</td>
<td>56.4</td>
<td>38.0</td>
<td>32.6</td>
</tr>
<tr>
<td>0.50°</td>
<td>24.2</td>
<td>19.2</td>
<td>17.7</td>
</tr>
<tr>
<td>0.75°</td>
<td>14.1</td>
<td>12.0</td>
<td>11.5</td>
</tr>
<tr>
<td>1.00°</td>
<td>10.1</td>
<td>8.8</td>
<td>8.6</td>
</tr>
<tr>
<td>1.50°</td>
<td>6.3</td>
<td>5.8</td>
<td>5.7</td>
</tr>
<tr>
<td>2.00°</td>
<td>4.6</td>
<td>4.3</td>
<td>4.2</td>
</tr>
</tbody>
</table>

~ 48% difference for narrow peaks (large sizes)
Smaller difference (~ 10%) for broad peaks (small sizes)
Pyroxene: increasing grain sizes

Collected by *Curiosity* rover, Gale crater, Mars

- Small grains, No texture
- Non uniform rings (texture)
- Spotty rings (large grain size)


Strain effects in diffraction lines

Macrostrain:
- Uniform tensile or compressive stress (lattice expansion or contraction)

Microstrain:
- Nonuniform strain (both tensile and compressive stresses) (lattice distortion).
  - Dislocations, vacancies, defects, thermal effects.

No strain

Uniform strain

Nonuniform strain

Peak position shift (lattice constant change)

Peak width change (symmetric broadening)

$\Delta(2\theta)$

FWHM

Dislocations, vacancies, defects, thermal effects.
Size and strain in peak shape analysis

\[(\text{FWHM})\cos(\theta) = \frac{k\lambda}{\text{size}} + (\text{strain})\sin(\theta)\]

FWHM\text{strain} = 4 \times (\text{strain}) \times \tan \theta

Williamson-Hall Method

Intercept \sim 1/\text{size}
Slope \sim \text{micro strain}
X-ray parallel beam methods

Rough, irregular surfaces

Film / Substrate systems

Glancing / grazing angle applications.
Phase, stress gradients (depth profiles)
Parallel beam configuration

Negligible sample displacement issues (rough and curved samples OK)

Primary Optics: mirror, crystal monochromator, lens

Specific optics to maximize intensities

Detector

Single crystal monochromator ($\lambda$)

Detector rotation ($2\theta$)

X-ray source

Parallel plates collimation

Parallel beam

Parallel beam configuration

Angle of incidence ($\omega$)

Excellent for glancing angle (fixed $\omega$) applications

specimen
Thin film analysis walkthrough:

- **TaN film**
- **MgO (001) substrate**

Cube on cube epitaxy:

- $(001)_{\text{TaN}}//(001)_{\text{MgO}}$
- $(100)_{\text{TaN}}//(100)_{\text{MgO}}$

After Shin et al, TSF (2002)
Thin film analysis walkthrough:

Peak shape analysis: TaN(002) rocking curve omega scans

After Shin et al, TSF (2002)
Glancing incidence x-ray diffraction (GI-XRD)

- **conventional** Bragg-Brentano configuration
  - $2\theta$--$\omega$ scans probe only grains aligned parallel to the surface
- + parallel-beam glancing incidence configuration
  - $2\theta$ scans probe grains in **all** directions
X-ray penetration depth vs. angle of incidence

- Type of radiation
- Angle of incidence
- Material (Z, A, r, m)
## Regular 2θ–ω scan vs. glancing incidence 2θ scan

### Regular 2θ–ω scan

- **Probe depth:**
  - Variable (deep)
  - Constant (shallow)

### Glancing incidence 2θ scan

- **ω (fixed, small)**

### Table

<table>
<thead>
<tr>
<th></th>
<th>Regular 2θ–ω scan</th>
<th>Glancing incidence 2θ scan</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Grain orientations</strong></td>
<td>Directions ⊥ to surface</td>
<td>Various directions</td>
</tr>
<tr>
<td><strong>Depth resolution</strong></td>
<td>Constant, many mm</td>
<td>• From few nm to mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Depth profiling possible by</td>
</tr>
<tr>
<td></td>
<td></td>
<td>varying angle of incidence</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Sensitive to surface</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Ideal for ultra-thin layers</td>
</tr>
<tr>
<td><strong>Best configuration</strong></td>
<td>Bragg Brentano</td>
<td>Parallel beam (less sensitive to</td>
</tr>
<tr>
<td></td>
<td>Parallel beam</td>
<td>sample displacement)</td>
</tr>
</tbody>
</table>
Glancing incidence x-ray analysis

Example: Poly-Si gate

| Poly-Si (~100 nm) | Si(001) substrate |

Glancing incidence
<table>
<thead>
<tr>
<th>Method</th>
<th>Measurement</th>
<th>Principle</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lotgering factor (L_{hkl})</td>
<td>2θ-ω scans</td>
<td>Compare I_{peak} or A_{peak} with expected values from random samples (PDF)</td>
<td>L_{hkl} as measure of texture strength</td>
</tr>
<tr>
<td>March-Dollase (MD)</td>
<td>2θ-ω scans</td>
<td>Use I_{peak} or A_{peak} with MD formalism</td>
<td>% of grains that are more oriented along a specific direction</td>
</tr>
<tr>
<td>Rocking curve</td>
<td>ω scans</td>
<td>Measure FWHM from ω scan for a particular (hkl)</td>
<td>FWHM decreases with stronger texture</td>
</tr>
<tr>
<td>Pole figure</td>
<td>φ scans at various tilts ψ</td>
<td>Pole plots of intensities from a particular (hkl)</td>
<td>Texture distribution for a single (hkl)</td>
</tr>
<tr>
<td>Orientation Distribution Function (ODF)</td>
<td>Pole figures from various (hkl) 's</td>
<td>Calculate ODF from various pole figures with background and defocussing correction</td>
<td>% of grain orientation distribution in all directions (Euller angles).</td>
</tr>
</tbody>
</table>
Pole figure measurement

Detector

sample

$2\theta$

X-rays

$\phi$

$\omega$
Pole figures

Tilt $\psi = 54.7^\circ$

Azimuth
$\phi = 45^\circ, 135^\circ, 225^\circ, 315^\circ$

$\psi$: [100],[111]
Basics of pole figure analysis

Example: (100) cubic crystal

(100) Pole figure

Azimuth
\( \phi = 0, 90^\circ, 180^\circ, 270^\circ \)

Tilt
\( \psi = 0, 90^\circ \)

\( \psi: [100],[100] \)

(111) Pole figure

Azimuth
\( \phi = 45^\circ, 135^\circ, 225^\circ, 315^\circ \)

Tilt \( \psi = 54.7^\circ \)

\( \psi: [100],[111] \)

(110) Pole figure

Azimuth
\( \phi = 0, 90^\circ, 180^\circ, 270^\circ,45^\circ, 135^\circ, 225^\circ, 315^\circ \)

Tilt \( \psi = 45^\circ,90^\circ \)

\( \psi: [100],[110] \)
Cu (111) pole figure

(111) single crystal

Rolled foil

Thin film
Fiber texture

(100) single crystal
X-ray pole figure analysis of textured materials

- Texture orientation and quantification.
- Volume fraction of textured grains, twinning and random distributions.
- Texture strength and sharpness.
- Crystallographic orientation.
- Crystallographic relationship between layers and substrate.

Texture results from a rolled Cu foil

Pole figures

Orientation distribution function (ODF)

Data: Sardela, UIUC
X-ray pole figure analysis of textured materials

- Texture orientation and quantification.
- Volume fraction of textured grains, twinning and random distributions.
- Texture strength and sharpness.
- Crystallographic orientation.
- Crystallographic relationship between layers and substrate.

Texture results from a rolled Cu foil

Pole figures

Pole figure: Distribution of grains with a particular (hkl) orientation

ODE: fraction of grain orientation distribution for all directions

Orientation distribution function (ODF)

Data: Sardela, UIUC
High resolution XRD methods

**Single crystals:**
Accurate measurements of $a$, $b$, $c$, $\alpha$, $\beta$, $\gamma$
Detailed peak shapes: defects, mosaicity.

**Film / substrate epitaxial systems:**
Measure small variations $\Delta a$, $\Delta c$, … ($\sim 10^{-5}$).
Measure layer tilts $\Delta \phi$, ...
Detailed peak shapes: defects, strain, mosaicity.
Multiple rlp’s
Relative position
Orientation
Shape
Instrument resolution in reciprocal space

\[ \delta(2\theta) \]

\( q = k_1 - k_0 \)

Ewald’s sphere
Instrument resolution in reciprocal space

“Real” space

Reciprocal space

Ewald’s sphere

$\delta(\omega)$

$q = k_1 - k_0$

$q = \frac{2\pi}{\lambda}$

$Ewald's sphere$

$k_0 (= radius)$

$k_1$

$2\theta$

$\omega$

$w$

$k_0$

$(= radius)$

Instrument resolution in reciprocal space
Instrument resolution in reciprocal space

"Real" space

Reciprocal space

\[ \delta(2\theta) \]

\[ \delta(\omega) \]

Ewald’s sphere

\[ q = k_1 - k_0 \]
**Instrumentation: high resolution configuration**

- 2-bounce monochromator
- X-ray source
- Slit
- Sample

3-bounce analyzer crystal

- \(\Delta \theta = 0.008^\circ\)
- \(\Delta \lambda/\lambda = 5 \times 10^{-5}\)

Open detector

- (open: < 1° acceptance)

1D detector

- 1D mode for ultra-high speed

Triple axis detector

- (triple axis: 12 arc-sec acceptance)
High resolution x-ray analysis

- Lattice distortions within $10^{-5}$.
- Rocking curve analysis.
- Film thickness.
- Strain relaxation and lattice parameter measurements.
- Alloy composition and superlattice periods.
- Interface smearing in heterostructures (dynamical simulation).

Data: Wu et al, UIUC

Data: Sardela, UIUC

Data: Zhang et al
High resolution x-ray analysis

Example: strained $\text{In}_x\text{Ga}_{1-x}\text{As}$ on GaAs (001) substrate

Lattice structure

$a_{// \text{film}} = a_{\text{substrate}}$

$a_{\perp \text{film}} > a_{\text{substrate}}$

$\text{In}_x\text{Ga}_{1-x}\text{As}$ (004)

GaAs (004)

High resolution $2\theta/\theta$ scan near GaAs(004)

\[
\frac{\Delta a}{a} = \frac{\sin \theta(\text{substrate})}{\sin \theta(\text{film})} - 1
\]

Thickness = \[
\frac{\lambda}{2 \Delta \theta \cos \theta}
\]

Data: Sardela
Sample: Highland, Cahill, Coleman et al, UIUC
High resolution x-ray analysis

Example: strained $\text{In}_x\text{Ga}_{1-x}\text{As}$ on GaAs (001) substrate

Lattice structure

$a_{// \text{ film}} = a_{\text{substrate}}$

$a_{\perp \text{ film}} > a_{\text{substrate}}$

In$_x$Ga$_{1-x}$As (004)

GaAs (004)

Takagi-Taupin dynamical scattering simulation

High resolution 2θ/θ scan near GaAs(004) and dynamical scattering simulation

Data: Sardela
Sample: Highland, Cahill, Coleman et al., UIUC
Reciprocal space mapping

Direct space:

Reciprocal space:
Reciprocal space mapping

- Separation of strain and mosaicity
- Lattice distortions within $10^{-5}$.
- Accurate lattice parameters in and out of plane
- Strain and composition gradients
- Strain relaxation
- Mosaic size and rotation
- Misfit dislocation density
- Nanostructure dimensions,
- Lattice disorder and diffuse scattering.

No strain relaxation: $a_{//} = a_s$

<table>
<thead>
<tr>
<th>film</th>
<th>$a_{//}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate</td>
<td>$a_s$</td>
</tr>
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</table>

Strain relaxation: $a_{//} \neq a_s$

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<td>$a_s$</td>
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Data: Sardela et al
High resolution reciprocal space mapping

Layer structure

- Strained Si (top layer, very thin)
- Relaxed Si\(_{1-x}\)Ge\(_x\) (thick, many microns)
- Si(001) substrate

Lattice structure

- Strained Si
- Relaxed Si\(_{1-x}\)Ge\(_x\) (virtual substrate)
- Si(001) substrate

Strain?
Lattice distortion?
% of relaxation?
% of Ge?
Defects?

High resolution 2\(\theta/\omega\) scan near Si(004)

Example: strained Si layer on Si\(_{1-x}\)Ge\(_x\) / Si substrate

Reciprocal lattice

(004)  (224)

\(\Delta q_{\perp}\)  \(\Delta q_{\parallel}\)

- Strained Si
- Si substrate
- Si\(_{1-x}\)Ge\(_x\)
High resolution reciprocal space mapping

Map near Si(224)

Strained Si (top layer)

| Relaxed Si$_{1-x}$Ge$_x$ | Si(001) substrate |

Strained Si

Si substrate

Si$_{1-x}$Ge$_x$

$\Delta q_{\perp}$

$\Delta q_{//}$

Data: Sardela
Sample: Zuo, UIUC
High resolution reciprocal space mapping

Strained Si
\( \varepsilon_\perp = -0.77\% \)
\( \varepsilon_\parallel = 0.64\% \)

4.60 at\% Ge

7.52 at\% Ge

11.45 at\% Ge

Relaxed Si_{1-x}Ge_x
18.70 at\% Ge
100% strain relaxation

Map near Si(224)

Data: Sardela
Sample: Zuo, UIUC

Strained Si (top layer)
Relaxed Si_{1-x}Ge_x
Si(001) substrate
High resolution reciprocal space mapping

Finite size

Vertical coherent length: 14 nm

Composition and strain gradients

Mosaicity and dislocations

Misfit dislocations:
average separation: 21 nm
density: $5 \times 10^5 \, \text{cm}^{-1}$

Misfit dislocations:
average separation: 21 nm
density: $5 \times 10^5 \, \text{cm}^{-1}$

Coherent length in any direction:
$2\pi / \Delta q_i$
i = x, y, z, //, ⊥

Data: Sardela
Sample: Zuo, UIUC
The “shape” of the reciprocal lattice point

- Changes in lattice parameter (radial direction)
- Lateral sub-grain boundaries (along \( q_{//} \))
- Mosaicity, curvature, orientation (circumferential direction)

CTR, finite layer thickness, superlattice (along \( q_{\perp} \))
X-ray reflectivity

Bulk materials:


Liquids:


Multilayered systems:


Near surface and interface information on:
- Density
- Porosity
- Roughness
- Thickness in films (ultra thin to thick)
- Amorphous or crystalline materials
**X-ray reflectivity**

- **One sharp interface** (density $\rho_e$ variation: $\delta$ function at interface)
- **One rough interface** ("broad" $\rho_e$ variation at interface)
- **Two interfaces**

Critical angle $\theta_c$  
$\sim \rho_e$

$R \sim \theta^{-4}$

Thickness fringes  
$\Delta \theta = \lambda/[2*(\text{thickness})]$  
$\Delta I \sim \Delta \rho_e$

$D_I \sim D_r$  

$D_{q} = l/[2*(\text{thickness})]$
X-ray reflectivity analysis of thin films

Ultra-thin film

- 2.3 nm thick polymer on Si

Data: Heitzman et al, UIUC

Multilayers

Metallic multilayer

Data: Sardela, UIUC
Sample: Auodai et al, SIU

Non crystalline

Amorphous PZT film

Data: Mikalsen et al, UIUC

Intercept: refractive index $\eta$

Slope: periodicity $d$

$\sin^2\theta = \left(\frac{\lambda^2}{2d}\right)^2 n^2 - (\eta^2 - 1)$
(modified Bragg’s law to include refractive index)

Data: Sardela, UIUC
Sample: Auodai et al, SIU
X-ray reflectivity data fitting in ultra-thin films

Data: Sardela
Sample: Zhang, Rogers et al, UIUC
X-ray reflectivity data fitting

Simulation using Parrat’s formalism and generic algorithm fitting

- Polymer: 2.0 nm, 1.30 g/cm³, rms: 0.26 nm
- SiO₂: 98.9 nm, 2.19 g/cm³, rms: 0.45 nm
- Si substrate: rms: 0.24 nm
X-ray reflectivity: summary

* Non destructive method
* Applicable to whole wafers (wafer mapping option)
* Fast method (in most cases)
* Do not depend on crystalline quality of the films (can also be used in amorphous layers).

Quantification of:

* Layer thickness in thin films and superlattices: 1 nm ~ 1 μm (± 0.5-1%).
* Layer density and porosity (± 1-2%).
* Interface roughness: 0.1 – 10 nm (model dependent; reproducibility ~ 3%).
* Layer density gradients (variations > 2%).
* Interface roughness correlation in superlattices and multilayers.

Alternative techniques:

* Thickness: optical methods (TEM, SEM) poor contrast issues.
* Density: RBS (issues for ultra thin layers).
* Interface roughness: AFM (surface only – not buried interfaces).
Small angles... large things...

2\theta < 3^\circ
\quad d > 2.7 \text{ nm}

Air scattering

SAXS

WAXS

Intensity

2\theta (degrees, Cu K-\alpha radiation)
Cu k-α (point focus)

0.8 x 1 mm² slit

Sample

Pilatus 300K areal detector (172μm pixel)

Evacuated path

1.6 m

1.4 m (SAXS)

(0.136 m WAXS)
Small angle x-ray scattering

x-ray source → evacuated path → slit → sample → aperture → evacuated path → detector

1.6 m → 1.4 m

SAXS
$q \sim 0.3-3 \text{ nm}^{-1}$
$d \sim 24-4 \text{ nm}$

x-ray source → evacuated path → slit → sample → evacuated path → detector

1.6 m → 0.136 m

WAXS (wide angle)
$q \sim 1.3-13 \text{ nm}^{-1}$
$d \sim 5-0.5 \text{ nm}$
SAXS and GI-SAXS

X-rays

capillary

Substrate or membrane

θ ~ θ_c

GI-SAXS
Sample holder for powders
Temperature control stage for capillaries

-20°C up to 120°C
Silver behenate
AgC$_{22}$H$_{43}$O

\[
\frac{q_n}{q_1} = 1, 2, 3, 4 \ldots
\]

lamellar
SAXS applications:

Analysis:

- Crystalline structure
- Degree of crystallinity and orientation
- Particle shape, size, distribution
- Radius of gyration
  Guinier plot $\ln I(q)$ vs. $q^2$
- Folded, partially or unfolded proteins
  Kratky plot $I(q)q^2$ vs. $q$
- Distance distribution function $p(r)$

Materials:

- Nanoparticles
- Membranes
- Lipids
- Polymers
- Proteins
- Solutions
- Nanocomposites
- Polymers
- Thin films...
Residual stress analysis methods

Residual stress?
How much? (MPa – GPa)
Type?
Direction (s)?
Stress gradients?

XRD measures strain ($\Delta d$)

\[ \text{Hooke’s law} \quad \text{Stress tensor} \]

\[ \text{Elastic properties (E, v)} \]
X-ray analysis of residual stress

- Quantification of residual stress.
- Compressive (-) and tensile (+) stress.
- Crystallographic orientation of stress.

- Sin²ψ method. Linear for rotationally symmetric biaxial stress where the only non-zero components are \(\sigma_{11} = \sigma_{22} = \sigma_{/}/\)
- \(\psi\) and \(\omega\) scan methods.

- Glancing angle method (texture).
- Determination of stress tensor.

- Requires crystallinity (no amorphous).
Structure information
- Stress, texture, lattice distortions
- Non destructive
- No sample prep
- No vacuum required
- Large volume technique

\(~0.5\%\)
\(30\ \mu m\)
Chemical information
~ EDS, ~ AES
< XPS
<< SIMS
No vacuum required
Large volume technique
XRF > XRD

Detection limits

Analytical lateral resolution
Surface information:
- Roughness (buried interfaces)
- AFM (surface only)
- SEM, TEM (contrast, prep)
- < XPS chemical info (vacuum)

Analytical lateral resolution

~0.5% 30 μm
Typical analysis depth for common analytical techniques

- **Top Surface**: 3 nm
- **Near Surface**: 10 nm
- **Thin Film**: $10^2$ nm
- **Thick Film**: $10^3$ nm
- **Bulk Substrate**: $>2 \times 10^3$ nm

**GI-XRD** can reduce depth.
X-ray analysis summary

(+) Non destructive
Quantitative
Finger printing (chemical info)
Very accurate crystalline structure info
Averages over large volume (~ $30 \text{ \mu m} \times 0.5$-$2$ cm’s)
Levels of complexity: simple to complex
Microdiffraction, pair distribution function, fast areal detectors

(-) Localized info (below 100 \text{ \mu m})
Defects identification and quantification
Direct imaging