Short Course on
X-ray diffraction analysis of thin films
and surfaces:
  i. Glancing/grazing incident XRD (GIXRD)
  ii. Residual stress analysis (RSA)

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FACTS Scientist

http://research.ntu.edu.sg/facts
Content

- Background: X-ray analysis of thin film materials
- Glancing/grazing incident X-ray diffraction
- Residual stress analysis by XRD
- Summary
What is a thin film sample?

- Prepared by:
  - Coating or deposition
  - Chemical or Physical reaction

- Characteristics:
  - Thickness, roughness, density, porosity, residual stress, topology, structures
  - Crystallinity, orientation, ordering, composition, defects, epitaxial strain

- Applications:
  - Electronic devices
  - Sensors & MEMS devices
  - Surface science & engineering

<table>
<thead>
<tr>
<th>Type</th>
<th>Thickness</th>
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<tbody>
<tr>
<td>Film</td>
<td>1 µm to 10 µm</td>
</tr>
<tr>
<td>Thin film</td>
<td>10 nm to 1 µm</td>
</tr>
<tr>
<td>Ultra thin film</td>
<td>10 nm</td>
</tr>
<tr>
<td>Surface or monolayer</td>
<td>&lt; 1 nm</td>
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</table>
X-ray interaction with thin films

**Incident X-rays**
- Laboratory source
- Synchrotron source

**Incident X-rays are reflected/scattered/diffracted:**
- X-ray reflectivity (XRR)
- X-ray scattering (SAXS, GISAXS)
- X-ray Diffraction (PXRD, GIXRD, GIWAXS, HRXRD)

**Incident X-rays excites the sample to produce signals:**
- X-ray Fluorescence (XRF)
- X-ray Photon Emission (XPS)
X-ray analysis of thin film materials

Amorphous
✓ Non-crystalline
✓ Thickness
✓ Roughness
✓ Density
✓ Nano-structure

Polycrystalline
✓ Crystalline, Phase ID
✓ Randomly oriented
✓ Thickness
✓ Roughness
✓ Density
✓ Nano-structure
✓ Residual stress

Textured
✓ Crystalline, Phase ID
✓ Preferred orientation
✓ Thickness
✓ Roughness
✓ Density
✓ Nano-structure
✓ Residual stress

Epitaxial
✓ Single crystal
✓ Orientation
✓ Thickness
✓ Roughness
✓ Density
✓ Nanostructure
✓ Epitaxy, strain, defects, composition

RSA XRD
GISAXS/WAXS
XRR

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## X-ray analysis of thin films and surfaces in FACTS

<table>
<thead>
<tr>
<th>Instrument</th>
<th>PXRD</th>
<th>TFXRD</th>
<th>PF</th>
<th>XRR</th>
<th>GISAXS GIWAXS</th>
<th>RSA</th>
<th>HRXRD</th>
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</tr>
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- **PXRD**: Powder XRD (Bragg-Brentanno, 2θ-θ scan)
- **TFXRD**: Thin film XRD (Glancing/grazing angle, 2θ scan)
- **PF**: Pole figure (phi-,chi-scan)
- **XRR**: X-ray reflectometry (specular and off-specular)
- **GISAXS**: Grazing Incidence Small Angle X-ray Scattering (in/out-of-plane)
- **GIWAXS**: Grazing Incidence Wide Angle X-ray Scattering (in/out-of-plane)
- **RSA**: Residual stress analysis (sin²ψ, multiple-hkl, whole pattern decomposition)
- **HRXRD**: High resolution XRD (2θ-ω, ω-2θ, rocking curve, phi-, chi-scan)

*In-situ cooling-heating, -150°C to 350°C
*Limited capability
PXRD and TFXRD
What’s the difference?
PXRD ($\theta/2\theta$) versus TFXRD (GIXRD)

1. Why is there a difference in diffraction geometry?
2. How much absorption and penetration depth?
\( \theta/2\theta \) diffraction geometry

- \( n\lambda = 2d\sin\theta \) Bragg condition
- Scattering/Diffraction vector is always normal to the surface
- \( \theta/2\theta \) is a symmetric scan
- \( hkl \) parallel to the surface
- Penetration depth is not controlled
- Coplanar configuration
θ/2θ : Bragg-Brentanno geometry

- Bragg-Brentanno (parafocusing) geometry
- Divergent beam optics:
  - Including crystals with tilted hkl normal
- Angular resolution can be improved with narrow slits

**Powder XRD:**

- Bragg-Brentanno (parafocusing) geometry

**Bragg-Brentanno geometry with optics**

Focus length

\[ B_p = R \frac{\sin \theta \sin \delta_{ds}}{\sin^2 \theta - \sin^2 (\delta_{ds} / 2)} \]
\(\theta/2\theta\): Bragg-Brentano geometry

- Focusing circle
- Goniometer circle

- \(R = 320\) mm (dashed curves)
- \(= 240\) mm (solid curves)

\[ B_p = R \left( \frac{\sin \theta \sin \delta_{ds}}{\sin^2 \theta - \sin^2 (\delta_{ds} / 2)} \right) \]

- \(\delta_{ds} = 2^\circ\)
- \(1/8^\circ, 1/4^\circ, 1/2^\circ, 1^\circ\)
$\theta/2\theta \rightarrow$ GIXRD diffraction geometry

- Only one point is in focus
- Requires narrow/parallel incident beam
GIXRD diffraction geometry

Thin film XRD:
- Glancing or Grazing incident angle
- Asymmetric scan, non-parafocusing
- Incident/diffracted parallel beam
- Controlled penetration depth
- Sample surface flat alignment is important (surface & height)
- Diffraction vector is not parallel to the sample surface normal
Beam footprint in GIXRD (parallel beam)

Beam footprint (B):

\[ BW = \text{beam width} \]

\[ B = \frac{BW}{\sin \alpha} \]
Goebel mirror

Figure 4.1 Laterally graded multilayer mirror: (a) principle of operation in top view and (b) schematic of combination with x-ray tube in side view (from Ref. [2]).
Examples: GIXRD versus BBG scan

GIXRD:
✓ Probes the thin film region only
✓ Relative Intensity is lower

Bragg-Brentanno (θ/2θ scan):
✓ Additional contribution from the substrate
✓ Very high intensity

How much difference in the absorption and penetration depth?
X-ray absorption and penetration depth

**X-ray absorption effects on materials:**
- **X-ray absorption** follows *Lambert-Beer law* which relates the *attenuation of light* (electromagnetic radiation) travelling through a material to the material’s properties.
- **Penetration depth** is the depth at which the intensity of radiation incident on a material is attenuated to $1/e$ (37%).

**Lambert-Beer law (X-ray absorption):**

$$ I = I_0 \exp(-\mu l) $$

- $\mu = \text{linear absorption coefficient} = \mu_m \rho$
- $\mu_m = \text{mass absorption coefficient}$
- $\rho = \text{mass density}$
- $l = \text{X-ray path length}$

**Penetration depth**

$$ \tau_{1/e} = \frac{1}{\mu} \text{ (normal incidence)} $$

$$ \tau_{1/e} = \frac{\sin \theta}{\mu} \text{ (non-normal incidence)} $$
\( \theta/2\theta \) scan: Absorption factor

Absorption factor:
\[
A_{\theta/2\theta} = 1 - \exp\left(-\frac{2\mu t}{\sin\theta}\right)
\]

Intensity is attenuated by:
\[
\int_0^{l_{\text{max}}} \exp(-2\mu l) \, dl
\]

where: \( l = \frac{z}{\sin\theta} \)

Solution of the integral:
\[
\frac{1}{2\mu} \left\{ 1 - \exp\left( -\frac{2\mu t}{\sin\theta} \right) \right\}
\]

Infinitely thick sample: \( t \to \infty \)
\[
\frac{1}{2\mu}
\]

Ref: Thin Film analysis by X-ray Scattering, Birkholtz
Absorption factor:

$$A_{\theta/2\theta} = 1 - \exp \left( -\frac{2\mu t}{\sin \theta} \right)$$

Diffraction intensity from a polycrystalline sample:

$$I = |F|^2 \rho \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) A(\theta) e^{-2M}$$

Al: $\mu_m = 486.7 \text{ m}^2 \text{ kg}^{-1}, \rho = 2700 \text{ kg m}^{-3} \Rightarrow \mu = 1.31 \times 10^6 \text{ m}^{-1}$

Nb: $\mu_m = 1492 \text{ m}^2 \text{ kg}^{-1}, \rho = 8550 \text{ kg m}^{-3} \Rightarrow \mu = 1.276 \times 10^7 \text{ m}^{-1}$
\( \theta / 2\theta \): Penetration depth

\[
\tau_{1/e} = \frac{1}{\mu} \text{ normal incidence}
\]

Penetration depth
\[
\tau_{1/e} = \frac{\sin \theta}{\mu}
\]

Table 2.2  Atomic masses of selected elements; and density \( \rho \), linear absorption coefficient \( \mu \) and penetration depth \( \mu^{-1} \) of selected solids for Cu K\( \alpha \) radiation.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic mass (( m ))</th>
<th>Modification</th>
<th>Structure type</th>
<th>Density, ( \rho ) (g cm(^{-3}))</th>
<th>( \mu ) (mm(^{-1}))</th>
<th>( \mu^{-1} ) (( \mu m ))</th>
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<tbody>
<tr>
<td>C</td>
<td>12.01</td>
<td>Diamond</td>
<td>Diamond</td>
<td>3.51</td>
<td>1.58</td>
<td>632</td>
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<td>Graphite</td>
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<td>985</td>
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<td>Si</td>
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<td>Zn</td>
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<td>Cubic ZnS</td>
<td>Sphalerite</td>
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<td>S</td>
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<tr>
<td></td>
<td></td>
<td>Hexagonal ZnSe</td>
<td>Wurtzite</td>
<td>5.39</td>
<td>43.7</td>
<td>22.9</td>
</tr>
</tbody>
</table>

Ref: Thin Film analysis by X-ray Scattering, Birkholtz
GIXRD: Absorption factor

\[ A_{GIXRD} = 1 - \exp(-\mu t k_\alpha) \]

\[ k_\alpha = \frac{1}{\sin \alpha} + \frac{1}{\sin(2\theta - \alpha)} \]

X-ray path length:

\[ l = \frac{z}{\sin \alpha} + \frac{z}{\sin(2\theta - \alpha)} \]
GIXRD: X-ray penetration depth

1. Attenuation of X-rays to 1/e of its initial value
   \[ \tau_{1/e} = \frac{\sin \alpha}{\mu} \]

2. \( \tau_{63} \) for \( A_{\text{GIXRD}} = 1 - 1/e \) (\( \mu \tau_{63} k_\alpha = 1, 63\% \))
   \[ \tau_{63} = \frac{\sin \alpha \sin(2\theta - \alpha)}{\mu [\sin \alpha + \sin(2\theta - \alpha)]} \]

3. Information depth, based on weighted average over the sampling depth
   for infinitely thick-layer it approaches \( \tau_{63} \)
   \[ \bar{\tau}_\alpha = \frac{1}{\mu k_\alpha} + \frac{1}{1 - \exp(\mu t k_\alpha)} \]

May exceed the thickness of a thin layer
penetration depth for Au63Cu35Al2 (ρ=15.36) @ 8040.0eV

---Note-----

i) Porosity, columnar grains, voids, defects in the material could reduce the effective density of the film and therefore the penetration depth could be deeper.

ii) Thin film density could be measured using XRR.
Glancing-incidence X-ray diffraction of Ag nanoparticles in gold lustre decoration of Italian Renaissance pottery

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3 ISTM and Centro di Eccellenza SMAAit, Dipartimento di Chimica, Università di Perugia, via Elce di Sotto 8, 06123 Perugia, Italy

FIGURE 1 At low incident angle ($\alpha_1$) diffraction occurs from the surface layer, at higher incidence angle ($\alpha_2$) the beam increases penetration depth in the sample and the contribution of deeper layers appear in the diffraction patterns

FIGURE 4 111 silver peak integrated area as a function of the incidence angle for GIXRD measurements. The circles represent the experimental data, the solid line the expected value obtained by simulating an 200 nm thick layer of Ag nanoclusters buried under 600 nm of glaze
Useful links for X-ray penetration depth

- **Online penetration depth calculator:**
  [http://gixa.ati.tuwien.ac.at/tools/penetrationdepth.jsf](http://gixa.ati.tuwien.ac.at/tools/penetrationdepth.jsf)

- **Absorption coefficient reference:**

---

penetration depth for Au \(_1\) \((\rho = 19.3)\) @ 8040.0eV

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GIXRD at $\alpha \sim \alpha_c$

4. Penetration depth:

$$\tau_{1/e} = \frac{\sqrt{2} \lambda}{4\pi} \sqrt{\left[(\alpha^2 - \alpha_c^2)^2 + \beta^2\right]^{1/2} - (\alpha^2 - \alpha_c^2)}$$

penetration depth for Au63Cu35Al2 ($\rho=15.36$) @ 8040.0eV

Near $\alpha_c$:
- Very surface sensitive
- GIXRD (in-plane scattering/diffraction)
GIXRD: Out-of-plane scattering/diffraction

- $\alpha$ is constant
- $\alpha \approx \arcsin(\mu t)$
- Thickness/depth information profile (microstructure, strain, phase)
- Coplanar configuration
- GISAXS, GIWAXS out plane scattering
GIXRD: In-plane scattering/diffraction

- Scattering plane is almost parallel to the surface
- $\alpha_i$, $\alpha_f$ are constant and very small almost near the surface plane
- Evanescent wave (few nm of the surface)
- depth information: $\alpha_i \rightarrow \alpha \sim \arcsin(\mu t)$
- hkl-planes perpendicular to the surface
- GISAXS, GIWAXS, -inplane scattering
GIXRD: 2D diffraction

2D detector:

* Captures the out-of-plane and in-plane diffraction
* Good for GISAXS/GIWAXS experiments
* Anisotropy or preferred orientation
GIXRD: 2D diffraction

Diffraction/scattering vector

2D diffraction:
- Makes sense with point X-ray source

This will not work for a Line beam X-ray source

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2D diffraction: GIWAXS in-plane and out-of-plane example

More of this technique in GISAXS/GIWAXS short course
Residual stress analysis by X-ray Diffraction
Residual stress in materials

Origin:

- Thin-film/substrate
  - difference in mechanical properties
  - multi-layer stack
- Surface deformation
  - nanocrystallization or amorphization by mechanical deformation
- Micro(nano)-structures
  - porosity, defects
  - 2D or 3D structures
  - Composite structures

Extrinsic or Intrinsic

Why do we need to quantify it?

- Reliability & performance
- Processing & product development
- Functional properties
- Failure analysis
Residual stress

Macrostress:
- Average over many grains
- $\sigma_I$
- Diffraction peak shifts
- $\sin^2\psi$ method and its variants

Microstress:
- Grain-specific, internal
- $\sigma_{II}$ & $\sigma_{III}$
- Diffraction peak shift and broadening
- Diffraction peak shape analysis:
  - Warren-Averbach
  - Whole pattern fitting
X-ray residual stress analysis

Specimen

homogeneous

polycrystalline

Inhomogeneous

Single-crystalline

Isotropic material
- Simple
- Mechanical constants (E, v)

Quasi-isotropic
- Relatively simple
- hkl dependent elastic constants
- X-ray elastic constants (XEC)

Anisotropic
- Complicated
- Texture, grain-interaction models
- X-ray stress factors (XSF)

Data collection?
Data analysis?
Basic elasticity equations

Stress tensors in the sample reference frame

Hooke’s law

\[ \varepsilon_{ij} = S_{ijkl} \sigma_{kl} \]
\[ \sigma_{ij} = C_{ijkl} \varepsilon_{kl} \]

\( \varepsilon_{ij} \): strain
\( \sigma_{ij} \): stress
\( S_{ijkl} \): compliance tensor
\( C_{ijkl} \): elastic stiffness

Isotropic materials:

\[ \varepsilon_{ij} = \frac{(1 + \nu)}{E} \sigma_{ij} - \delta_{ij} \frac{\nu}{E} \sigma_{kk} \]
\[ \sigma_{ij} = \frac{E}{(1 + \nu)} \varepsilon_{ij} + \frac{\nu E}{(1 + \nu)(1 - 2\nu)} \delta_{ij} \varepsilon_{kk} \]

E (Young’s modulus) and \( \nu \) (Poisson’s ratio) are materials dependent mechanical constants
Elastic constants

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<th>Crystal System</th>
<th>Description</th>
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<tr>
<td>Triclinic</td>
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<tr>
<td>Monoclinic</td>
<td>1 twofold rotation</td>
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<tr>
<td>Orthorhombic</td>
<td>2 perpendicular twofold rotation</td>
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<tr>
<td>Hexagonal</td>
<td>1 sixfold rotation around [0001]</td>
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<td>Cubic</td>
<td>4 threefold rotations around &lt;111&gt;</td>
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### Cubic

Anisotropy factor

\[ C' = \frac{C_{11} - C_{12}}{2} \]

<table>
<thead>
<tr>
<th>Material class</th>
<th>Material</th>
<th>( C_{11} ) (10^{10}) N/m(^2)</th>
<th>( C_{12} ) (10^{10}) N/m(^2)</th>
<th>( C_{44} ) (10^{10}) N/m(^2)</th>
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<td>1.3</td>
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Table 2.2

Stiffness coefficients for selected cubic materials
Sample reference frame: SS₁ SS₂ SS₃
- SS₃ = Surface normal
- SS₁ & SS₂ are in-plane (surface) directions

Laboratory reference frame: L₁ L₂ L₃
- \( L_3 = L_{\phi \psi} \) = Diffraction vector
  \[ \rightarrow \varepsilon_{33}^L = \varepsilon_{\phi \psi} \]

- \( \phi \) in-plane rotation angle
- \( \psi \) azimuth angle

Tensor transformation applied to express the strain (stress) in the sample coordinate system

Fundamental equation for x-ray residual stress analysis:

\[
\varepsilon_{33}^L = \frac{1}{2} S_2 \left[ \left( \sigma_{11}^S \cos^2 \phi + \sigma_{22}^S \sin^2 \phi + \sigma_{12}^S \sin 2\phi \right) \sin^2 \psi + \left( \sigma_{13}^S \cos \phi + \sigma_{23}^S \sin \phi \right) \sin 2\psi + \sigma_{33}^S \cos^2 \psi \right] + S_1 \left( \sigma_{11}^S + \sigma_{22}^S + \sigma_{33}^S \right)
\]
**Fundamental equation for x-ray residual stress analysis:**

\[
\varepsilon_{\phi\psi}^{hkl} = \varepsilon_{33}^{L} = \frac{1}{2} S_2^{hkl} \left[ \left( \sigma_{11}^{S} \cos^2 \phi + \sigma_{22}^{S} \sin^2 \phi + \sigma_{12}^{S} \sin 2\phi \right) \sin^2 \psi + \left( \sigma_{13}^{S} \cos \phi + \sigma_{23}^{S} \sin \phi \right) \sin 2\psi + \sigma_{33}^{S} \cos^2 \psi \right] + S_1^{hkl} \left( \sigma_{11}^{S} + \sigma_{22}^{S} + \sigma_{33}^{S} \right)
\]

\[
L_3 = L_{\phi\psi} = \text{Diffraction vector}
\]

\[
\varepsilon_{33}^{hkl} = \varepsilon_{\phi\psi} = \varepsilon_{\phi\psi}^{hkl}
\]

*\textit{Bragg's law: }* \( \lambda = 2d_{hkl}^{hkl} \sin \theta_{hkl} \)

\[
\varepsilon_{hkl} = \frac{d_{hkl}^{hkl} - d_{o}^{hkl}}{d_{o}^{hkl}}
\]

**X-ray elastic constants:**

\[
S_1^{hkl} = -\frac{\nu_{hkl}}{E_{hkl}} \quad \frac{1}{2} S_2^{hkl} = \frac{1 + \nu_{hkl}}{E_{hkl}}
\]
How do we collect RSA data?

Conventional diffraction geometry:
✓ $\psi$: angle between sample ($S_3$) and diffractometer ($L_3$)
✓ Can be done as $\chi$ or $\omega$ tilt or both
✓ Single hkl (set at the Bragg angle $2\theta_{hkl}$)
How do we collect RSA data?

Conventional diffraction geometry:
- \( \psi \): angle between sample (\( S_3 \)) and diffractometer (\( L_3 \))
- Can be done as \( \chi \) or \( \omega \) tilt or both
- Single hkl (set at the Bragg angle \( 2\theta_{hkl} \))

- \( \omega \) tilt

- Maximum \( \psi \) tilt is limited by \( \theta \)
- Penetration depth is not controlled
- \( 2\theta-\omega \) scan mode
How do we collect RSA data?

Conventional diffraction geometry:
- \( \psi \): angle between sample (\( S_3 \)) and diffractometer (\( L_3 \))
- Can be done as \( \chi \) or \( \omega \) tilt or both
- Single hkl (set at the Bragg angle \( 2\theta_{hkl} \))

- \( \psi \)-tilt is not limited by \( \theta \)
- Chi (\( \chi \)) scan in a Eulerian cradle
- \( \psi \)-tilt in GIXRD is possible (fixed \( \alpha \)), penetration depth is controlled
How do we collect RSA data?

Conventional diffraction geometry:
- $\psi$: angle between sample ($S_3$) and diffractometer ($L_3$)
- Can be done as $\chi$ or $\omega$ tilt or both
- Single hkl (set at the Bragg angle $2\theta_{\text{hkl}}$)

- 2D-diffraction simultaneously captures various $\psi$-tilt ($\chi$ azimuth)
- GIXRD, penetration depth controlled
How do we collect RSA data?

Grazing incident geometry:
- $\psi$: angle between sample ($S_3$) and diffractometer ($L_3$)
- $\psi$ tilt by 2$\theta$ scan
- multiple hkl (as set by the Bragg angle $2\theta_{hkl}$)
- 2D diffraction will require no tilting
- Penetration depth is controlled

Scattering plane

$\psi$-tilt by 2$\theta$ scan will require multiple hkl

$\psi = \theta_{hkl} - \alpha$
FACTS XRD

D8 Advance: vertical goniometer

\[ \psi = 0 \]


D8 Discover: Horizontal goniometer

\[ \theta/\omega \]

\[ \phi \text{ manual} \]

\[ \checkmark \omega \text{-tilt} \]

\[ \checkmark \chi \text{-tilt} \]

\[ \checkmark \text{GIXRD} \]

\[ \checkmark \phi \text{-rotation} \]
Residual stress data analysis

I. Single hkl
   - Triaxial, biaxial, uniaxial

II. Multiple hkl
   - \( g(\psi, hkl), f(\psi, hkl) \)

III. General least-squares analysis of any stress state
   - Non-linear least square fitting algorithms

\[
\varepsilon_{\psi \psi}^{hkl} = \varepsilon_{33}^{hkl} = \frac{1}{2} S_{2}^{hkl} \left[ \left( \sigma_{11}^{S} \cos^{2} \phi + \sigma_{22}^{S} \sin^{2} \phi + \sigma_{12}^{S} \sin 2\phi \right) \sin^{2} \psi + \left( \sigma_{13}^{S} \cos \phi + \sigma_{23}^{S} \sin \phi \right) \sin 2\psi + \sigma_{33}^{S} \cos^{2} \psi \right] \\
+ S_{1}^{hkl} \left( \sigma_{11}^{S} + \sigma_{22}^{S} + \sigma_{33}^{S} \right)
\]

**Fundamental equation for x-ray residual stress analysis:**

**X-ray Elastic Constant:**

\[
S_{1}^{hkl} = -\frac{\nu_{hkl}}{E_{hkl}}
\]

\[
\frac{1}{2} S_{2}^{hkl} = 1 + \frac{\nu_{hkl}}{E_{hkl}}
\]

**X-ray Stress Factor:**

\[
\left\{ \varepsilon_{33}^{L} \right\}_{\psi \psi}^{hkl} = F_{ij} \left( \phi, \psi, hkl \right) \left\{ \sigma_{ij}^{S} \right\}
\]
Fundamental equation for x-ray residual stress analysis:

\[ \varepsilon_{\phi\psi}^{hkl} = \frac{1}{2\nu^2} \left[ (\sigma_{11}^S \cos^2 \phi + \sigma_{22}^S \sin^2 \phi + \sigma_{12}^S \sin 2\phi) \sin^2 \psi + (\sigma_{13}^S \cos \phi + \sigma_{23}^S \sin \phi) \sin 2\psi + \sigma_{33}^S \cos^2 \psi \right] \\
+ S_1^{hkl} (\sigma_{11}^S + \sigma_{22}^S + \sigma_{33}^S) \]
Single hkl analysis

Triaxial stress analysis:

Stress tensor (MPa) =
\[
\begin{bmatrix}
402 & 7 & -7 \\
7 & 391 & 3 \\
-7 & 3 & -3 \\
\end{bmatrix}
\]

Principal stress tensor (MPa) =
\[
\begin{bmatrix}
406 & 0 & 0 \\
0 & 387 & 0 \\
0 & 0 & -3 \\
\end{bmatrix}
\]

Biaxial stress!

\[\phi = 0\]
\[\phi = -45\]
\[\phi = -90\]
### Single hkl analysis: \( \sin^2 \psi \) variants

#### Triaxial principal stress

\[
\begin{bmatrix}
\sigma_{11} & 0 & 0 \\
0 & \sigma_{22} & 0 \\
0 & 0 & \sigma_{33}
\end{bmatrix}
\]

\[
\varepsilon_{0 \psi}^{hkl} = \frac{1}{2} S_{1 \psi}^{hkl} (\sigma_{11}^S - \sigma_{33}^S) \sin^2 \psi + S_{1 \psi}^{hkl} (\sigma_{11}^S + \sigma_{22}^S + \sigma_{33}^S) + \frac{1}{2} S_{2 \psi}^{hkl} \sigma_{33}^S
\]

\[
\varepsilon_{90 \psi}^{hkl} = \frac{1}{2} S_{2 \psi}^{hkl} (\sigma_{22}^S - \sigma_{33}^S) \sin^2 \psi + S_{1 \psi}^{hkl} (\sigma_{11}^S + \sigma_{22}^S + \sigma_{33}^S) + \frac{1}{2} S_{2 \psi}^{hkl} \sigma_{33}^S
\]

\[
\varepsilon_{0 \psi}^h = S_{1 \psi}^{hkl} (\sigma_{11}^S + \sigma_{22}^S + \sigma_{33}^S) + \frac{1}{2} S_{2 \psi}^{hkl} \sigma_{33}^S
\]

#### Biaxial principal stress

\[
\begin{bmatrix}
\sigma_{11} & \sigma_{12} & 0 \\
\sigma_{12} & \sigma_{22} & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

\[
\varepsilon_{0 \psi}^{hkl} = \frac{1}{2} S_{1 \psi}^{hkl} \sigma_{11}^S \sin^2 \psi + S_{1 \psi}^{hkl} (\sigma_{11}^S + \sigma_{22}^S)
\]

\[
\varepsilon_{45 \psi}^{hkl} = \frac{1}{2} S_{2 \psi}^{hkl} \left( \frac{\sigma_{11}^S + \sigma_{22}^S}{2} \right) \sin^2 \psi + S_{1 \psi}^{hkl} (\sigma_{11}^S + \sigma_{22}^S)
\]

\[
\varepsilon_{90 \psi}^{hkl} = \frac{1}{2} S_{2 \psi}^{hkl} \sigma_{22}^S \sin^2 \psi + S_{1 \psi}^{hkl} (\sigma_{11}^S + \sigma_{22}^S)
\]

#### Biaxial Rotationally symmetric

\[
\begin{bmatrix}
\sigma_{11} & 0 & 0 \\
0 & \sigma_{22} & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

\[
\varepsilon_{0 \psi}^{hkl} = \frac{1}{2} S_{1 \psi}^{hkl} \sigma_{11}^S \sin^2 \psi + S_{1 \psi}^{hkl} (\sigma_{11}^S + \sigma_{22}^S)
\]

\[
\varepsilon_{90 \psi}^{hkl} = \frac{1}{2} S_{2 \psi}^{hkl} \sigma_{22}^S \sin^2 \psi + S_{1 \psi}^{hkl} (\sigma_{11}^S + \sigma_{22}^S)
\]

#### Biaxial Rotationally symmetric

\[
\begin{bmatrix}
\sigma_{11} & 0 & 0 \\
0 & \sigma_{12} & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

\[
\varepsilon_{0 \psi}^{hkl} = \frac{1}{2} S_{1 \psi}^{hkl} \sigma_{11}^S \sin^2 \psi + S_{1 \psi}^{hkl} (\sigma_{11}^S + \sigma_{22}^S)
\]

\[
\varepsilon_{0 \psi}^{h} = \frac{1}{2} S_{2 \psi}^{hkl} \sigma_{11}^S \sin^2 \psi + 2 S_{1 \psi}^{hkl} \sigma_{11}^S
\]

#### Uniaxial

\[
\begin{bmatrix}
\sigma_{11} & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

\[
\varepsilon_{0 \psi}^{hkl} = \frac{1}{2} S_{2 \psi}^{hkl} \sigma_{11}^S \sin^2 \psi + S_{1 \psi}^{hkl} \sigma_{11}^S
\]

5/March/2019

FACTS short course, Buenconsejo
Multiple hkl analysis

GIXRD

\[ \psi = \theta^hkl - \alpha \]

Material: Au\textsubscript{71}Cu\textsubscript{25}Al\textsubscript{4} thin film
fcc-AuCu(Al) phase
thickness = 725 nm

Young’s modulus = 79 GPa
Poisson’s ratio = 0.44
Arx = 2.8
Multiple hkl analysis

\( g(\psi, hkl) \) method:
Biaxial stress state

\[
g(\psi, hkl) = \frac{1}{2h^2 k^l} S_1 S_\text{hkl} \sin^2 \psi
\]

\[
\frac{\varepsilon_{0,\psi}^\text{hkl}}{S_1^\text{hkl}} = g(\psi, hkl) \sigma^{S}_{11} + (\sigma^{S}_{11} + \sigma^{S}_{22})
\]

\[
\frac{\varepsilon_{45,\psi}^\text{hkl}}{S_1^\text{hkl}} = g(\psi, hkl) \left( \frac{\sigma^{S}_{11} + \sigma^{S}_{22}}{2} + \sigma^{S}_{12} \right) + \sigma^{S}_{11} + \sigma^{S}_{22}
\]

\[
\frac{\varepsilon_{90,\psi}^\text{hkl}}{S_1^\text{hkl}} = g(\psi, hkl) \sigma^{S}_{22} + (\sigma^{S}_{11} + \sigma^{S}_{22})
\]

\( f(\psi, hkl) \) method:
Rotationally symmetric
Biaxial stress state

\[
f(\psi, hkl) = 2S_1^\text{hkl} + \frac{1}{2} S_2^\text{hkl} \sin^2 \psi
\]

\[
\varepsilon_{\psi}^\text{hkl} = f(\psi, hkl) \sigma^{S}_{ll}
\]

5/March/2019 FACTS short course, Buenconsejo
General least-square analysis of any stress state

\[ \chi^2 = \sum_i \omega_i^2 [\varepsilon_i^{calc}(\sigma^s, hkl, \phi, \psi) - \varepsilon_i^{exp}(hkl, \phi, \psi)]^2 \]

- \( \omega_i \) is weighting factor
- \( \sigma^s \) is a fitting parameter

- Most general solution
- Requires more computing power
- Non-linear least squares fitting
- Can combine single hkl and multiple hkl data
- Works well with textured (highly anisotropic) samples
- For highly anisotropic samples it requires use of grain-interaction models (XSF)

**Figure 14**
Textured copper film. Measured (open circles) and simulated (dashed line) diffraction strain data for two reflections as function of \( \sin^2 \psi \). For details of the simulation, see text. The error bars indicating statistical errors on the lattice strains are about twice the size of the circles for the 200 reflection and less than the size of the circles for the 420 reflection.

Summary

θ/2θ scan vs GIXRD
✓ geometry
✓ X-ray absorption & penetration depth
✓ in-plane & out of plane diffraction

Residual stress analysis
✓ background on residual stress
✓ how to collect the data
✓ how to analyse the data

Suggested reading materials:
- “Residual Stress (Measurement by Diffraction and Interpretation)” Noyan, Cohen, 1987 Springer
- “Thin film analysis by X-ray Scattering” Mark Birkholz