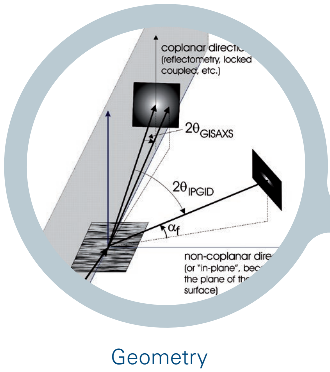
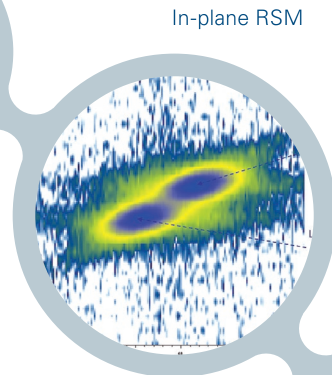
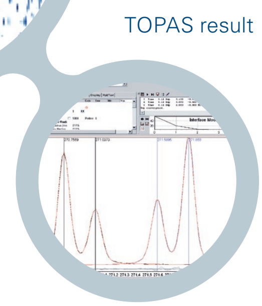





Lab Report XRD 68

# Non-Coplanar or "In-Plane" GID Solutions for Soft Matter and Crystalline Materials

## Introduction

Non-coplanar GID (Grazing Incidence Diffraction) emerged in the early 1990s as a technique for investigating the near-surface region of samples (ten or fewer nm beneath the air-sample interface). It exploits the high intensity of the total external reflection condition while simultaneously Bragg-diffracting from planes that are nearly perpendicular to the sample surface. Figure 1 shows the experimental geometries used for coplanar and non-coplanar or "in-plane" GID. More extensive information about the theory and practice can be found in the review article by Pietsch (Current Science, vol. 78, no. 12, 2000) and in the Bruker AXS Analytical Application Note #377, Laboratory X-ray Diffraction Setup for Studies of Ultra Thin Films and Nanostructures and the references therein. Related techniques include reflectometry and GISAXS (Grazing Incidence Small-Angle X-ray Scattering), as shown in figure 1.

## Questions Answered by Non-Coplanar or "In-Plane" GID

Non-coplanar GID is used for determining information in the plane of the sample surface, which is why it is also referred to as "in-plane" diffraction. In particular, lattice parameters, surface-plane relaxation, texture and crystallite size are among the sample information that can be obtained with GID. Soft matter such as gels, polymers and liquids, single crystals, polycrystalline sheets and powders can be investigated. Particular applications include:

- Polycrystalline materials: Phase ID and lattice parameters, lateral grain size, in-plane preferred orientation.
- Single crystals: in-plane lattice parameter (high accuracy using the bond method), azimuthal orientation of layers with respect to the substrate, evidence of twinning.
- Soft matter: in-plane size and shape of colloids, distance correlation functions, length scales of in-plane density modulations.
- Any other in-plane applications where standard diffraction geometries fail due to lack of scattered intensity

## Instrumentation

Bruker AXS Diffraction Solutions offer two optimized configurations for performing non-coplanar or "in-plane" GID. Both are extensions of commonly configured D8 DISCOVER instruments for thin film and powder applications. For both configurations, the full functionality of the underlying D8 DISCOVER without compromises is included. This means that a wide range of experiments, in addition to the non-coplanar GID measurements, can be performed.

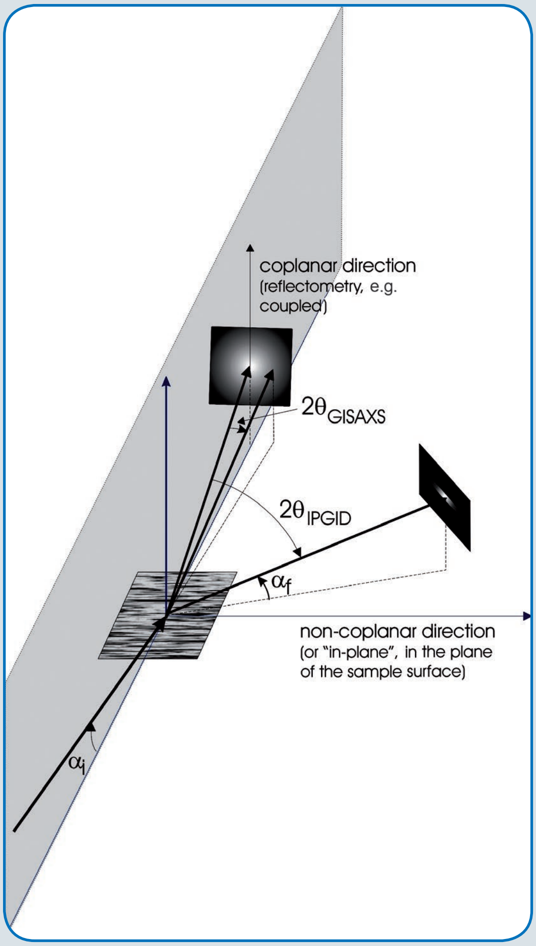



Figure 1: The scattering geometries involved in IP-GID („in-plane“ Grazing Incidence Diffraction), GISAXS, and reflectometry.
$\alpha_i$ = incident angle, commonly in the regime of total external reflection
$\alpha_f$ = exit angle
$\theta$ = diffraction angle

The first configuration, the D8 DISCOVER Ultra-GID, enables switching between coplanar and non-coplanar geometries by changing the orientation of the x-ray tube and sample relative to the detector. With the Ultra-GID configuration, it is also possible to add various types of Ge channel-cut monochromators, enabling high-resolution thin-film measurements. The Ultra-GID is shown in figure 2, and more detailed information is available in the Ultra-GID application note #377.

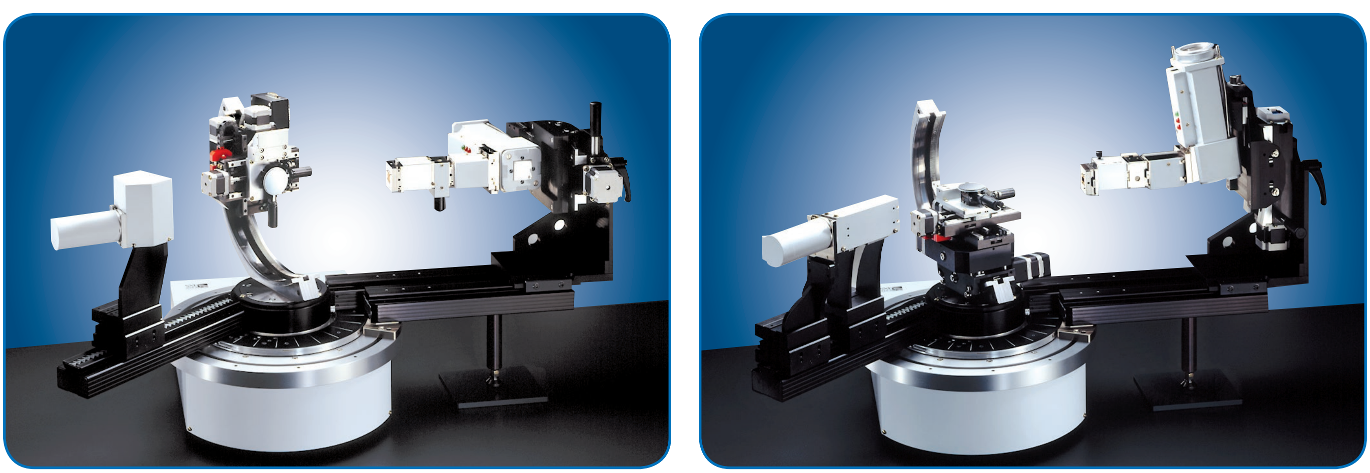


Figure 2: The D8 DISCOVER Ultra-GID, which can be configured for coplanar (left) or non-coplanar („in-plane“) measurements.

The second non-coplanar GID configuration is a dual-goniometer system, with one detector for coplanar measurements and one detector for non-coplanar measurements. Figure 3 shows a dedicated set-up with an Eulerian cradle mounted to the horizontal goniometer, which enables rotation, tilting and surface mapping of the sample. Alternatively, the horizontal goniometer can be used to support relatively bulky troughs for the measurement of liquids. The set-up incorporates a motorized z stage for the height alighment of the trough in combination with an anti-vibration table (not shown). A variety of other sample stages and environments are available as well.

Either the D8 DISCOVER Ultra-GID or the dual-goniometer system offers the following advantages for performing non-coplanar GID:

- Exact positioning of $\alpha_i$, the incident angle.
- Perfect adaptation of the resolution to sample properties.
- Illumination of large sample areas, allowing greater intensity.
- Easy performing of in-plane reciprocal space mapping.

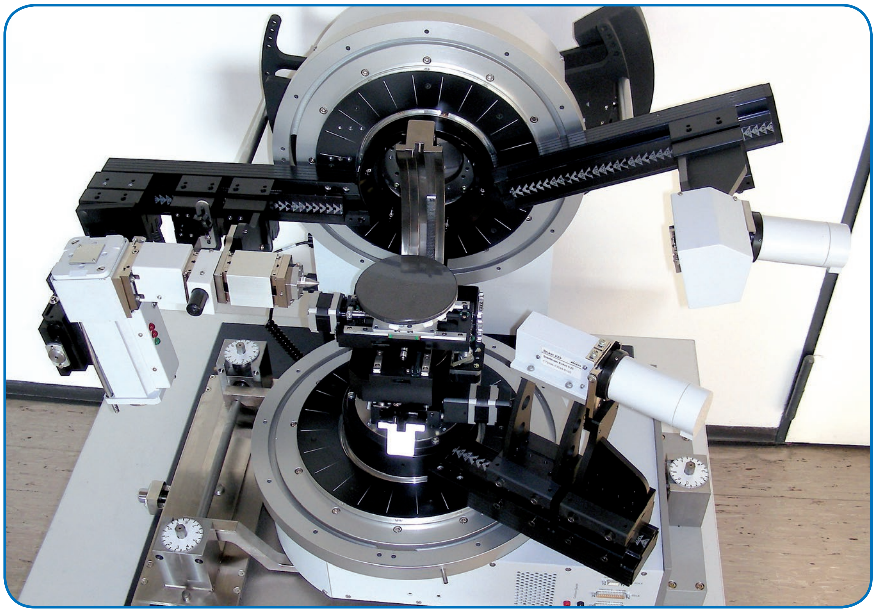


Figure 3: The dual-goniometer system. Shown in this configuration is a Pathfinder for the coplanar measurements, and an equatorial Soller coolimator plus scintillation counter for the non-coplanar or "in-plane" measurements. Incident beam side: line focus X-ray tube, Göbel Mirror, Auto-absorber, 2-bounce channel-cut, pin-hole collimator.

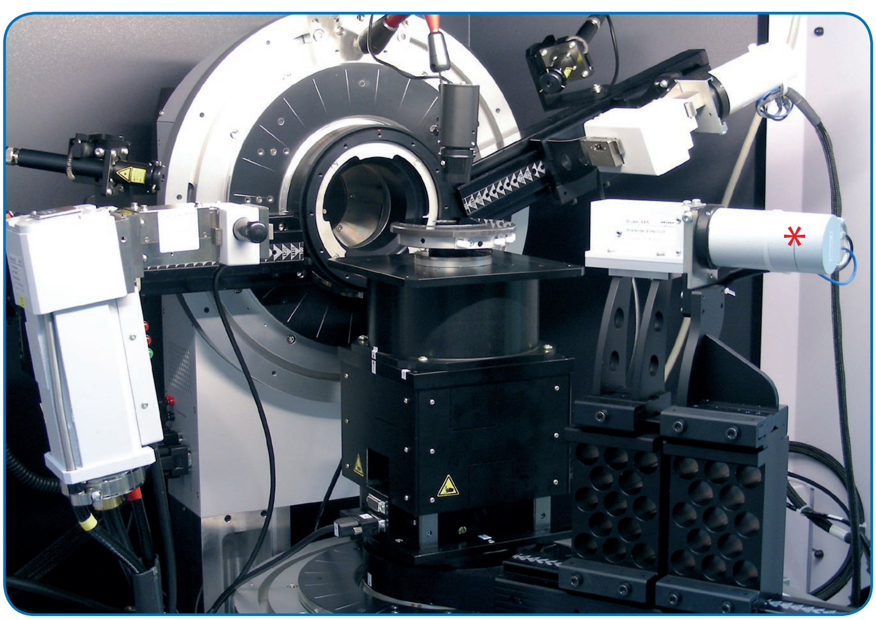


Figure 4: A similar instrument to that shown in Figure 3, with the Eulerian cradle replaced by a Universal Motion Concept (UMC) z-stage. * Note that the detectors can be upgraded to 1-D detector for information in the $\alpha_f$, or vertical direction (refer to figure 1 for the illustration of $\alpha_f$).

## Example Application #1: In-Plane Lattice Parameter of Strained Si

Background: To increase the mobility of the conduction electrons in Si, a thin silicon layer is grown on top of a substrate with a slightly larger lattice constant. This causes the Si-lattice to stretch in the direction along the surface. Non-coplanar GID measures the amount of stretching, as revealed in the angular position of the reflections. In addition, since the substrate signal is quite large, non-coplanar GID is useful for enhancing the relatively small signal coming from the thin, surface Si layer.

| | |
|---|---|
| **Method:** | In-Plane Bond Method (fig. 5) |
| **Source:** | Cu FL sealed tube operated at 1.6 kW |
| **Primary Optics:** | Goebel mirror, rotary absorber, 0.12° equatorial Soller |
| **Sample Stage:** | Vacuum chuck (optional DHS 1100 high-temperature chamber for non-ambient investigations) |
| **Secondary Side:** | 2 NaI scintillation counters |
| **Results:** | $a_{Si, strained}$ = 5.4728 (2) Å ($a_{Si, unstrained}$ = 5.4309 Å) (a = lattice parameter) |

The analysis of the measurement data was done using TOPAS P for profile fitting (fig. 6). The angular difference $\Delta\varphi$ of the reflection measured in both "+" and "–" geometry at very high diffraction angles is used to accurately determine the lattice spacing.

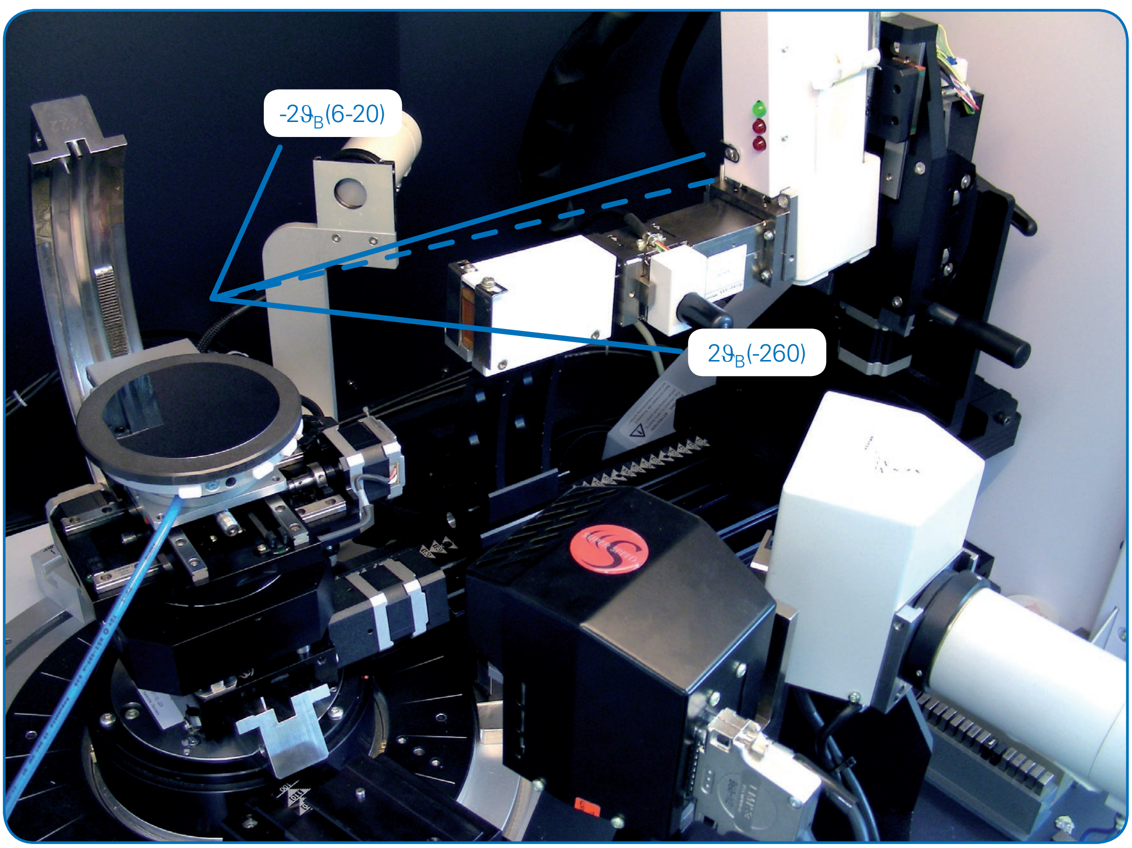
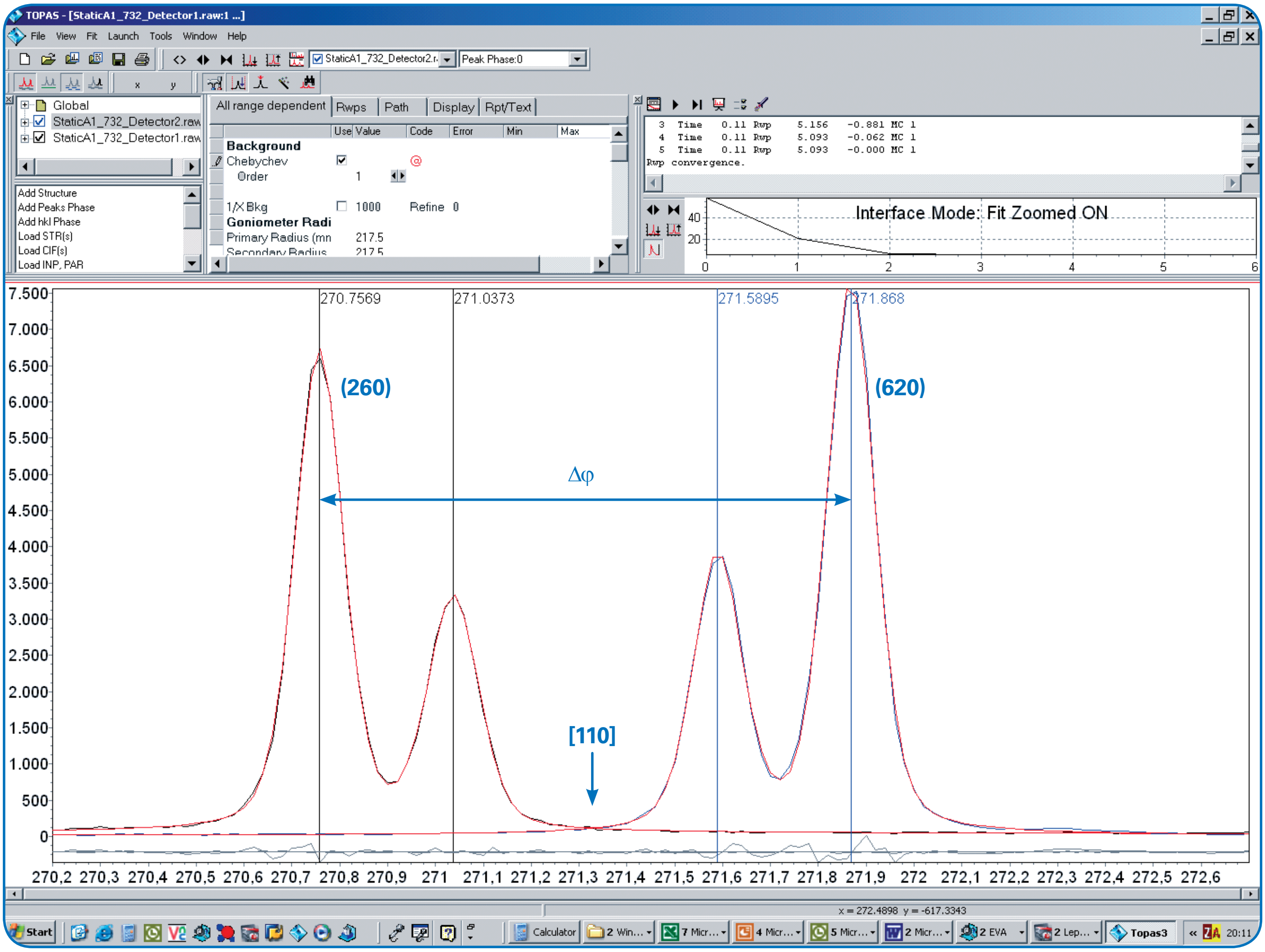



Figure 5: The experimental configuration for measuring strained Si. This is the in-plane Bond method, with two scintillation counters.




$\theta_{(620)} = \pi/4 + \mathrm{Arctan}(1/3) - \Delta\varphi/2$

Figure 6: The analysis for the in-plane Bond method.
Black line: measurement results
Red line: TOPAS P fit results
Bottom black line: difference plot

### Example Application #2: In-Plane Reciprocal Space Mapping

Background: Reciprocal space mapping is commonly used to measure the relaxation, tilt and mosaicity of a layer with respect to the substrate. The grazing incidence geometry can be used to 1) enhance the amount of signal from the layer, and 2) measure direction-dependent changes in the plane of the sample surface.

| | |
|---|---|
| **Method:** | Looped scans in angular space |
| **Source:** | Cu FL sealed tube operated at 1.6 kW |
| **Primary Optics:** | 60 mm Goebel mirror, rotary absorber, 0.35° equatorial Soller |
| **Sample Stage:** | Small goniometer head (optional motorized tilt stage) |
| **Secondary Optics:** | 0.35° equatorial Soller, NaI scintillation counter |
| **Results:** | The in-plane lattice constants of LSMO can be obtained. |

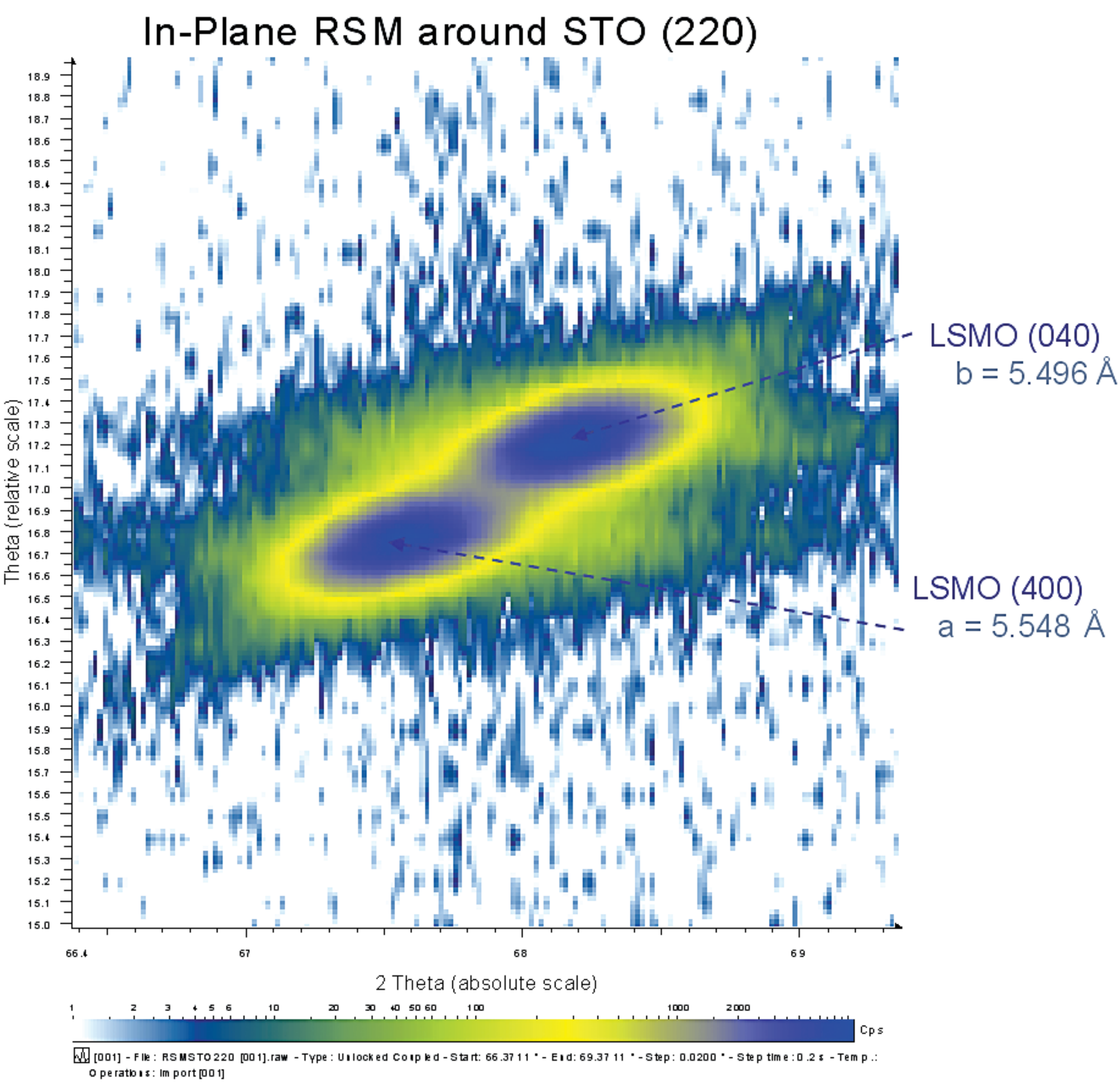



Figure 7: The reciprocal space map in the vicinity of the 220 reflection of LSMO ($LaSrMnO_3$) on STO ($SrTiO_3$) shows two domains due to orthorhombic symmetry.

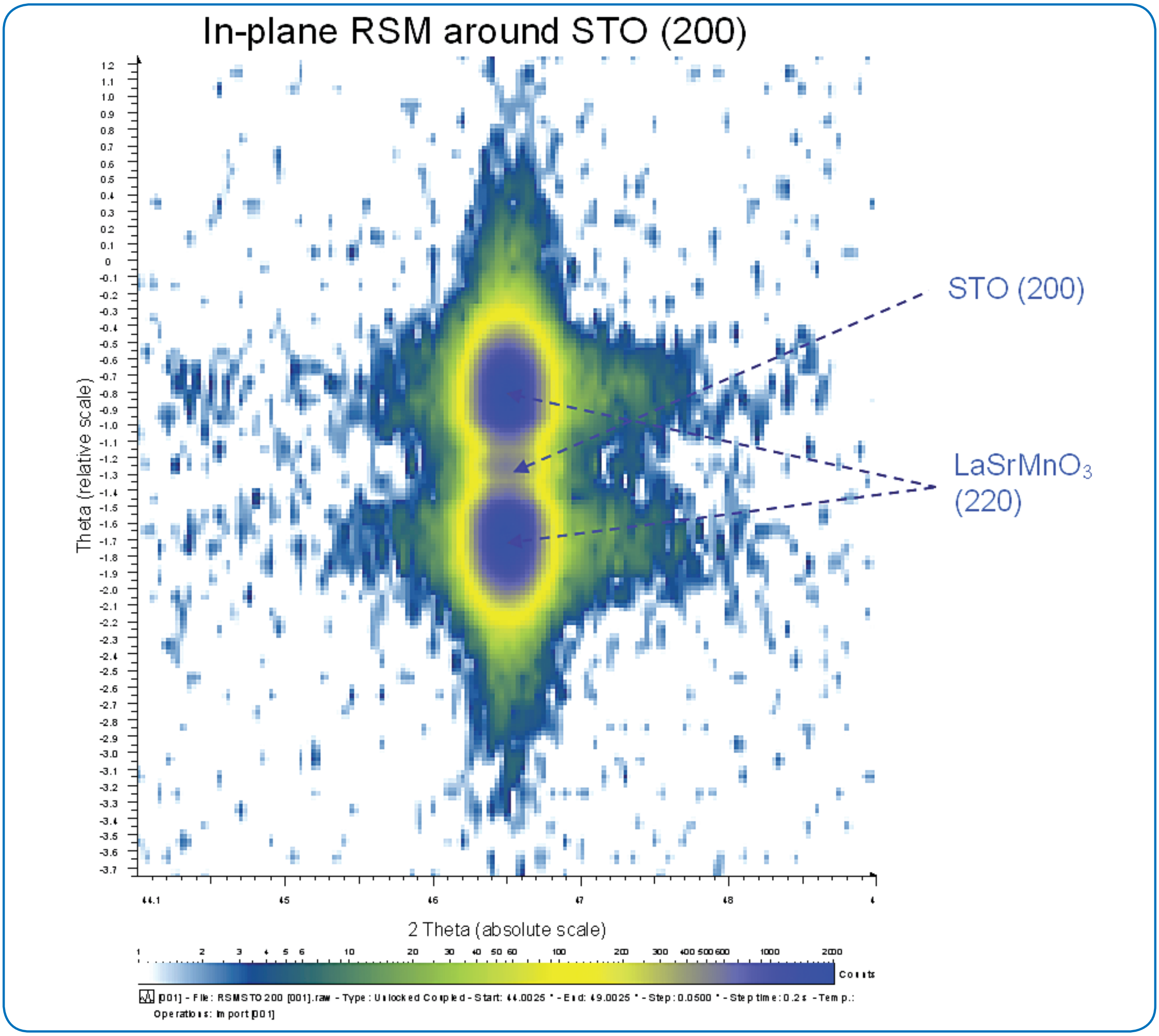



Figure 8: The reciprocal space map in the vicinity of the 200 reflection. Note that the layer reflection intensity is much greater than that of the substrate.

## Example Application #3: GISAXS on Porous Si

Background: GISAXS (Grazing Incidence Small-Angle X-ray Scattering) is a measurement technique that can be performed with the two instruments discussed in this report, the Ultra GID and the dual-goniometer system.

| | |
|---|---|
| **Method:** | Evaluate the scattering around the specularly reflected beam, in the "in-plane" or non-coplanar direction. This is the direction perpendicular to the direction explored in a reflectometry experiment. |
| **Source:** | Cu FL sealed tube operated at 1.6 kW |
| **Primary Optics:** | Goebel mirror, rotary absorber, 0.12° equatorial Soller |
| **Sample Stage:** | Centric Eulerian cradle with small goniometer head attachment (2 rotation arcs) |
| **Secondary Optics:** | 0.12° equatorial Soller, NaI scintillation counter |
| **Results:** (evaluation shown in figure 9)<br>Particle radius: 12.2 Å<br>Sigma of size distribution: 12.4 Å<br>Hard-Sphere particle radius: 10.2 Å<br>Hard-Sphere volume fraction: 0.65 | |

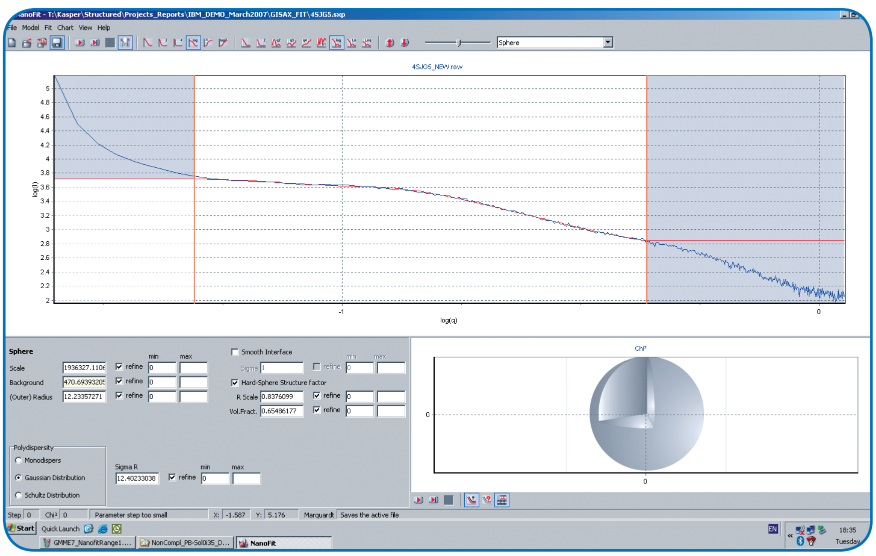


Figure 9: Nanofit results of the GISAXS data for porous Si.

## Conclusion

With the addition of a few components, the modularity and flexibility of the D8 DISCOVER platform was utilized to make two optimized configurations for IP-GID and GISAXS. For both configurations, the full functionality and flexibility of the underlying D8 DISCOVER without compromises is included. This was shown by the variety of sample stages (Eulerian cradle or UMC), detectors (LYNXEYE, scintillation and others) and primary optics (soller slits or Ge channel-cut monochromators).

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