High Resolution X-ray Diffraction

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Outline

• Watlab’s new tool: Panalytical MRD system

• Techniques:
  – introduction to XRD
  – high resolution XRD
  – glancing incidence XRD
  – x-ray reflectometry
Panalytical’s Materials Research Diffraction System (MRD-Pro)
Introduction to X-ray diffraction

**Bragg's Law:** \( n\lambda = 2d \sin \theta \)

\( \lambda = \) x-ray wavelength, CuK\( \alpha_1 = 1.540562 \) Å
\( d = \) crystal lattice spacing
\( \theta = \) incident angle

For a single crystal sample, Bragg’s law will result in diffracted spots in space. These can be mapped onto an *Ewald sphere*, and assigned to various diffraction planes.

For a multi-crystal powder sample, the large number of diffracted spots form rings.
Powder Diffraction is widely used to determine unknown inorganic phases.

A powder scan involves moving the incident angle (called $\theta$ or $\omega$), and the detector angle (called $2\theta$), simultaneously, so that $\omega$ is $\frac{1}{2}(2\theta)$. This will satisfy the Bragg condition for a range of d-spacings.

Cu nanoparticles on Si/Au/PPy. Only Au peaks are seen.

Fe nanoparticles on Si. Signal/noise is bad.
Single crystal diffraction is used widely for drug discovery and to analyze large biomolecules.

Large molecules can have thousands of diffracted spots, making it a challenge to determine the structure.

This technique also requires “large” single crystals of the biomolecule.
High Resolution X-ray Diffraction

What affects how accurately Bragg’s law is followed?

- monochromacity of the x-ray beam (i.e. how accurately do we know $\lambda$?)

- dispersion of the x-ray beam (i.e. how parallel is the beam?)

- accuracy and step-size of the goniometer

- noise in the detector

Sample Artifacts:
small sample size
defects/impurities in the crystal lattice
diffuse scattering from amorphous material
Triple-Axis HR-XRD System

Rocking Curve

Rotation

Tilt

Sample

Beam Conditioner

Detector

Analyzer

Provides detailed and finer information, but at the expense of intensity, hence increased time for acquisition.

First Axis: Adjustment of the Beam Conditioner (comprising of optical elements and slits)

Second Axis: Scan of the specimen through Bragg Angle

Third Axis: Adjustment of the Analyzer (comprising of optical elements and slits)

Differential movement of the three axis makes the measurement and determine the precision and accuracy of the instrument.
High resolution XRD : SrTiO$_3$ (002) Rocking Curve

Fix $\theta$ at a known Bragg reflection, and move (rock) $\omega$ about $\frac{1}{2}(2\theta)$.

The width of the peak indicates the perfection of the crystal.

This single crystal film is highly crystalline (i.e. few defects), but contains some mis-aligned grains.
SrTiO$_3$ (002) Reciprocal Space Map
A more detailed look at the Bragg reflection seen in the rocking curve.
SrTiO$_3$ (002) In-Plane Rocking Curve

Most of the film has the STO (002) crystal axis perpendicular to the film surface.

An in-plane rocking curve shows part of the STO film consists of mis-aligned grains that have the STO (002) crystal axis parallel to the film surface.

AFM or SEM shows small nano-crystals in the film.
Glancing Incidence X-ray Diffraction (GIXRD)

GIXRD can determine the diffraction pattern from a very thin film or layer.

This is sometimes difficult with ordinary diffraction, because
1) small volume of material in the film
2) strong contribution from the substrate swamps out film data

Parallel, monochromatic X-ray beam falls on a sample surface at a fixed angle of incidence ($\alpha_i$) and diffraction profile is recorded by detector only scan.
When the angle of incidence of the x-ray beam decreases, the beam will not penetrate (refract) as deeply into the sample.

Any light hitting an interface can have a reflected and refracted component.

Below a critical angle, $\alpha_c$, total external reflection will occur. Much of the x-ray beam is reflected, and the refracted beam propagates parallel to the interface, while being exponentially damped below the interface. This refracted beam is what is used by GIXRD.

The exact details of penetration depth, intensities etc., are found by solving Maxwell’s equations for the case with a boundary condition.
GIXRD shows Au and Cu phases for Cu nanoparticle on PPy/Au/Si
Au nano-particles on Si, seen using GIXRD
X-ray Reflectivity (XRR)

X-ray reflectivity occurs when x-rays hit the sample at low incident angles. The reflection occurs at the interface. So the film does not have to be crystalline. Amorphous, disordered films are also ok.
X-ray reflectivity limitations

If the films are rough, or do not have even thickness, the interference are washed out.

Also, the film layers must have different electron densities to get reflection from the interface.

Many orders of magnitude in x-ray intensity are needed. Therefore, big samples are better.
XRR on Cr/Glass sample (8x4 cm²)
Summary

- Thin film XRD system has varied capability.
- Complete analysis of SrTiO$_3$ structure in reciprocal space using HRXRD.
- Accurate phase identification of nanoparticles using GIXRD.
- Can determine of film thickness, density and roughness by XRR method.