Diffraction and Beyond: Thin Film Analysis by X-Ray Scattering with a Multipurpose Diffractometer

Scott A Speakman, Ph.D.
Interactions of X-rays with Thin Films

- **X-Ray Diffraction**
  - X-rays scatter elastically and constructively from the atomic structure
  - Probes features on the atomic scale: <nm

- **Small Angle X-Ray Scattering**
  - X-rays scatter elastically producing a mesostructural map of variations in electron density
  - Probes features on the micro and meso scale: 1 nm to 150 nm

- **X-Ray Reflectivity**
  - X-rays reflect from interfaces with different refractive indices
  - Probes layered information on the meso scale, 1 nm to 100 nm

- **X-Ray Fluorescence**
  - X-rays absorbed and fluoresced by individual atoms
  - Probes chemistry
## What information is provided by different X-ray scattering analyses of thin films

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**HRXRD**- High Resolution XRD using coupled scan or RSM  
**RC**- Rocking Curve  
**XRPD**- Bragg-Brentano powder diffraction  
**GIXD**- grazing incidence XRD  
**IP-GIXD**- in-plane grazing incidence XRD  
**PF**- pole figure  
**Psi**- sin²psi using parallel beam  
**XRR**- X-Ray Reflectivity  
**GI-SAXS**- grazing incidence small angle x-ray scattering  
*depending on degree of texture*
# Topics of Today’s Talk

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The scattering vector is an important concept in thin film analysis by X-ray scattering.

- The scattering vector, \( \mathbf{S} \), is the difference between the scattered and incident wave vectors.

- X-ray scattering always probes the direction of the scattering vector.
The scattering vector is normal to the sample in a typical Bragg-Brentano geometry

- Thin film analysis often requires the ability to re-orient the sample with respect to the scattering vector by tilting omega, chi (psi), and phi.
- X-ray scattering techniques requires:
  - an incident-beam mirror to produce a parallel or focused X-ray beam
  - Anti-scatter optics, such as slits and a beam tunnel
  - Detector with high dynamic range and low noise
X-Ray Reflectometry (XRR)
Schematic of X-Ray Reflectometry

- Specular reflection occurs at each interface that has a difference in electron density
  - Electron density and mass density are closely correlated.
- Interference between reflected X-ray waves produces interference
  - The X-ray probe deeper into the sample as \( \omega \) increases
Density information in XRR

- Critical angle increases with density
- Fringe amplitude may also vary with density
- Precision: ±1-2%

\[ \omega_c \sim \sqrt{\rho} \]

\[ \omega_0 < \omega_c , \text{ total reflection} \]
Thickness information in XRR

- Oscillation spacing varies with thickness
- Thickness can be quantified by Fourier transform, direct measurement, or simulation and fitting
- Precision: ±0.5-1% (max about 1000 nm)

\[ d = \frac{M\lambda}{2\left(\sqrt{\theta_1^2 - \omega_c^2} - \sqrt{\theta_2^2 - \omega_c^2}\right)} \]

(Profiles are vertically offset for clarity)
Roughness information in XRR

- RMS Roughness can be quantified by
  - the dampening of reflected signal
  - Curve shape
  - Amplitude
- Model dependent reproducibility ~3%
Diffuse scatter from a rough (non-perfectly smooth) interfaces

- Perfect layers: all X-rays scattered specularly
- Perfect layers: X-rays scattered specularly
- Imperfect interfaces: X-rays diffusely scattered (specular and off-specular)
Diffuse scatter can be measured using off-specular scans

\[ \omega = \theta \]

\[ \omega = \theta + \text{offset} \]
Off-specular scans provide important supporting information to XRR analysis

Why are no fringes observed from this thin film?
Roughness redistributes intensity away from specular reflection into diffuse scatter

Diffuse scatter indicates a very rough surface
Diffuse scatter analysis of surface roughness

DS of a single Ir layer on a Si substrate.

Fractal interface

Lateral correlation length ($\xi$) of Ir layer = 20 nm
Diffuse Scatter Map

High-angle Yoneda wing

Low-angle Yoneda wing

Resonant Diffuse Scattering

\( \omega \)-\( 2\theta \) offset scan

\( \omega \)- scan

\( \omega \)-\( 2\theta \) specular scan
Grazing Incidence Small Angle X-Ray Scattering (GISAXS)
GISAXS Geometry probes off-specular scatter in many directions respective to the sample.
Comparing diffuse scatter mapping and GISAXS

- Structural correlations parallel to surface
- Structural correlations in scattering plane
- Structural correlations perpendicular to scattering plane
Analysis and Simulation

- GISAXS pattern is a convolution of the scattering from the size and shape of the nanostructures (the form factor) and their arrangement (the structure function)

\[ I(q_x, q_z) \propto |F(q)|^2 \cdot |S(q)|^2 \]

- To deconvolute the effects typically requires simulation, but one can often times extract meaning for the structure function by direct measurement of the scattered information (once converted to q parameters)

- One must consider multiple scattering effects in both simple structural analysis but also when trying to determine the form factors through DWBA modelling.

- Simulation of entire patterns is both laborious and impractical as DWBA cannot account for specular beams, so line cuts are often made for fitting purposes to determine lateral or vertical correlation.

Terms in DWBA approximation

Term 1: \( q_z = k_{fz} - k_{iz} \)
Term 2: \( q_z = k_{fz} + k_{iz} \)
Term 3: \( q_z = -k_{fz} - k_{iz} \)
Term 4: \( q_z = -k_{fz} + k_{iz} \)
GISAXS contains information about nanoscale ordering

For example: lamellar films of block copolymers:

GISAXS 2D data

type of ordering

parallel

perpendicular

http://staff.chess.cornell.edu/~smilgies/gisaxs/GISAXS.php
Scattering from horizontally and vertically stacked pores

Vertically aligned Co filled pores in amorphous SiO2 thin film on Si wafer substrate

**vertical lines confirm pore periodicity of ~37nm**
Scattering from horizontally ordered and disordered pores

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<tr>
<th>calculation:</th>
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<th>size (nm)</th>
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<tbody>
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<td>↓ Ti size lower limit</td>
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<td>← surface modulation</td>
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Iron oxide nanoparticles on Si
GI-WAXS from polymer solar cell

25 deg

Empyrean

Literature (4C2 beamline, Pohang Light Source)
Summary

- Surface sensitive scattering techniques can be accommodated on a multipurpose diffractometer with proper optics to:
  - Control divergence, producing a parallel or focusing X-ray beam
  - Anti-scatter slits and beam knifes to reduce air scatter
  - Detector with high dynamic range and low noise
- These techniques complement thin film X-ray diffraction analyses
  - Coupled scan XRPD using variable divergence slits
  - Grazing incidence X-ray diffraction (GIXRD)
    - Grazing incidence residual stress analysis (multi-hkl technique)
  - In-plane grazing incidence X-ray diffraction (IP-GIXD)
  - Triple axis diffraction
    - Coupled scans, rocking curves, reciprocal space maps
The PANalytical award recognizes and praises groundbreaking research that required the use of a laboratory X-ray diffraction, X-ray fluorescence or X-ray scattering instrument as the primary analytical technique.

As such, recipients will not be limited to any brand of instrument, but rather to research that utilised an X-ray source to reach their conclusions.

The annual award consists of a €5,000 cash prize, a trophy and a certificate.

http://www.panalytical.com/Events-overview/The-PANalytical-Award.htm

Submissions for the PANalytical Award will be accepted until and including 1 December 2015. The full application form is to be completed by the first author of the journal article. Questions may be directed to award@panalytical.com
GISAXS Configuration

Diffractometer + Area Detector + Hardware = GISAXS

Empyrean + PIXcel\(^{3D}\) + PIXcel\(^{3D}\) 2x2

PANalytical
get insight