Grazing Incidence X-Ray Diffraction (GIXRD)

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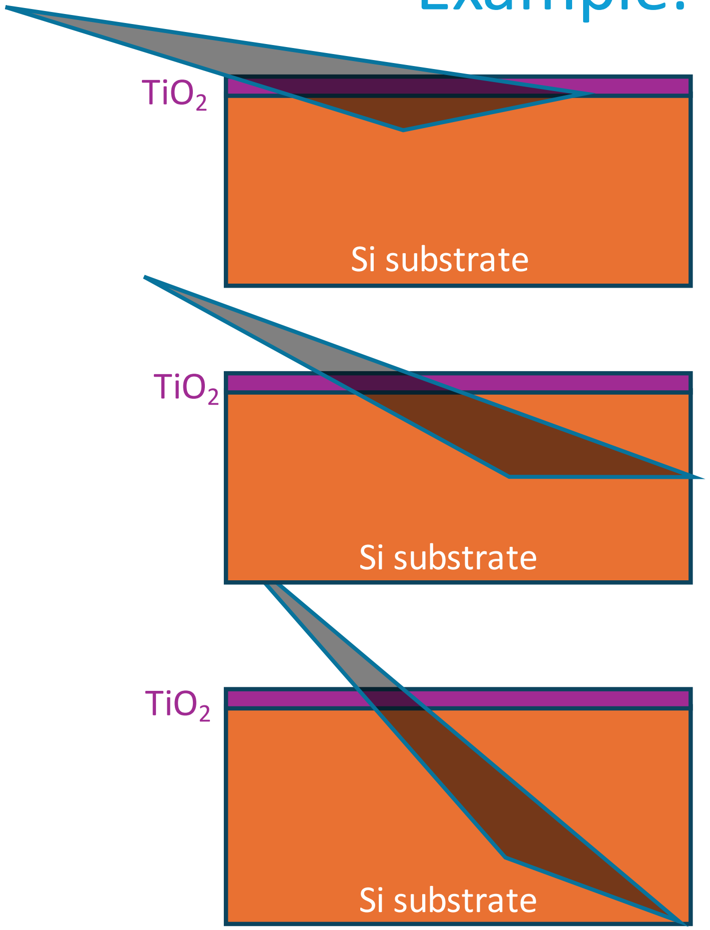
Challenges of Thin Film Analysis

Conventional X-Ray Powder Diffraction (XRPD) may struggle to provide useful data from thin film samples

Example: a 1 micron thick layer of TiO_2 on Si



At 10°2θ (ω=5°)

- 55% of X-rays go through the film and into the Si substrate
- The X-ray beam is 24mm long, the irradiated volume of the film is 0.24mm^3

At 50°2θ (ω=25°)

- 88% of X-rays go through the film and into the Si substrate
- The X-ray beam is 5mm long, the irradiated volume is 0.05mm^3

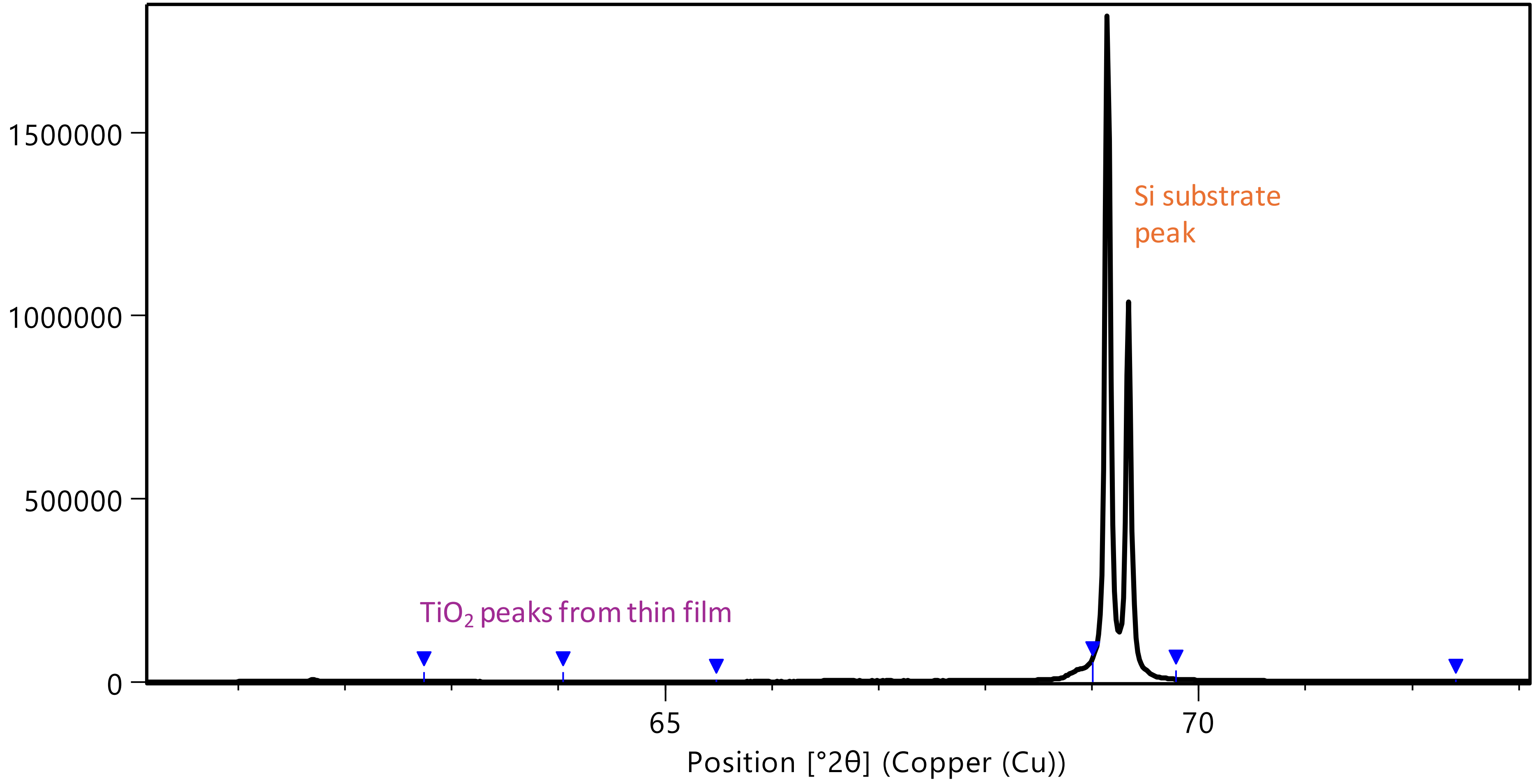
At 90°2θ (ω=45°)

- 93% of X-rays go through the film and into the Si substrate
- The X-ray beam is 3mm long, the irradiated volume of the film is 0.03mm^3

Challenges of Thin Film Analysis

Examples of problematic data produced using conventional bulk XRPD to collect data from thin films

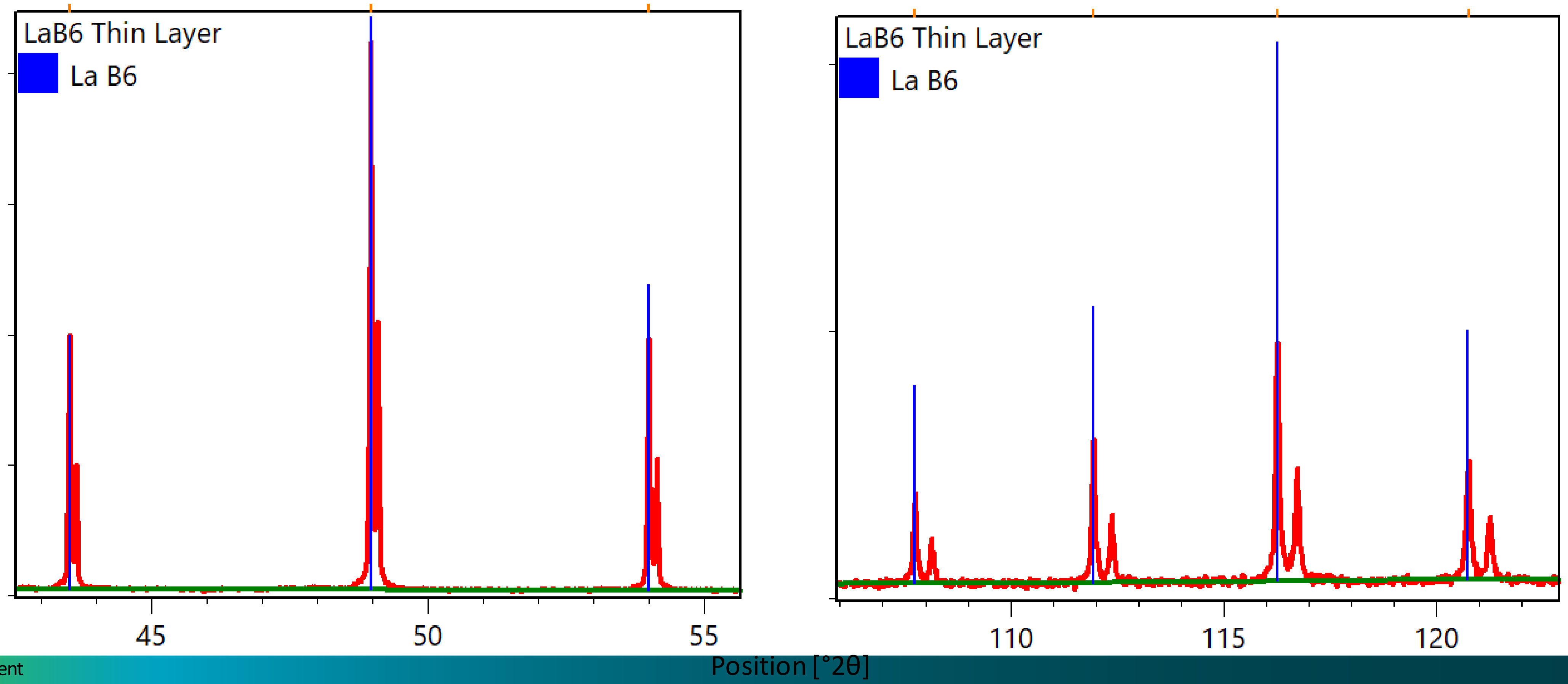
- Problem 1: Intensity from the substrate is stronger than intensity from the film



Challenges of Thin Film Analysis

Examples of problematic data produced using conventional bulk XRPD to collect data from thin films

- Problem 2: Irradiated volume decreases at higher 2theta angles, leading to loss of signal and inaccurate peak intensities



Challenges of Thin Film Analysis

There are two approaches to address the challenges of thin film analysis

1. Variable Divergence Slit

- The divergence slit is motorized
  - The divergence slit changes during the measurement to maintain a constant X-ray beam length
- Advantages
  - Maintains constant irradiated volume for accurate peak intensities
  - Optimal peak resolution (peak width)
  - Can utilize the full active length of a position sensitive detector (PSD) such as the PIXcel
- Disadvantage
  - Large fraction of X-rays still pass through the film into the substrate

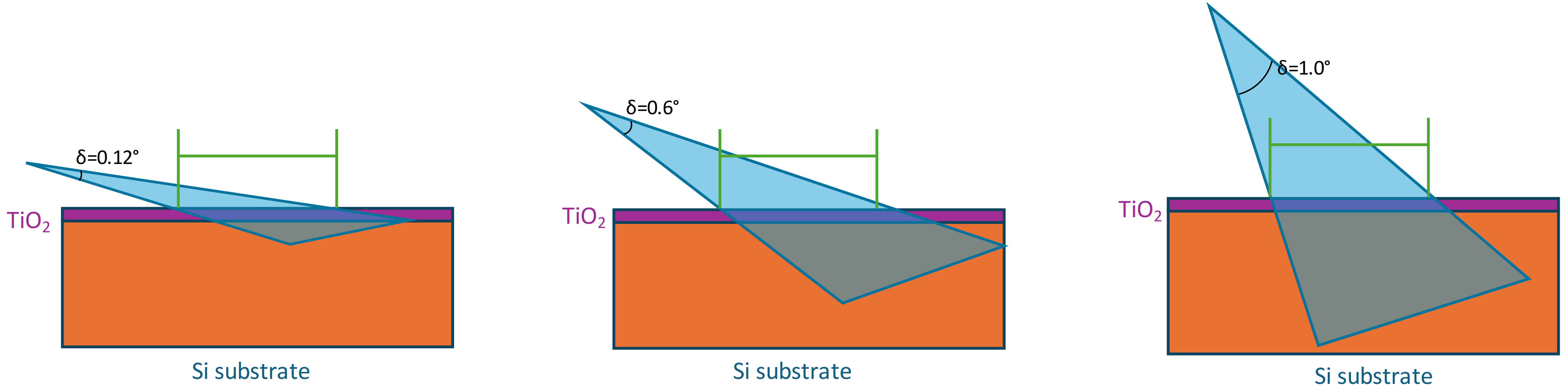
2. Grazing Incidence X-ray Diffraction (GIXRD)

- The incident angle (omega) is fixed at a low angle to focus the X-rays in the surface of the sample
- Advantages
  - Increases the fraction of X-rays that diffract from the film rather than the substrate.
  - The X-ray beam footprint does not change during the measurement
    - Constant irradiated volume for accurate peak intensities
    - Useful for inhomogeneous samples as well as thin films
  - Penetration depth can be controlled
- Disadvantages
  - Uses point detector (or PSD in point mode) so measurement is slower than XRPD scan
  - Limited peak resolution (eg broad peak widths)

Variable Divergence Slit

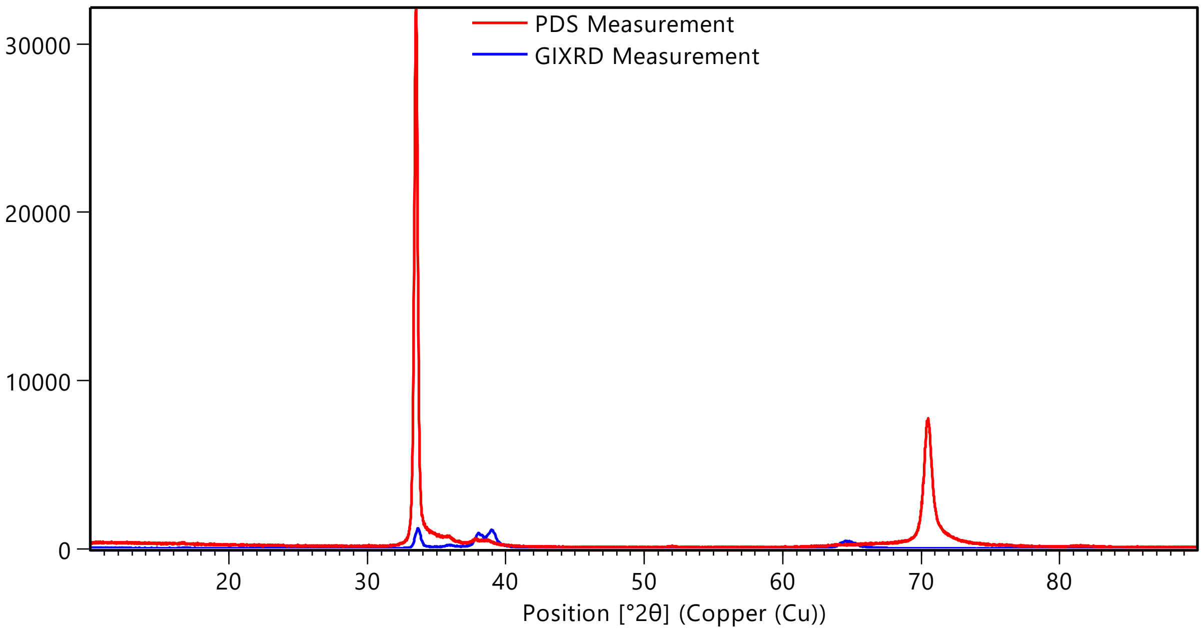
Overview of variable divergence slit measurements

- As omega increases, the divergence slit aperture (δ) opens larger so that the length of the X-ray beam on the surface stays constant.

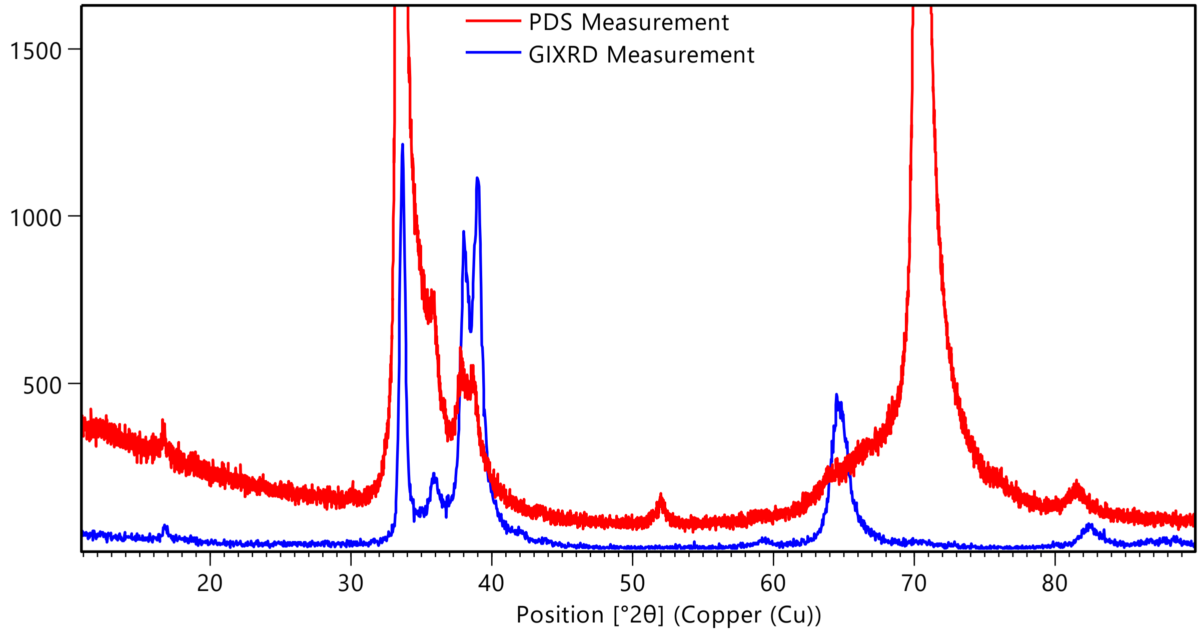


Variable Divergence Slit

Comparing 17min PDS measurement (red) to a 17min GIXRD measurement (blue) of a thin film



Unzoomed comparison of thin film data collected in 17min scans with PDS and GIXRD techniques. PDS gives much more raw intensity, but most of the intensity is from the substrate peak.

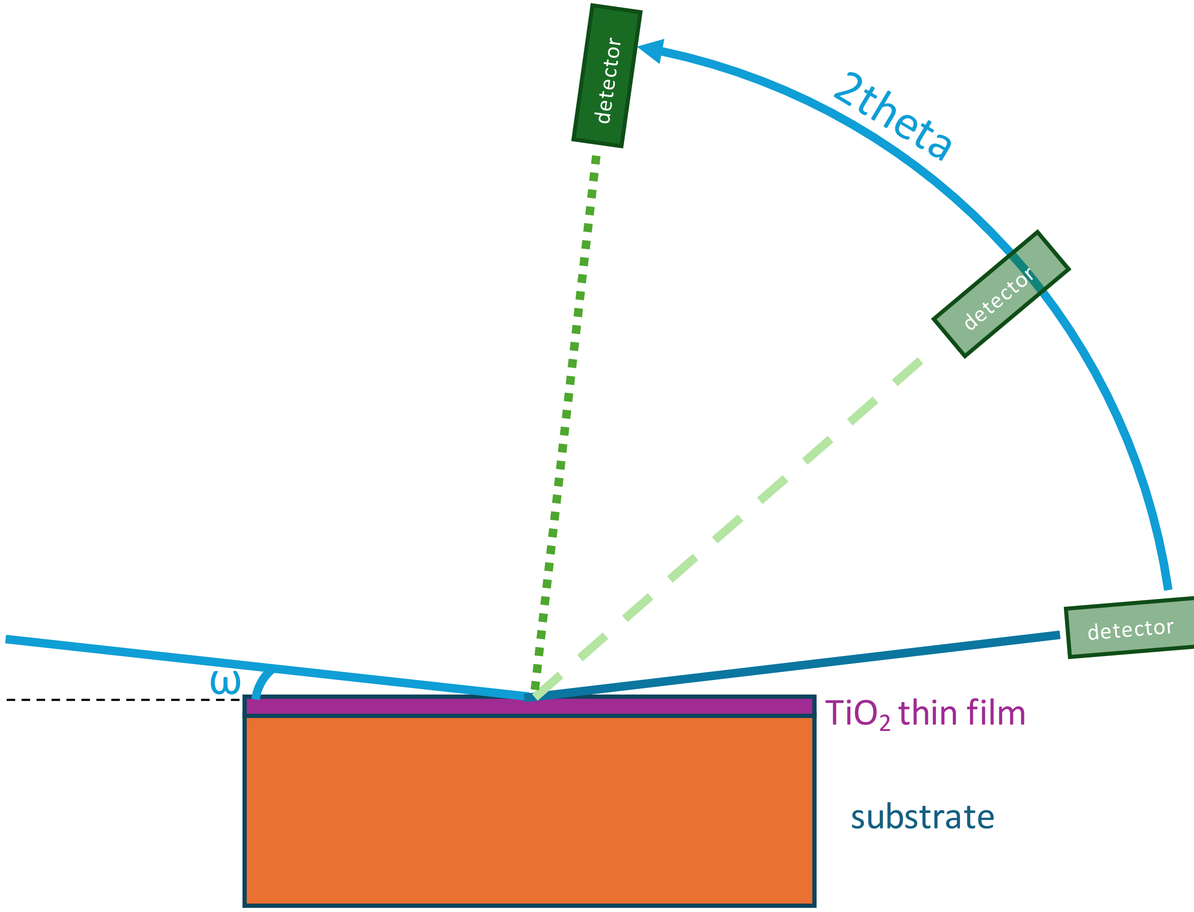


When zoomed in, it is apparent that the GIXRD provides more information about the film even though the overall intensity is less. However, PDS resolves some weak peaks not seen in the GIXRD measurement, such as the peak at 51 deg 2theta.

Grazing Incidence X-Ray Diffraction

Grazing Incidence X-ray Diffraction (GIXRD) measurements are useful for thin film analysis.

- the incident angle (omega) is fixed at a low angle. This focuses the X-ray beam on the top surface of the sample, providing several benefits:
    - Improves the ratio of X-rays scattering from the film compared to X-rays scattering from the substrate
    - The asymmetric geometry breaks the diffracting condition for single crystals, so single crystal substrate peaks and artifacts can be eliminated.
    - The beam footprint does not change during the measurement,
    - The penetration depth of X-rays is dependent on the incident angle (omega) and can be controlled or varied for depth profiling
- *GIXRD is also called a grazing incidence asymmetric Bragg diffraction (GIABD).*

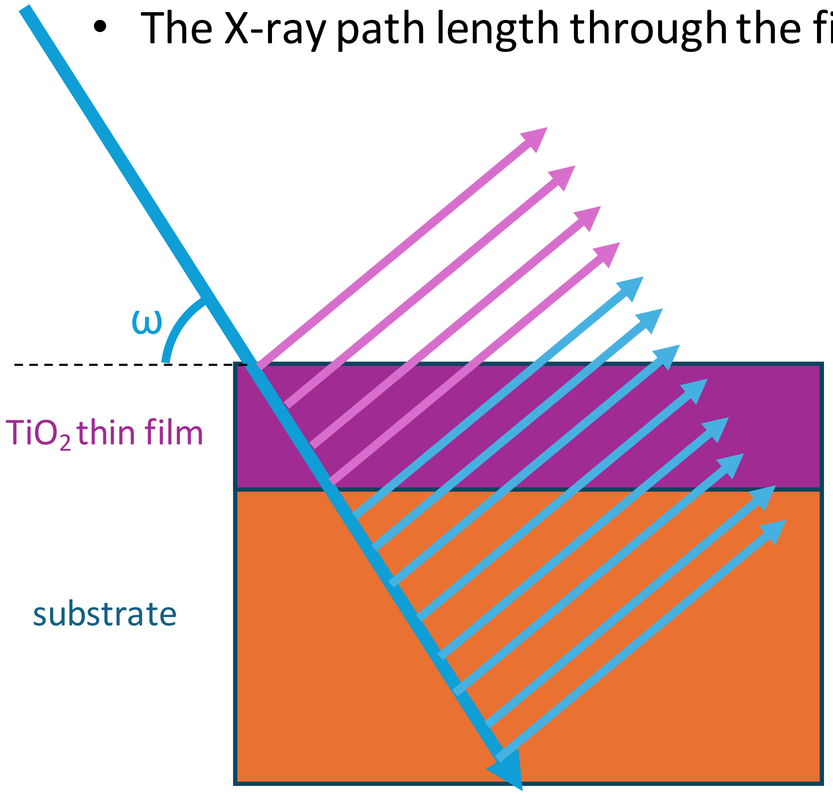


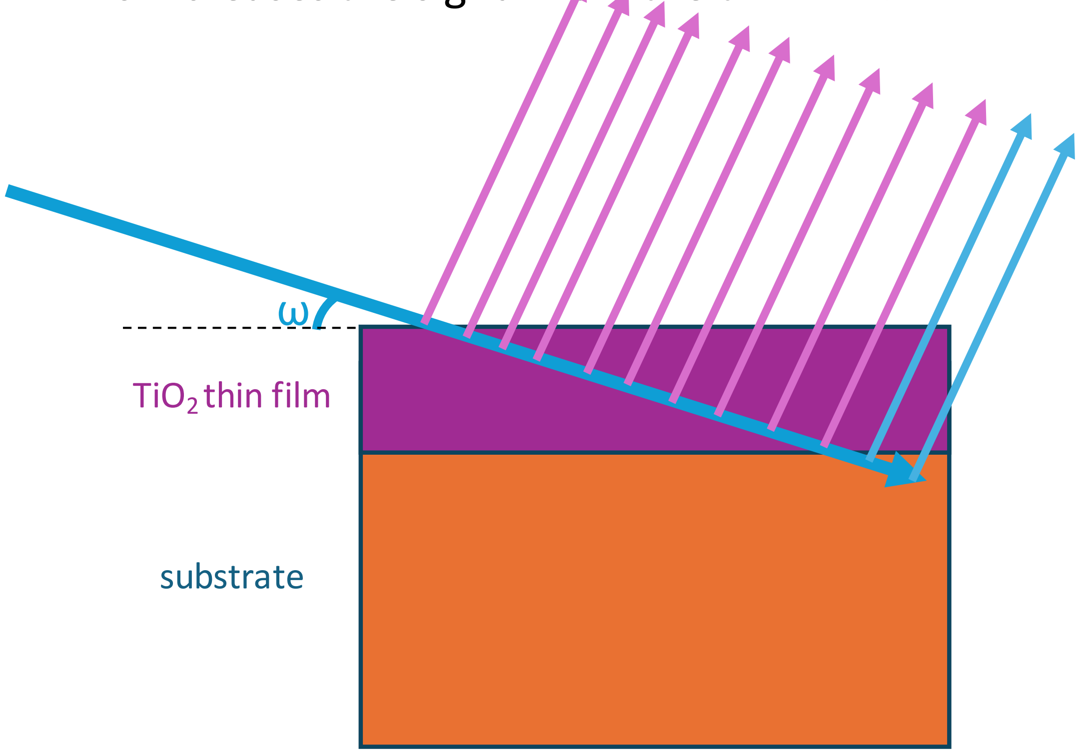
Grazing Incidence X-Ray Diffraction

GIXRD increases the volume of the thin film that is irradiated, improving the diffraction efficiency.

- At a large incident angle, omega, most of the X-rays pass through the thin film and into the substrate.
- The X-ray path length through the film is small.

- At a small omega, the X-ray path length through the film is substantially larger.
  - Typical ω is 0.5 to 2 deg
- This increases the signal from the thin film.



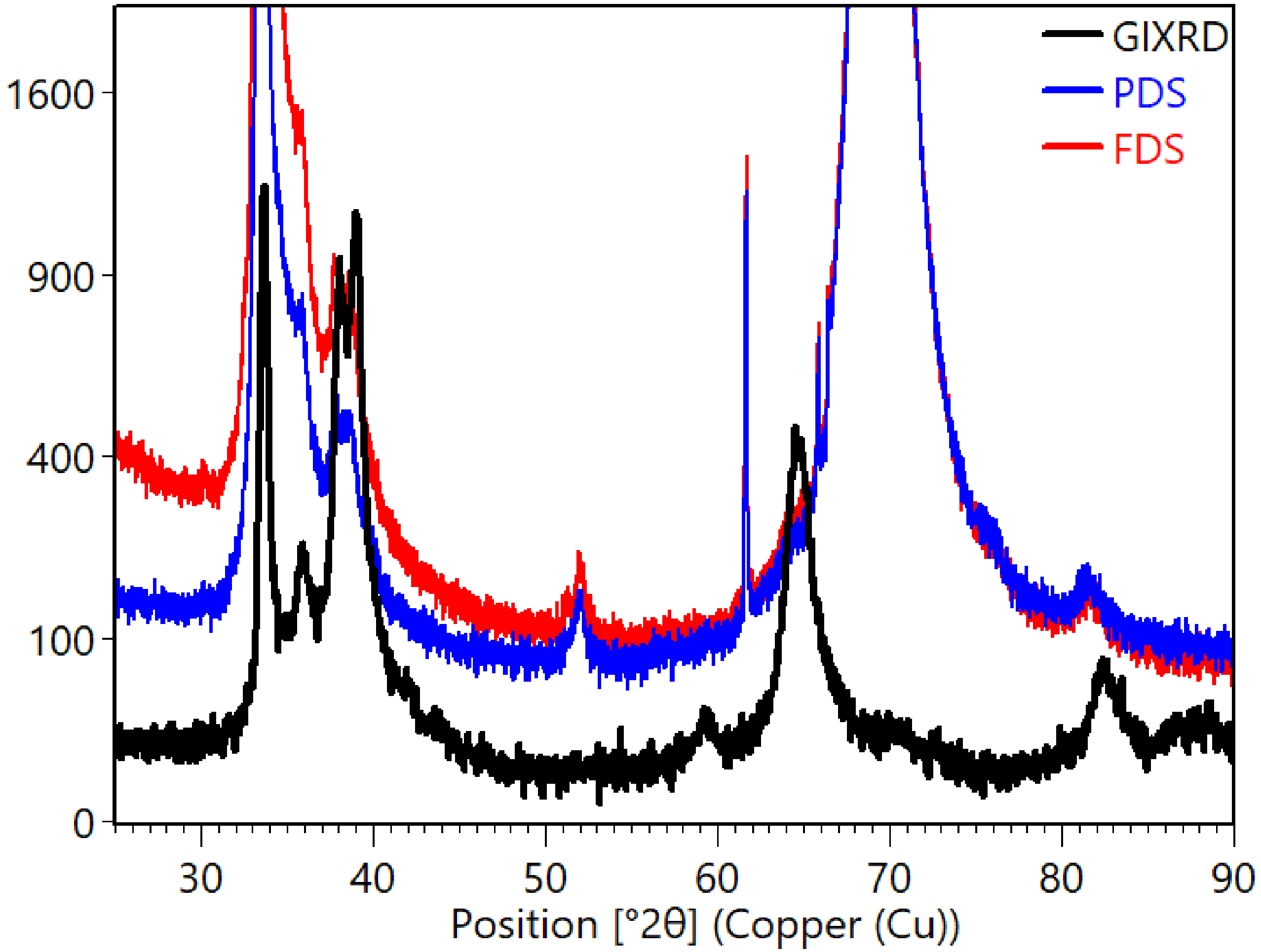


Grazing Incidence X-Ray Diffraction

Advantage of GIXRD: Improved intensity from thin films

- The figure to the right compares data from a thin film collected with:
  - Fixed divergence slit (FDS) in Bragg-Brentano geometry
  - Programmable divergence slit (PDS) in Bragg-Brentano geometry
  - GIXRD geometry

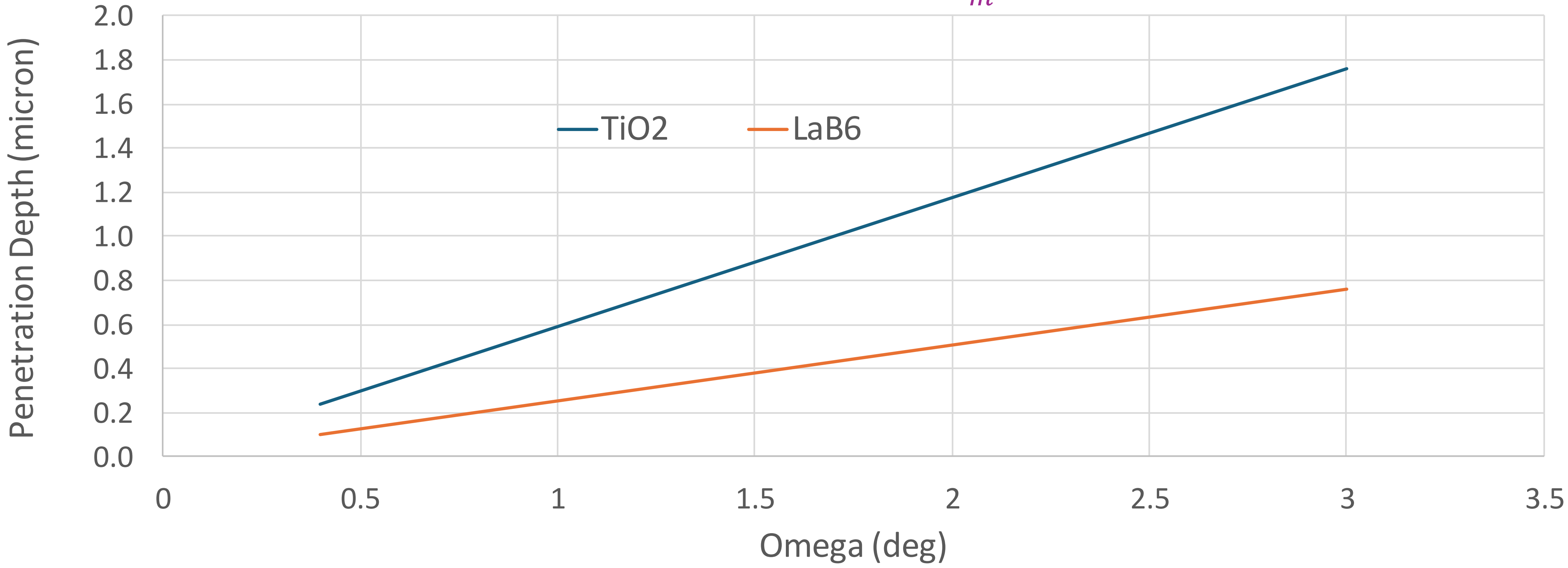
- The GIXRD geometry:
  - Eliminates the substrate peak intensity
  - Provides better peak intensity



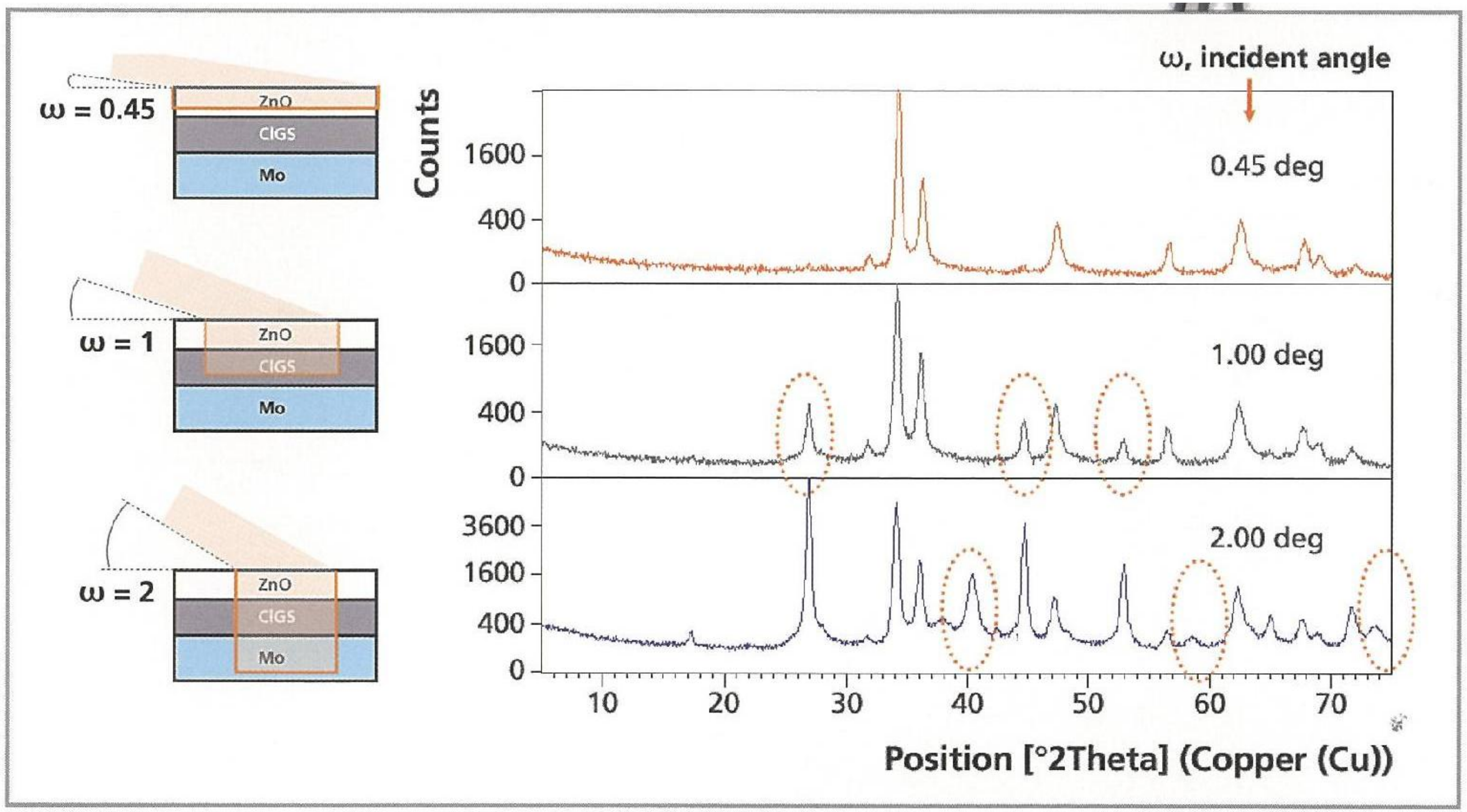
Depth of Penetration

Depth of penetration calculations vary depending on what % of the X-ray beam you assume is scattered. The plots shows penetration depth calculated for 99.9% X-rays scattered (I_L/I_0=0.001)

$$T = 0.5 * \sin(\omega) * \ln\left(\frac{I_L}{I_0}\right) * \left(\frac{\mu}{\rho}\right)_m * \rho_m$$



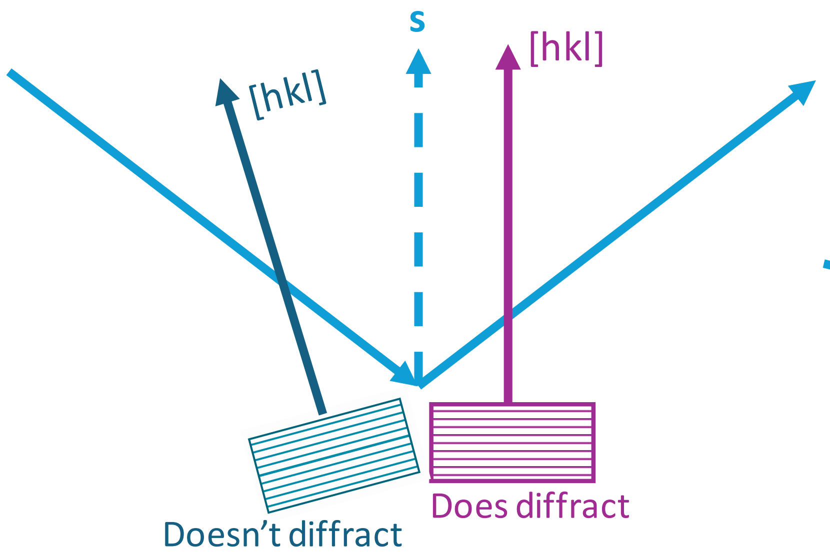
Depth Profiling with GIXRD

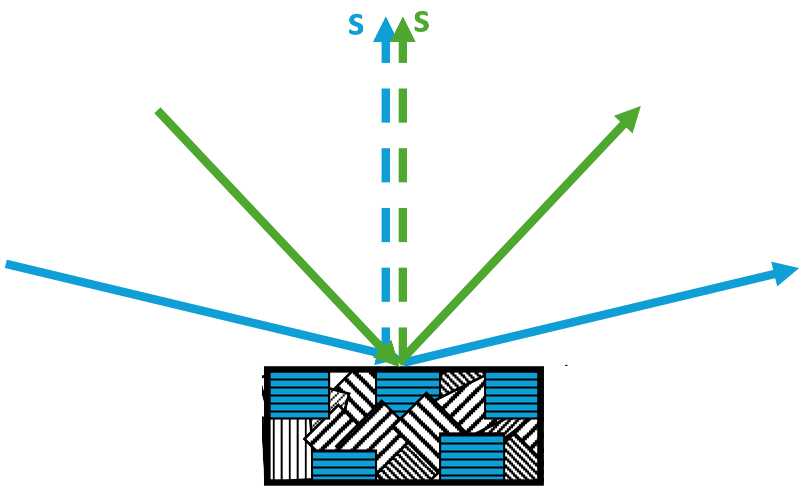


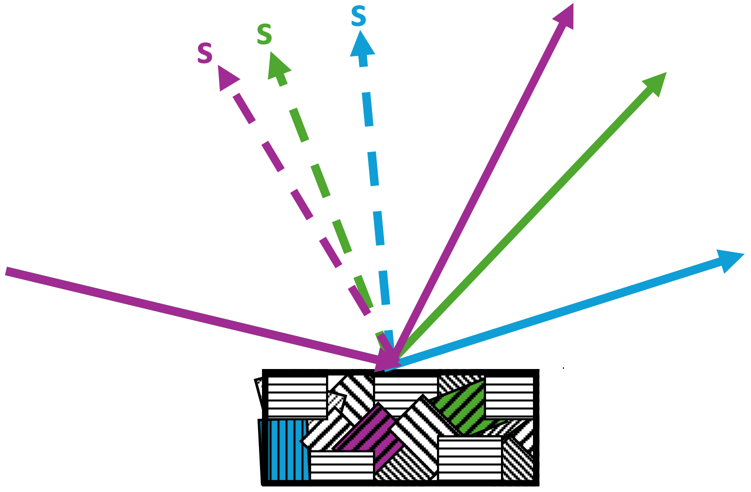
An example of depth probing on a CIGS solar structure, showing the different layers exposed to the parallel X-ray beam in a sequential mode by varying the incident angle . Top pattern is from the conductive oxide layer only, with CIGS coming in (middle, highlighted) and next the Mo metal contact layer appearing (bottom diagram, Mo peaks highlighted).

Analysis of Textured Thin Films

Films with preferred orientation (ie texture) diffract differently in Bragg-Brentano and GIXRD geometries.







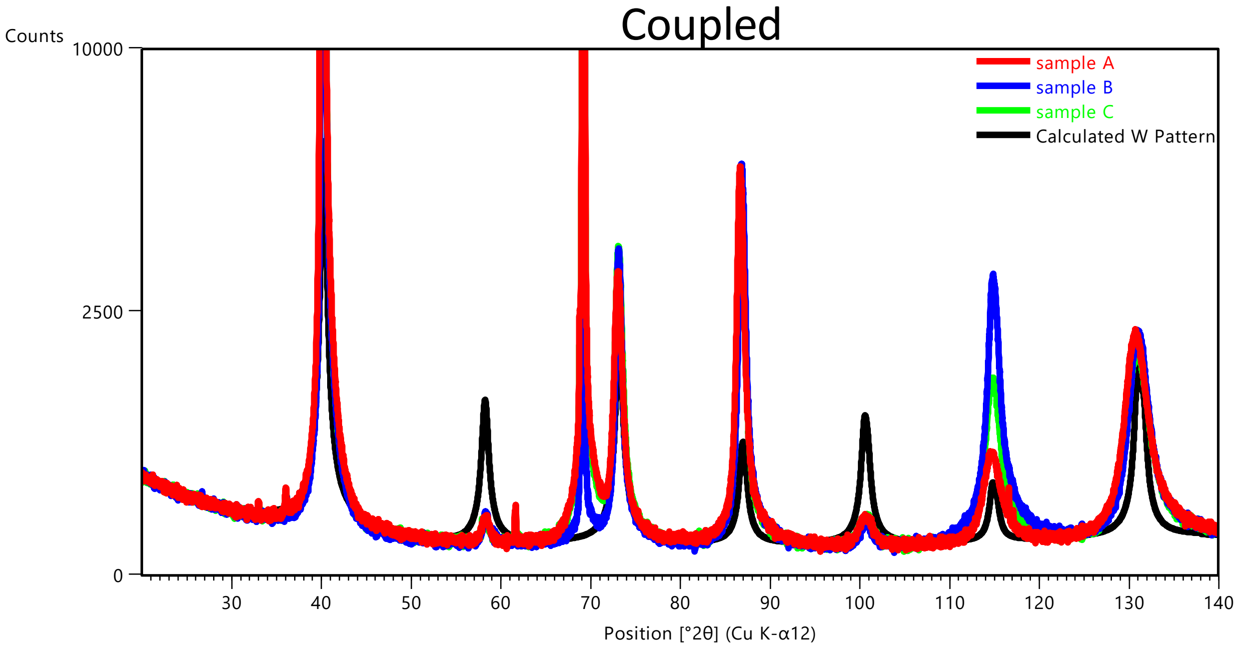
- In a powder diffractometer, diffraction from a crystal is only observed if:
  - The detector is at the Bragg angle
  - The diffraction vector **s** is parallel to the crystallographic direction **[hkl]**

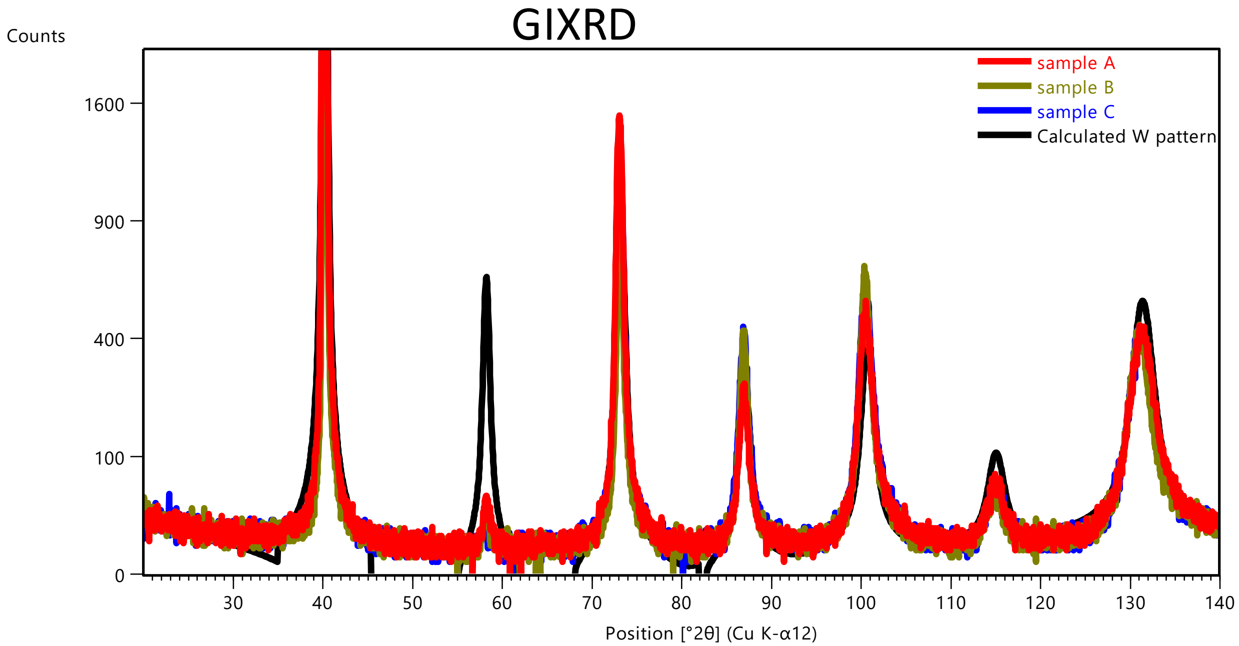
- In Bragg-Brentano geometry, the diffraction vector **s** does not change during the measurement
- Every observed diffraction peak is produced by [hkl] oriented in the sample direction

- In GIXRD geometry, the diffraction vector **s** changes with the detector angle **2Theta**
- Every observed diffraction peak is produced by [hkl] oriented in a different direction

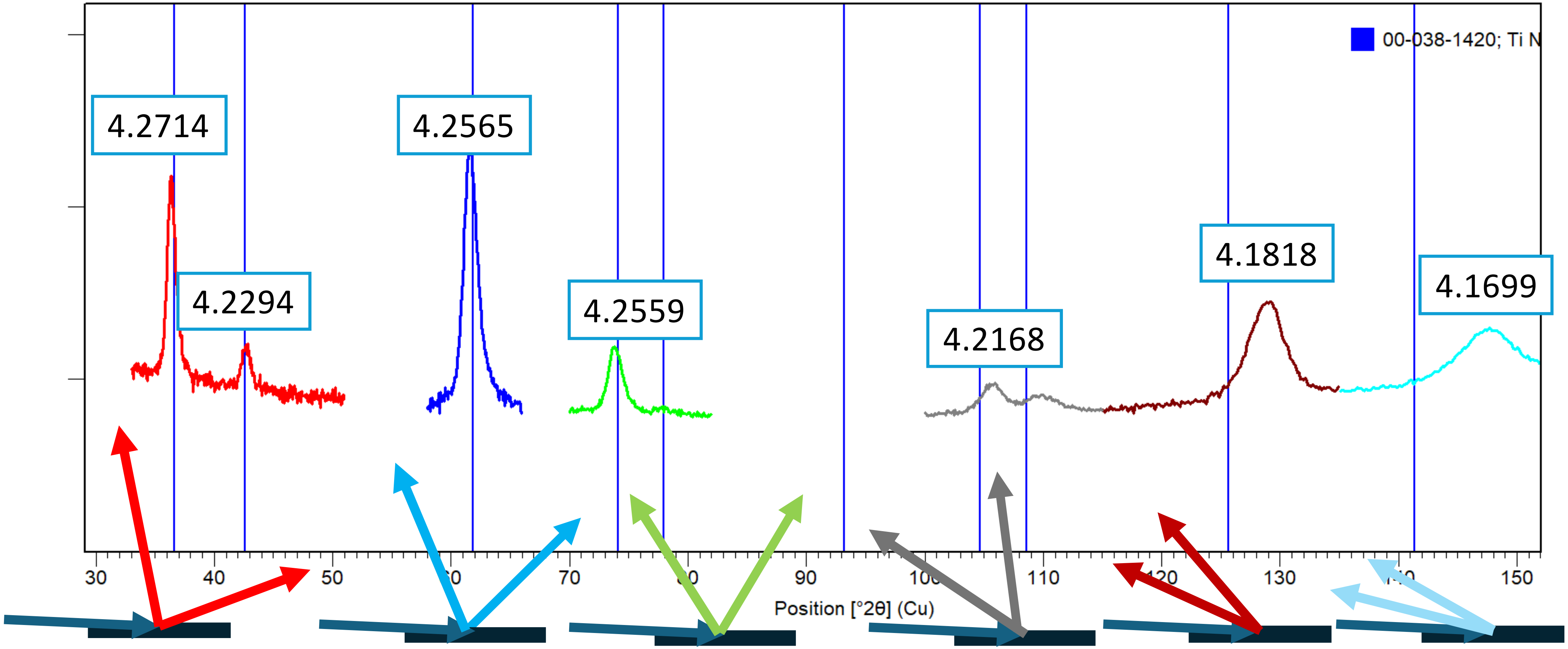
Analysis of Textured Thin Films

Bragg-Brentano and GIXRD scans sample a different population of grains



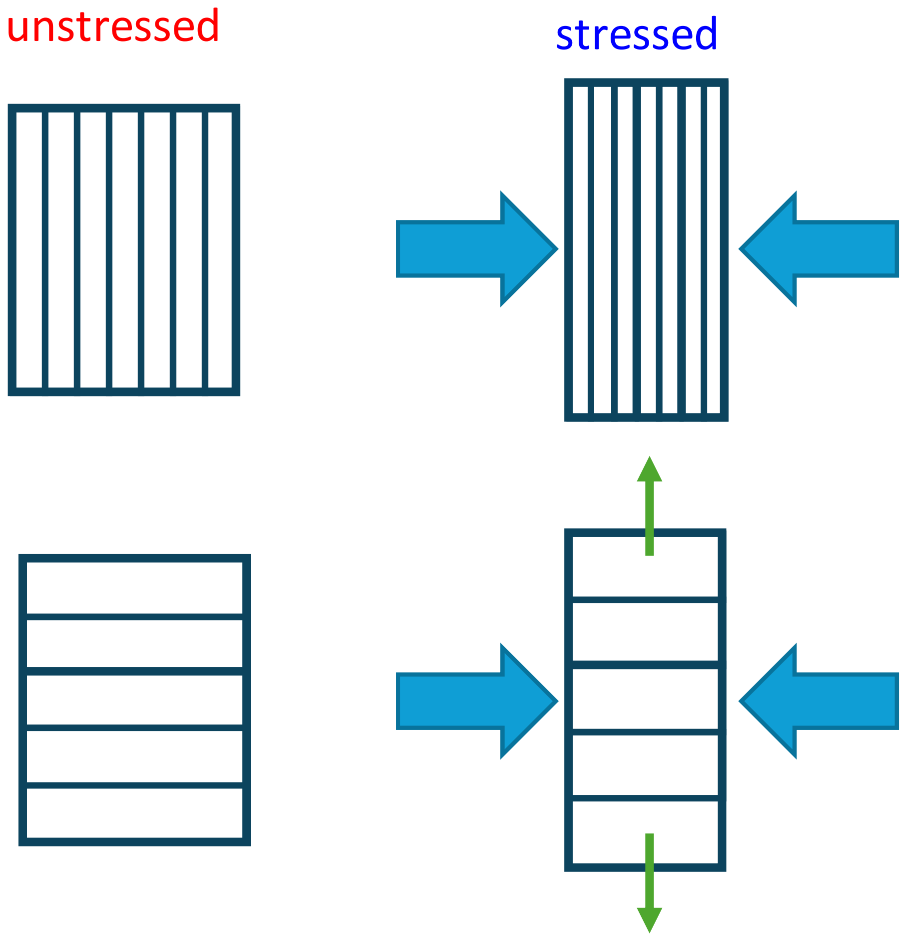


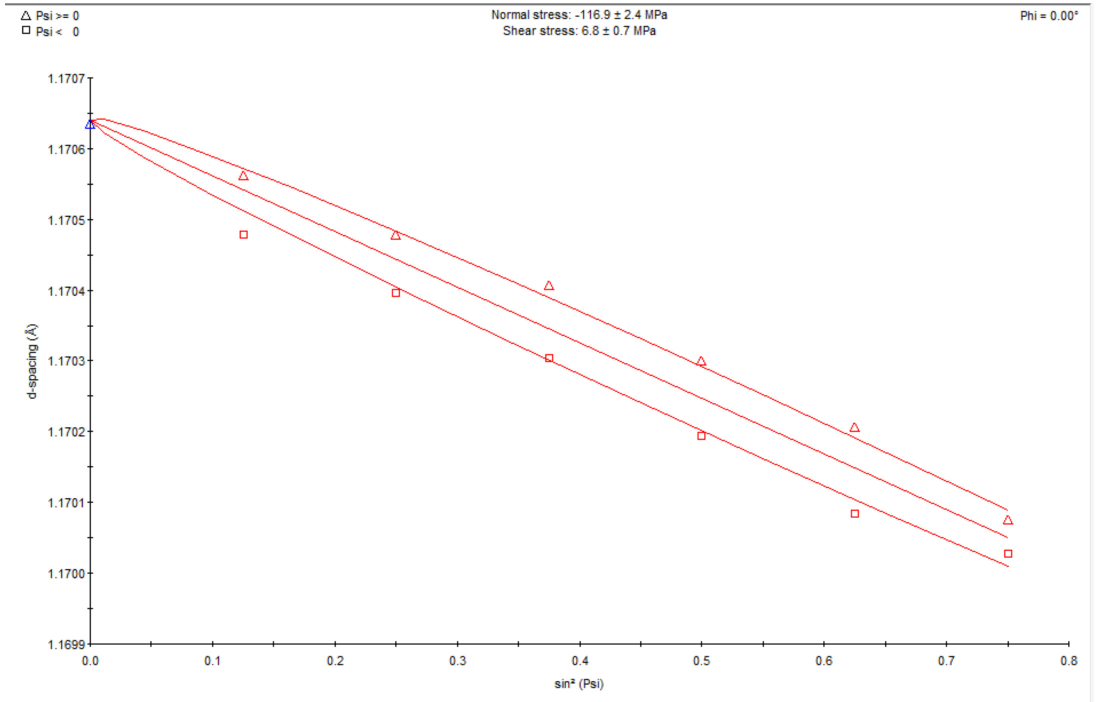
Peak Shift in GIXRD Data



Residual Stress Analysis

Stress analysis using GIXRD data is called "multi-hkl" method. Other methods include side-inclination (chi tilt) and iso-inclination (omega tilt), which measure the shift of one diffraction peak as the sample is physically tilted





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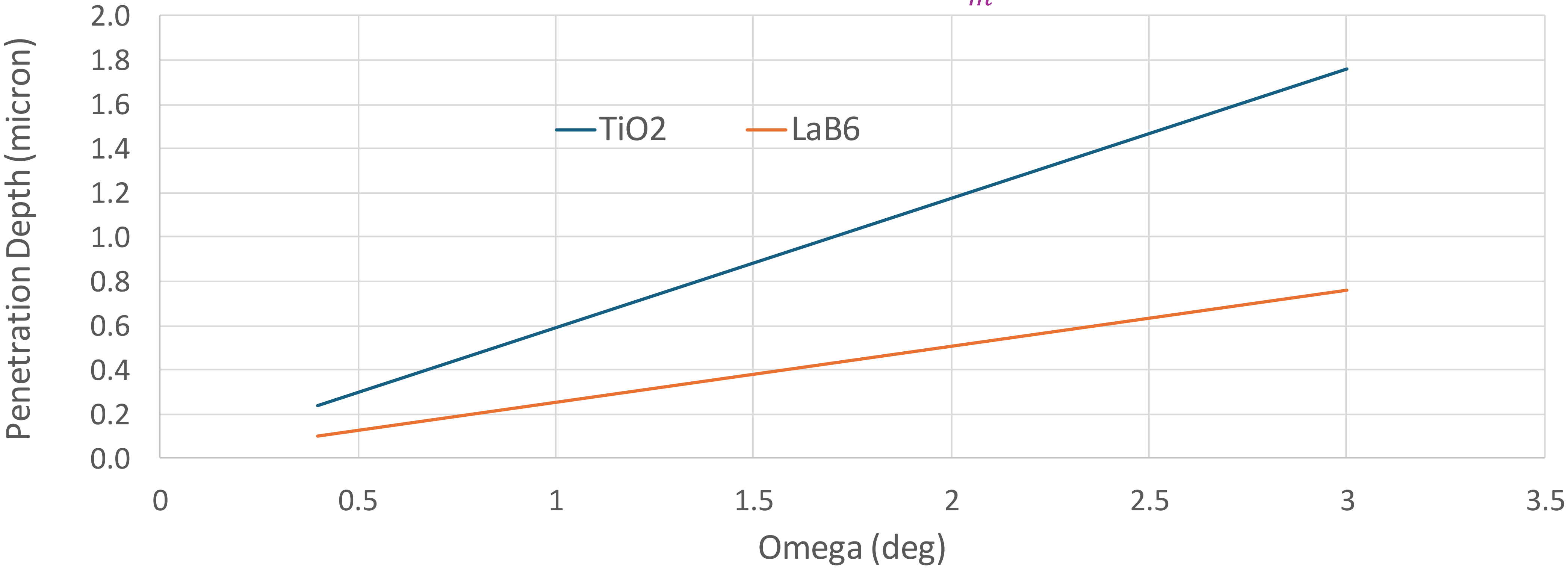
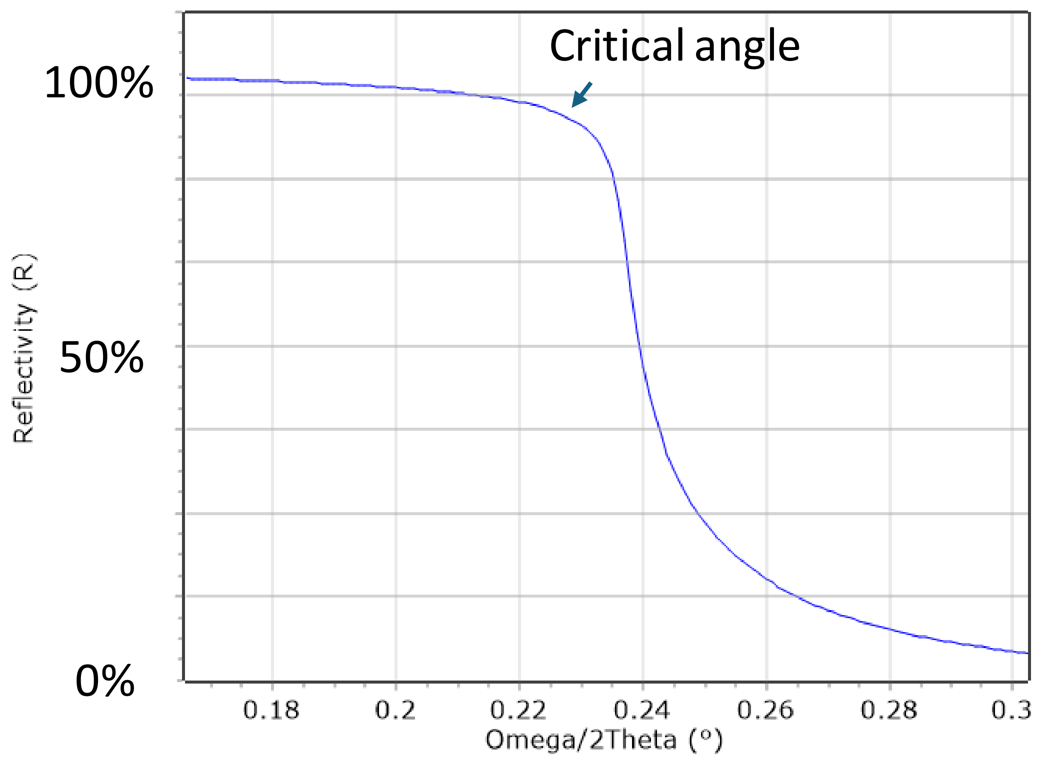
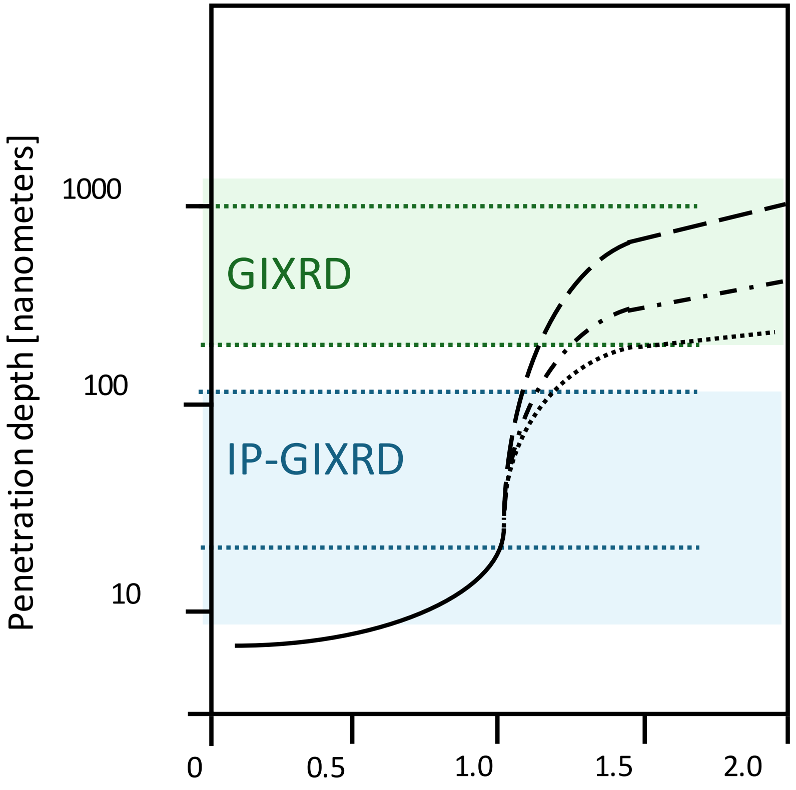


Analysis of *Very* Thin Films

Incident angle near the critical angle of a film will penetrate only nanometers into the film.



Reflectivity Curve

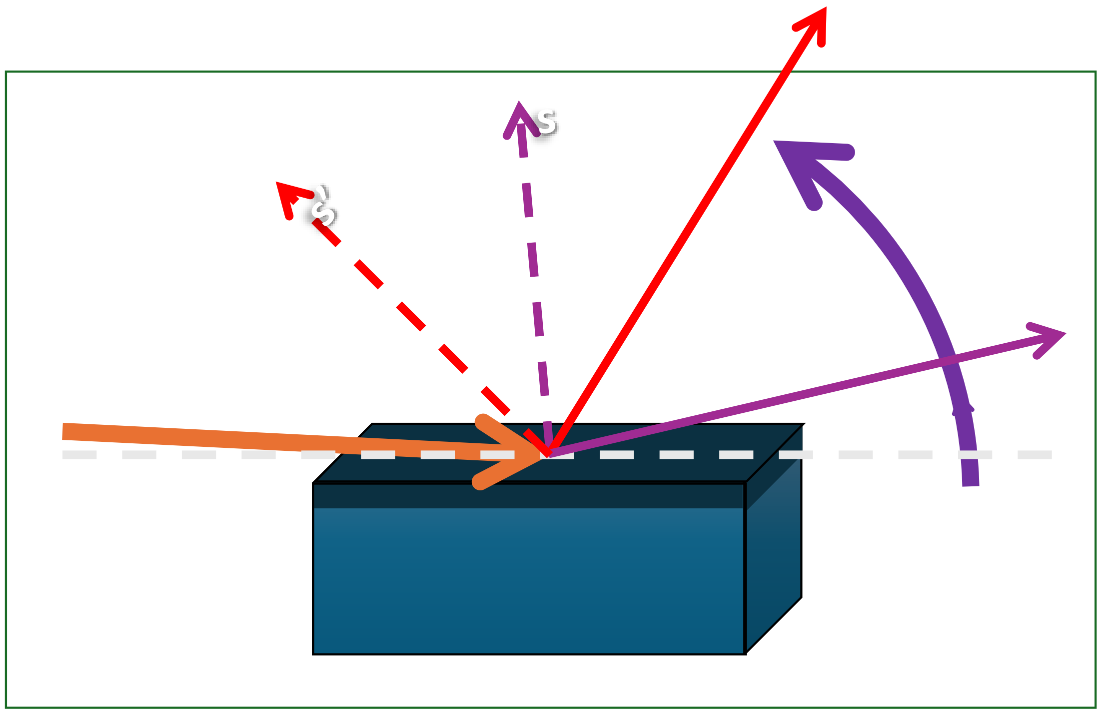


Incident angle {as ω/ϕ_c}

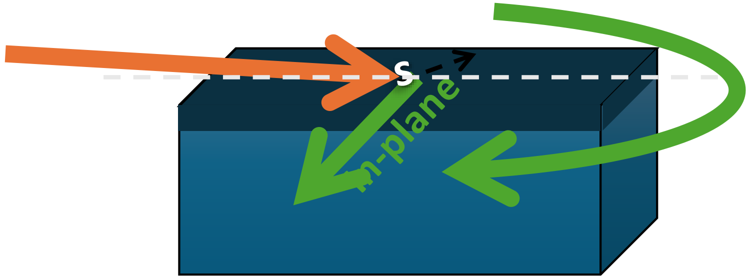
In-Plane Grazing Incidence XRD

When the incident angle is near the critical angle, the greatest signal is diffraction co-planar to the film.

- 'Out of Plane' GIXRD



- In-Plane GIXRD

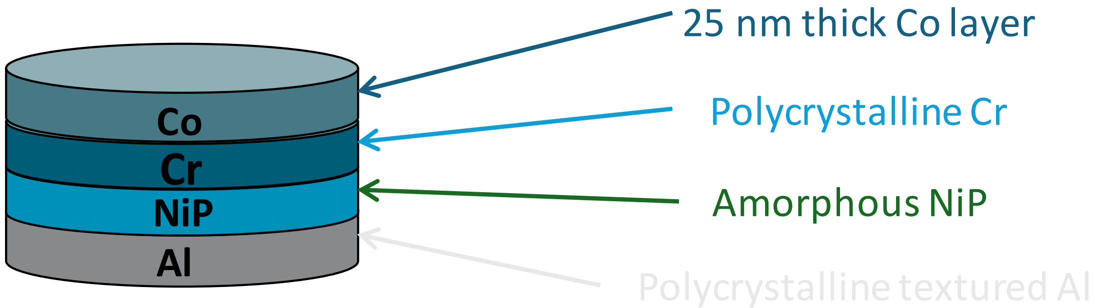


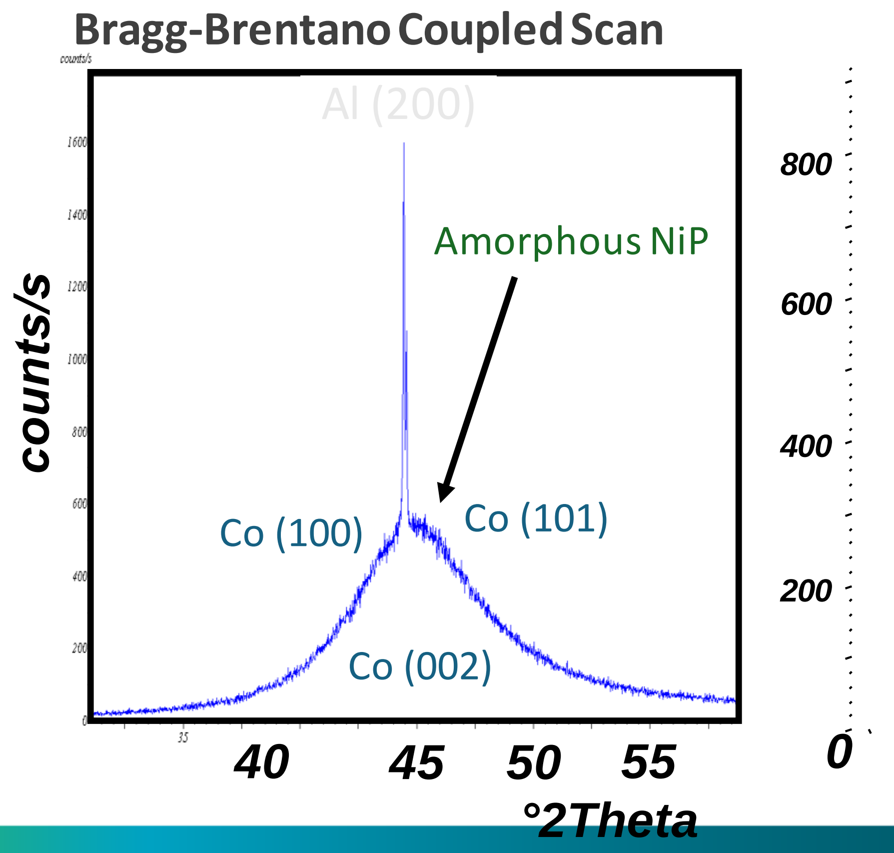
Advantages of GIXRD and In-Plane GIXRD

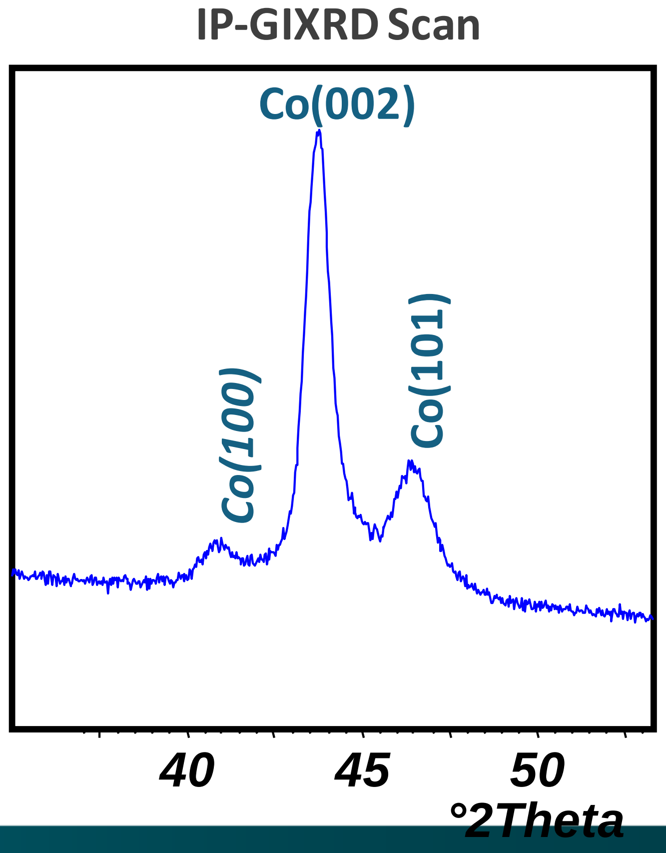
- There are 3 advantages **shared** by GIXRD and IP-GIXRD
  1. Enhance signal from thin films (less than 10 micron thick)
  2. Depth profiling of surfaces and thin films
  3. Minimize diffraction and background intensity from a substrate

- There are 3 **distinct** advantages of the **IP-GIXRD** technique
  1. Enhanced signal from ultra thin films (less than 100 nm thick)
  2. Enhanced measurement of textured thin films, which cannot be measured using GIXRD.
  3. Direct measurement of strain in epitaxial thin films

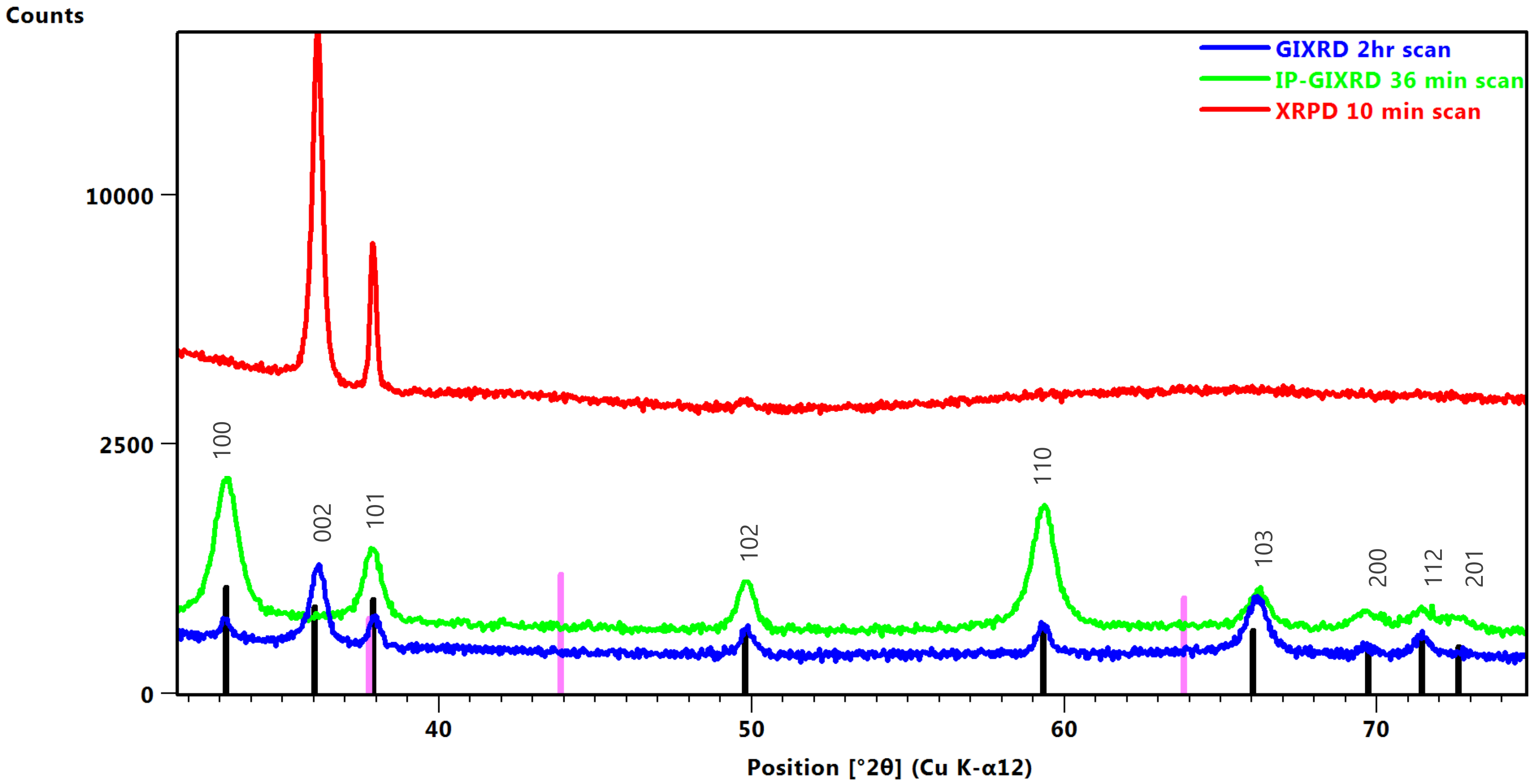
IP-GIXRD of a Hard Disk





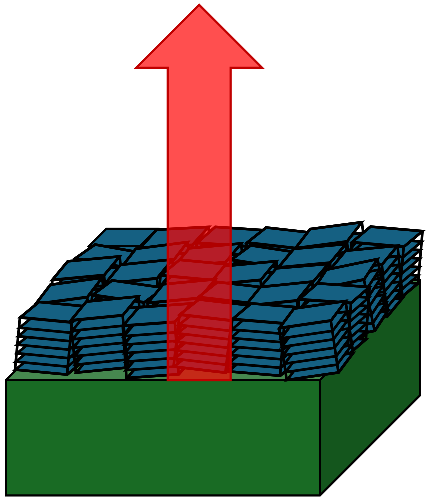


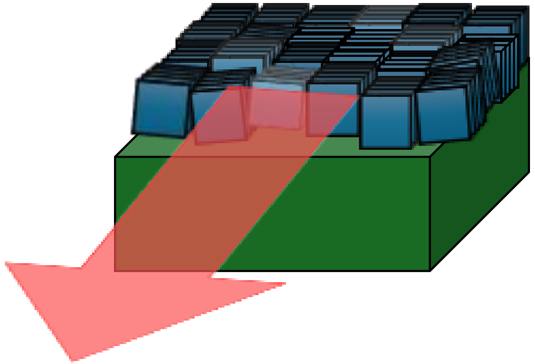
Comparison of methods for analyzing AlN film



IP-GIXRD

IP-GIXRD can measure d-spacing, and therefore calculate lattice parameters, within the plane of the film– which is often strained by the substrate

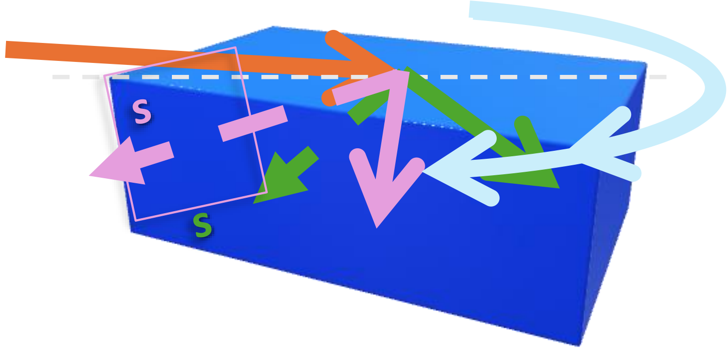


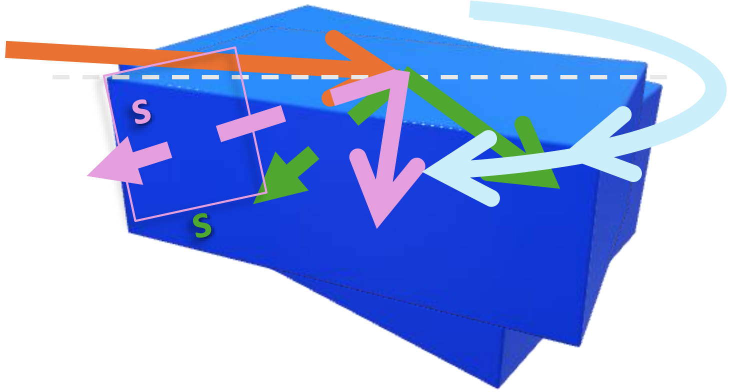


IP-GIXRD

The direction probed by IP-GIXRD can be varied by whether or not the sample rotates with the detector

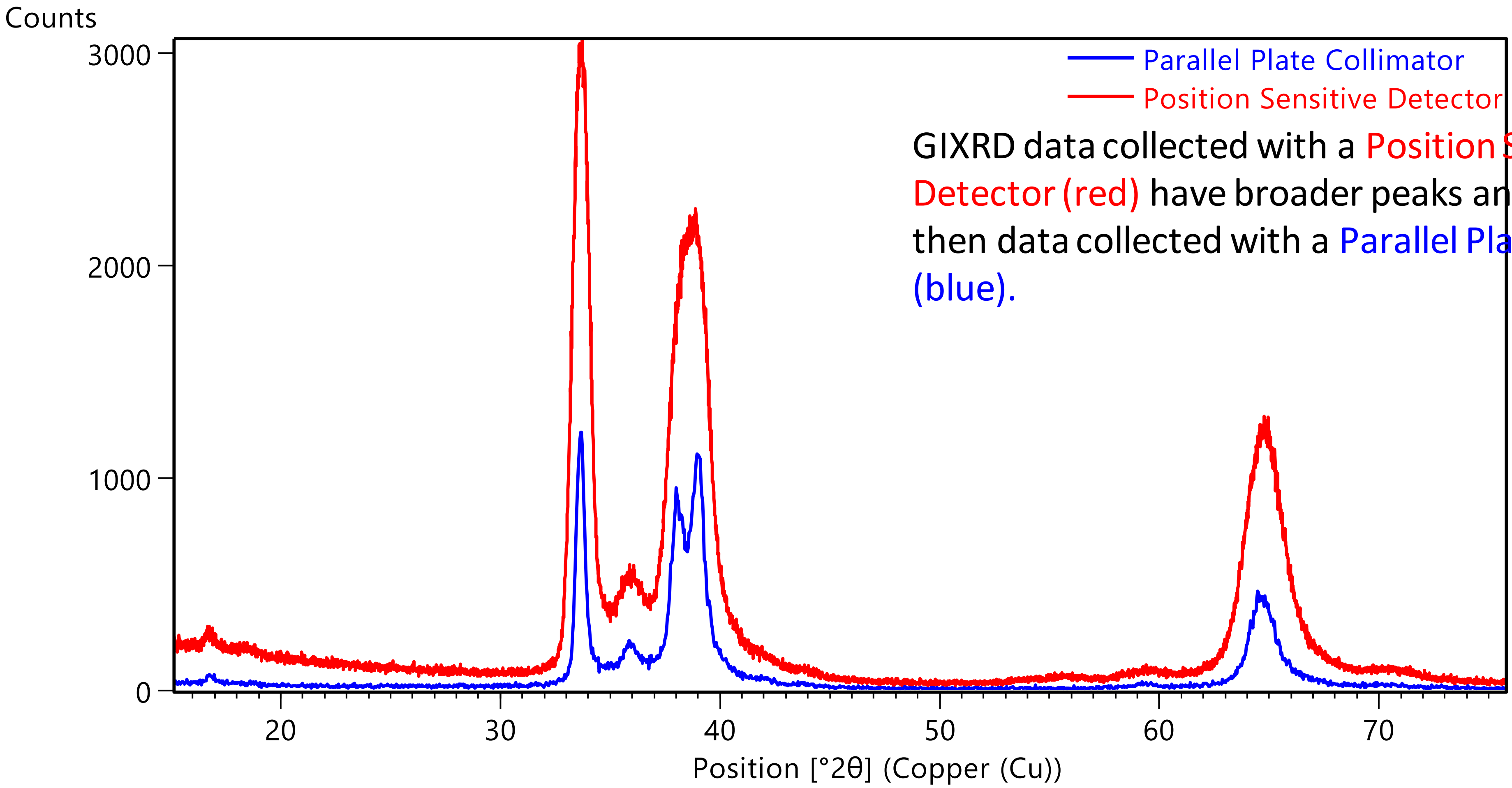
- If the sample is stationary while the detector moves, then the diffraction vector **s** moves with respect to sample orientation
  - This is similar to a out of plane GIXRD
- If the sample rotates with the detector, then the orientation between diffraction vector **s** and sample remains fixed





Grazing incidence X-ray diffraction

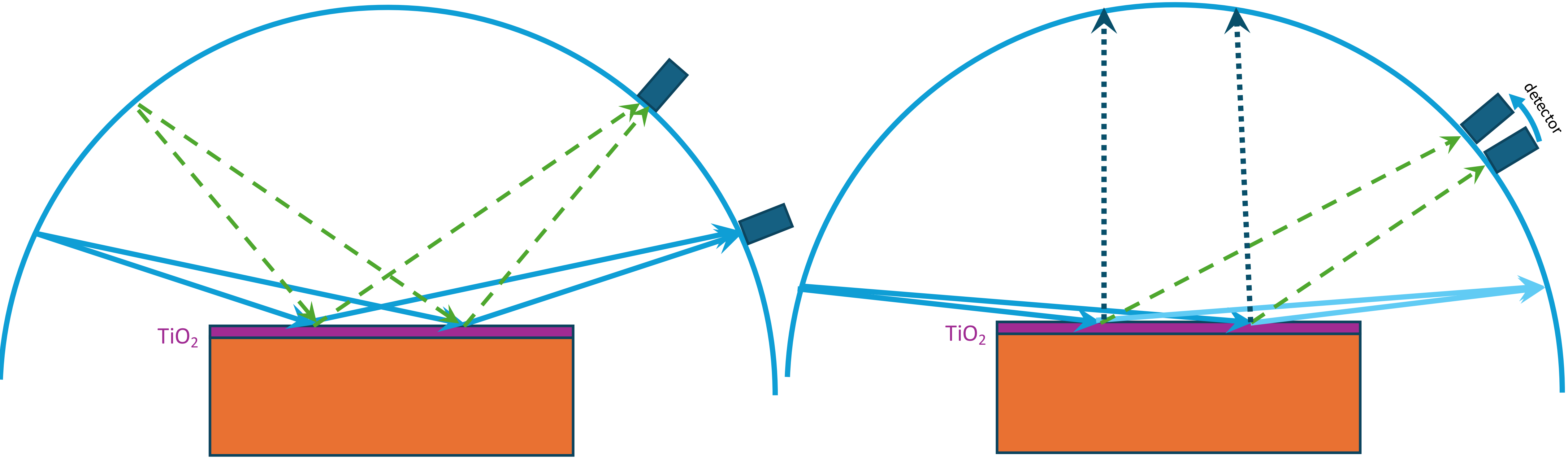
A common mistake is to collect GIXRD data using a 1D position sensitive detector instead of parallel-beam optics.



GIXRD data collected with a Position Sensitive Detector (red) have broader peaks and less resolution then data collected with a Parallel Plate Collimator (blue).

Grazing incidence X-ray diffraction

Why does a position sensitive detector provide poor data in the GIXRD geometry?



Grazing incidence X-ray diffraction

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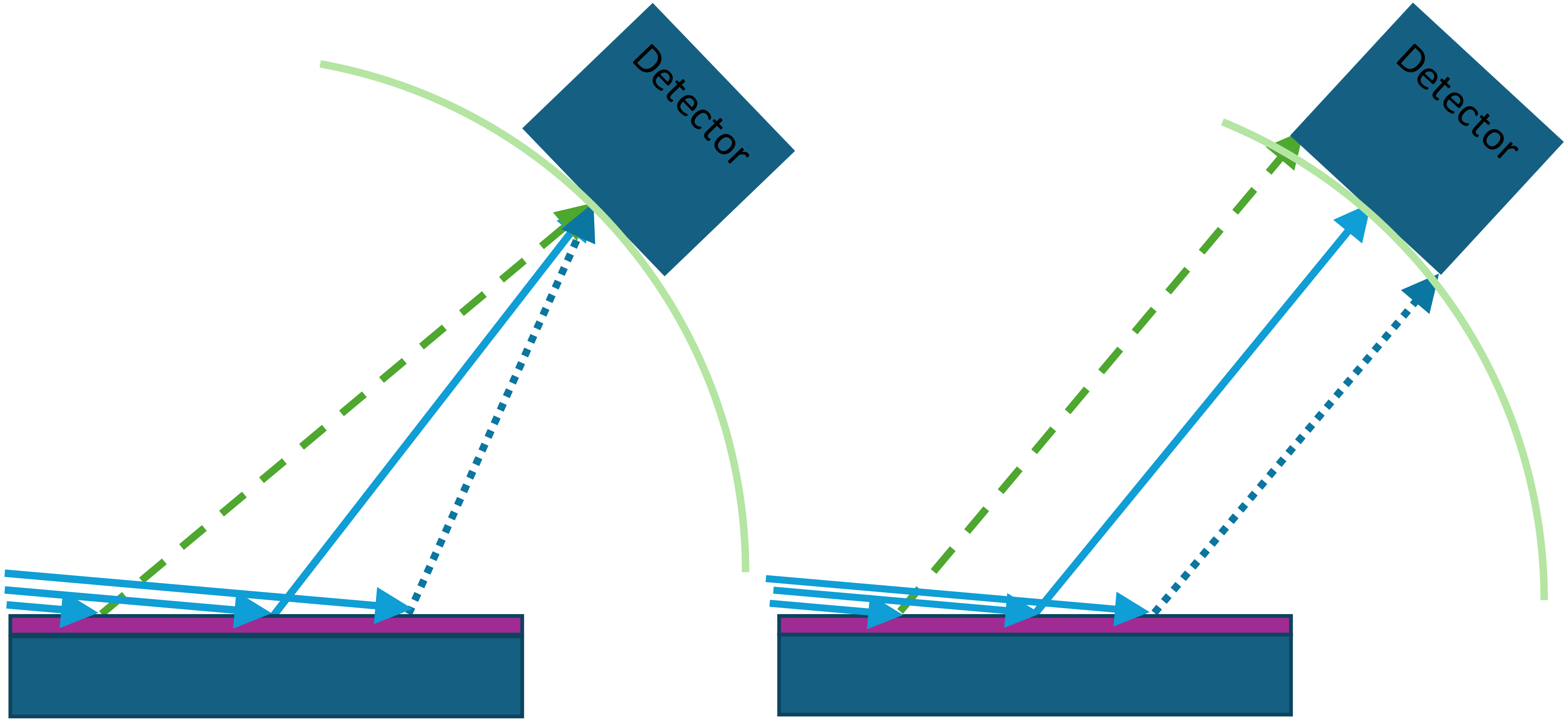
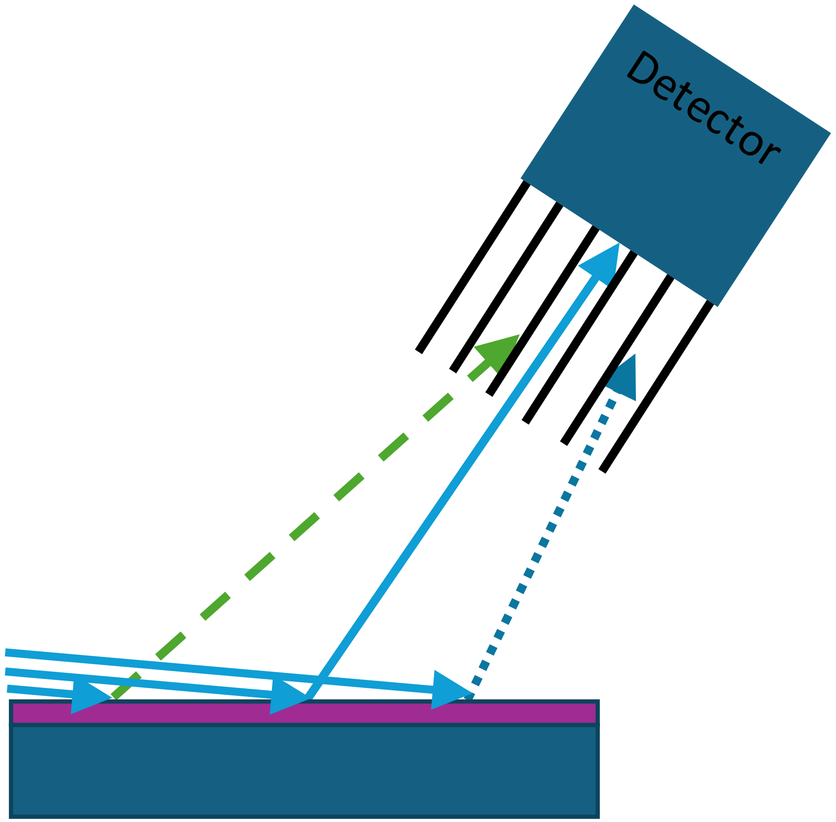
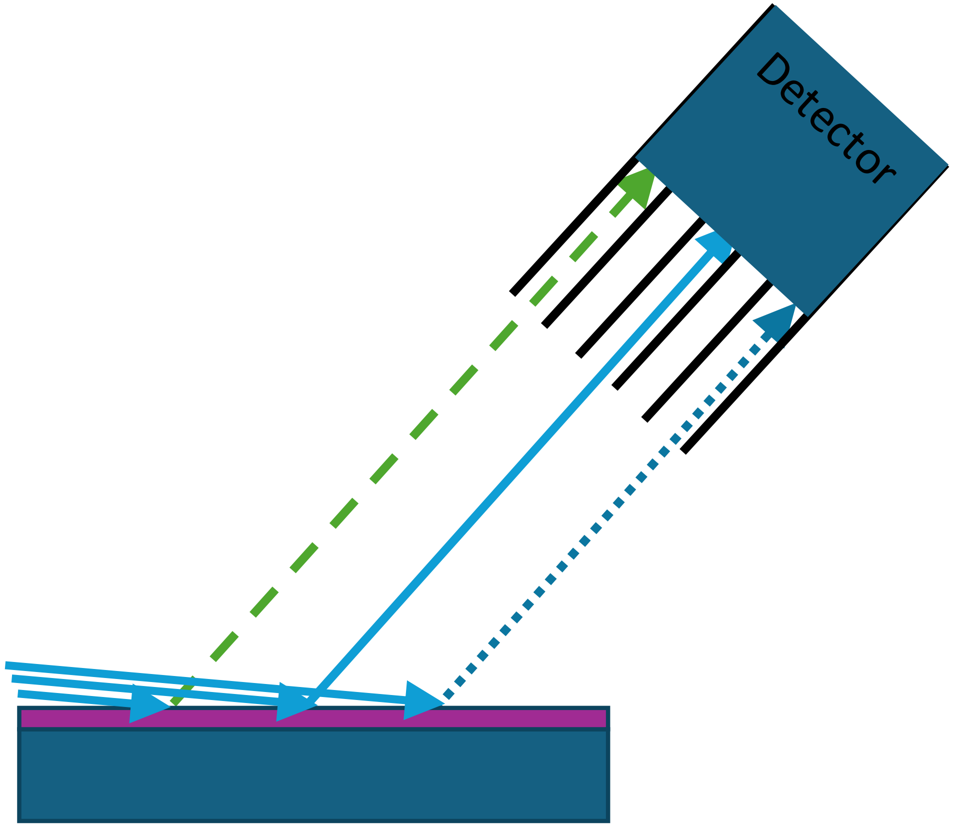


Grazing incidence X-ray diffraction

How does a parallel plate collimator improve GIXRD precision?





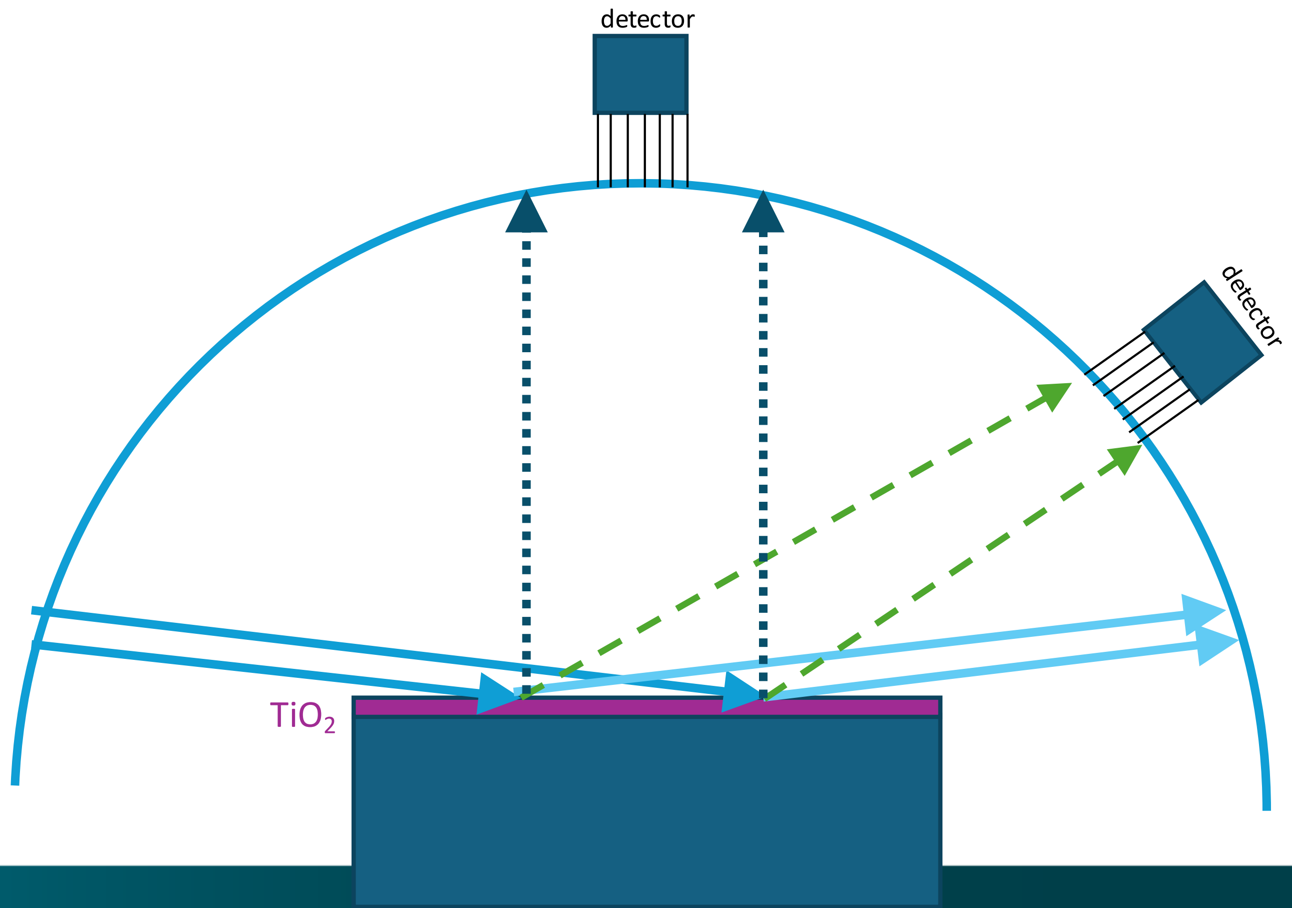
Grazing incidence x-ray diffraction

The X-ray beam footprint should be limited to create a constant observed irradiate volume

- The GIXRD geometry creates a constant irradiated volume because the X-ray beam footprint does not change during the measurement.

- However, as seen in the figure to the right:
    - The height of the scattered X-ray beam changes as a function of 2theta
    - As 2theta approaches 90, the scattered X-ray beam height is equal to the beam length on the sample
    - If the scattered beam height is larger than the collimator or detector, then some scattered X-rays are not observed. This will lead to a loss peak intensity and loss of accuracy.

- The next slide shows equations to calculate the X-ray beam length on the sample and the beam height at the detector.



Grazing incidence x-ray diffraction

Breaking the rules: collecting GIXRD data with a 1D position sensitive detector

- As discussed on slides 15-19, *precise* GIXRD data require a diffracted-beam parallel-beam optic.

- However, as seen in the graph below, GIXRD data collected with a 1D position sensitive detector may have more intensity than data collected with a parallel-plate collimator.
  - There are times when intensity is more important than

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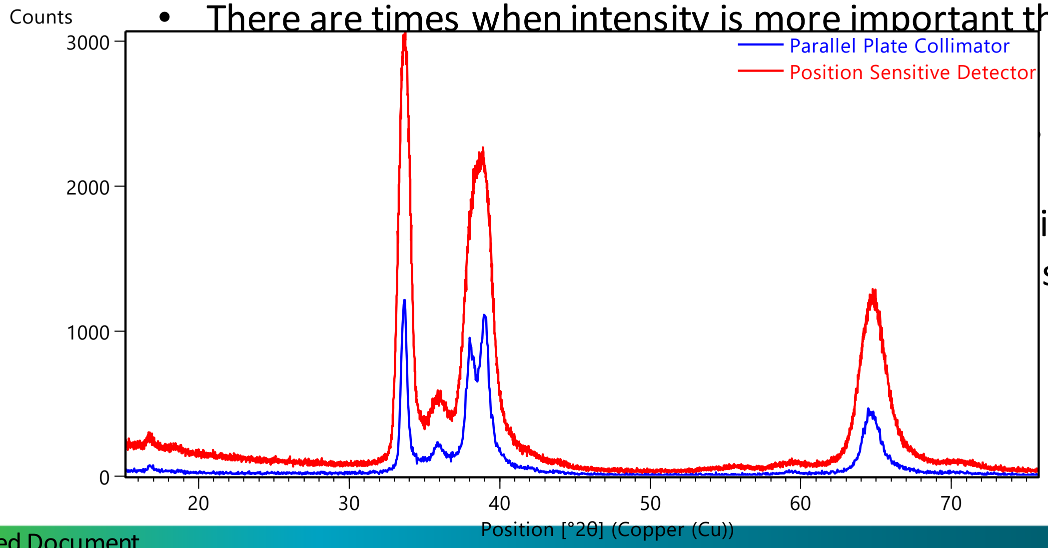
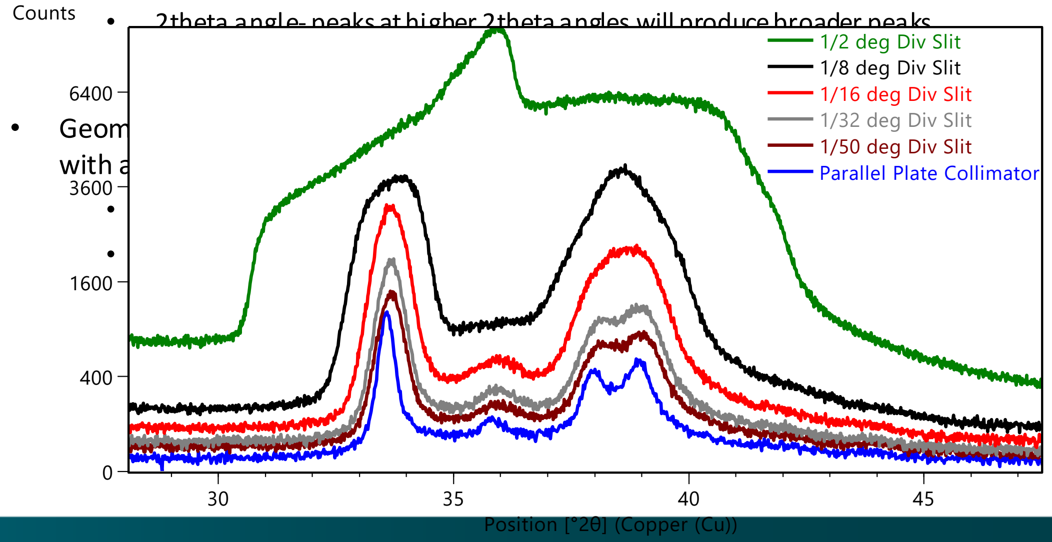


- The graph below compares data collected with different size divergence slits and a 1D position sensitive detector.
  - Precision GIXRD data collected with a parallel plate collimator are shown in blue for comparison.
  - Parallel beam optics also provide more accurate peak positions by eliminating specimen displacement error, accounting for the small peak shift in the data below.

- When using a 1D position sensitive detector, resolution is affected by:
  - Divergence slit- a smaller divergence slit produces sharper peaks
    - The divergence slit generally needs to be 1/8 deg or smaller.
  - Omega angle- a lower omega angle produces broader peaks
  - 2theta angle- peaks at higher 2theta angles will produce broader peaks

- Geom
  with a



Summary

- GIXRD can be used to probe coatings and surfaces
- GIXRD requires* parallel beam geometry
- Bragg-Brentano geometry and GIXRD are *complementary*, not exclusive
- The diffraction vector changes direction during GIXRD