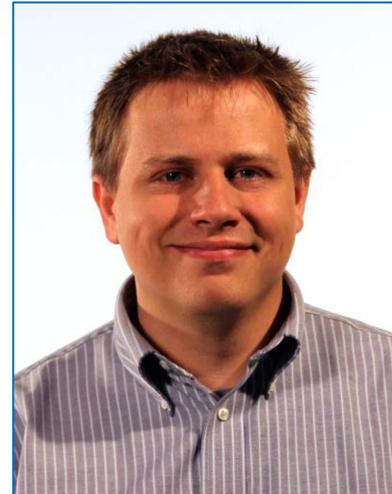
Good Diffraction Practice Webinar Series

Innovative 2D XRD Applications in Materials Science
June 4, 2013

www.bruker-webinars.com

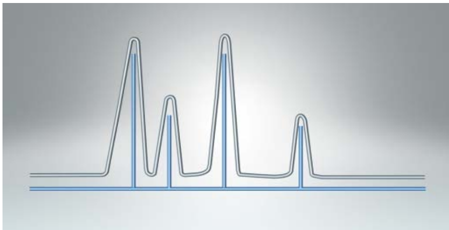
Welcome

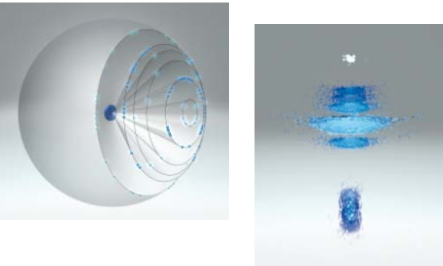
Dr. Brian Jones
Product Manager - XRD
Bruker AXS Inc.
Madison, Wisconsin, USA
brian.jones@bruker-axs.com
+1.800.234.9729

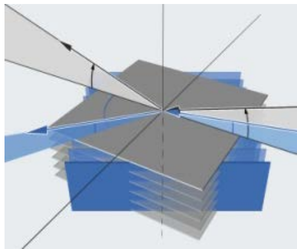


Jon Giencke
Applications Scientist - XRD
Bruker AXS Inc.
Madison, Wisconsin, USA
jon.giencke@bruker-axs.com
+1.800.234.9729

Topics to be discussed







Introduction to XRD^2

- What is XRD^2
- Instrument Effects on XRD^2 Resolution

Traditional XRD^2 Techniques

- Enhanced Phase Identification
- Residual Stress
- Texture

Innovative XRD^2 Techniques

- Quantitative Phase Analysis with XRD^2 (Retained Austenite)
- Gamma Profile Analysis for Crystallite Size
- Single Crystal Orientation Analysis via Laue Diffraction
- Rapid X-ray Reflectometry with XRD^2
- Surface Diffraction with XRD^2
- Large Scale Rapid Reciprocal Space Mapping

What is XRD❷?

Information from a 0D detector

What is XRD❷?

Information from a 1D detector

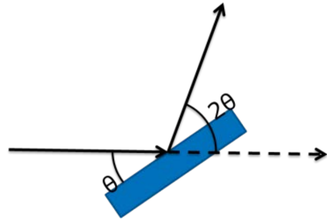
The **SAME** information, just faster!

What is XRD❷?

Information from a 2D detector

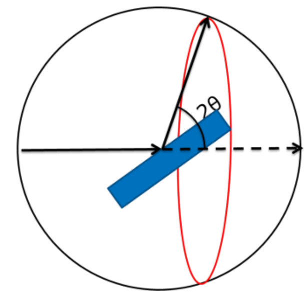
What is XRD❷?

Origin of Debye Rings



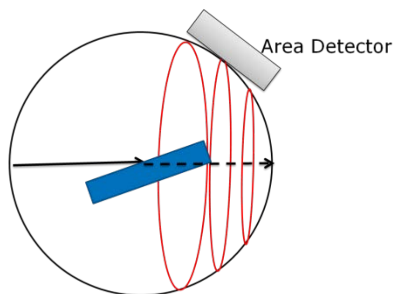
Bragg's Law

- $\lambda=2d\sin\theta$
- In a sample with discrete "d", we have discrete peaks
    - Discrete "d" = "Crystalline", Random "d" = "Amorphous"
- Due to "crystallography", there are many unique "d" present



Debye Rings

- If you rotate the sample, the same "d" still exists
- As 2θ approaches 90°, the Debye ring gets bigger!
- If you include the 2θ "arm", you can see a "Debye Cone"



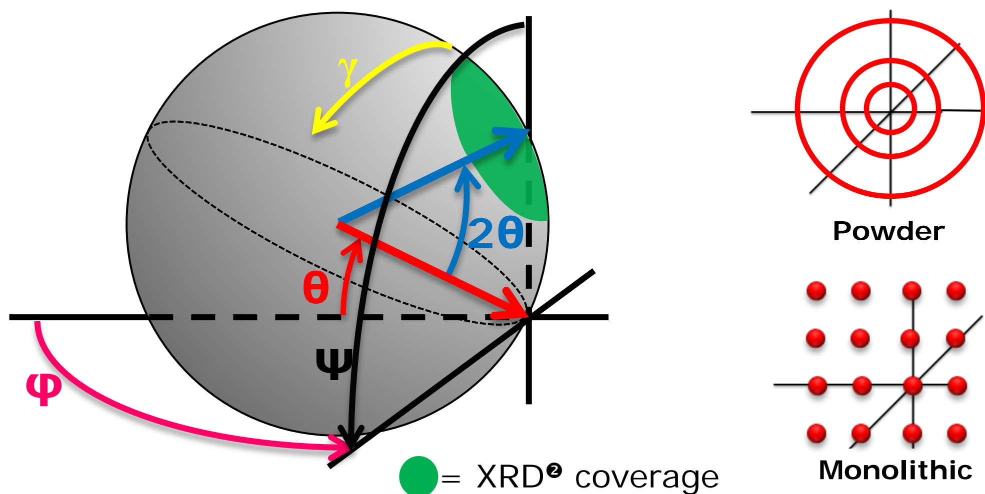
Area Detector

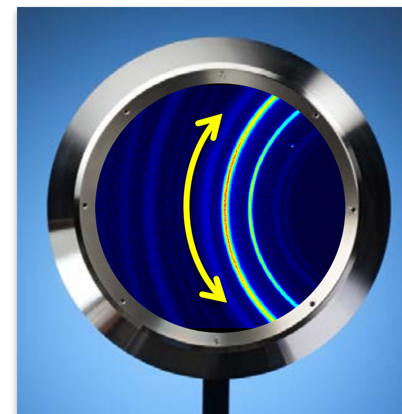
- The detector is a constant size, so its "tilt" coverage changes
- Due to geometry, this tilt is not the sample tilt "Psi", it is **Gamma**
- The larger the area detector, the greater the Gamma coverage

What is XRD²?

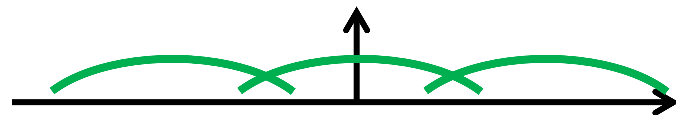
XRD² with a Four Circle Diffractometer

Ewald Sphere Construction of XRD²





Can you expand γ coverage with Ψ? No.

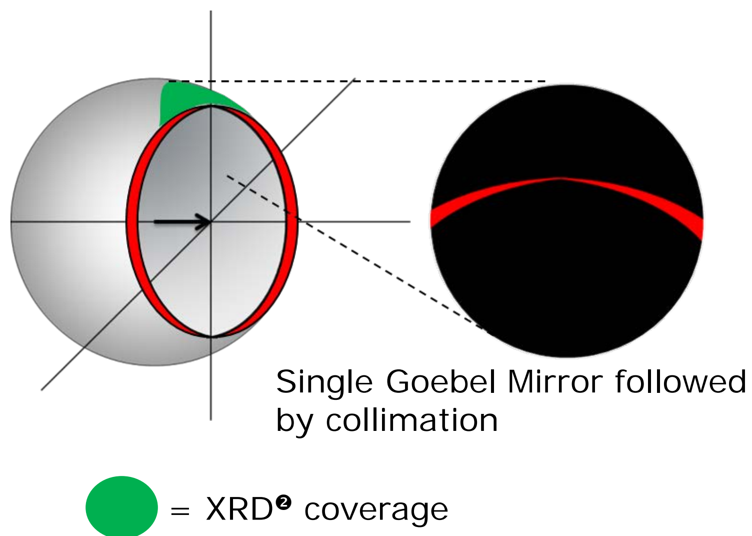


Physical detector size = Gamma coverage

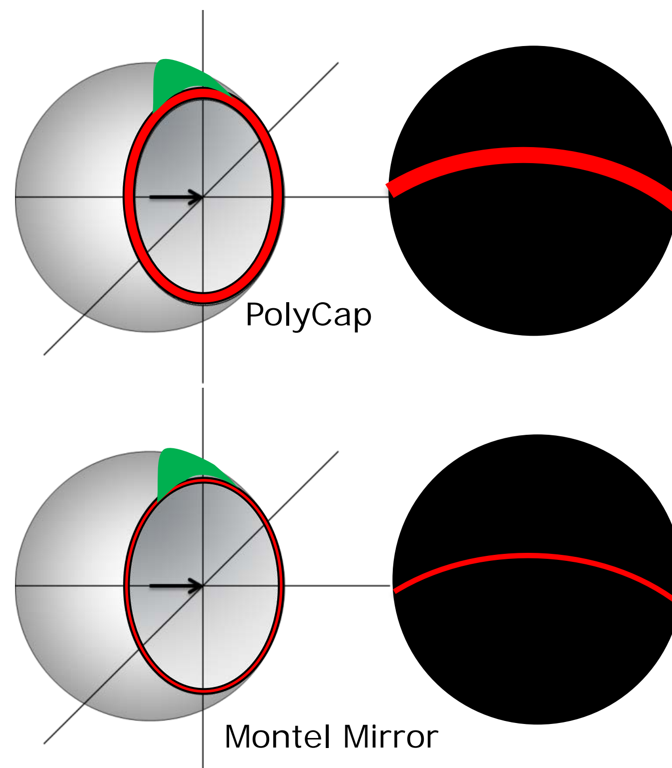
Instrument Effects on XRD² Resolution

Primary Optic Divergence

Line Focus Source

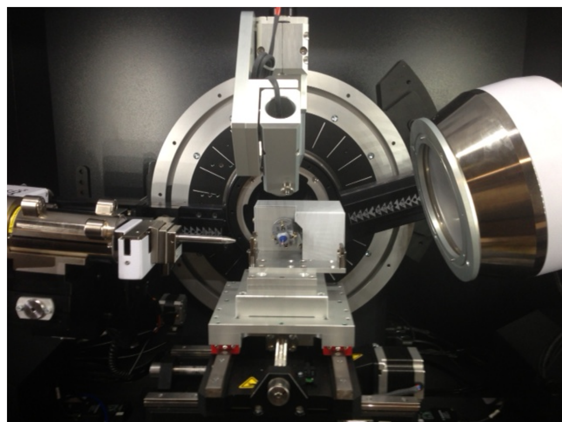


Point Focus Source



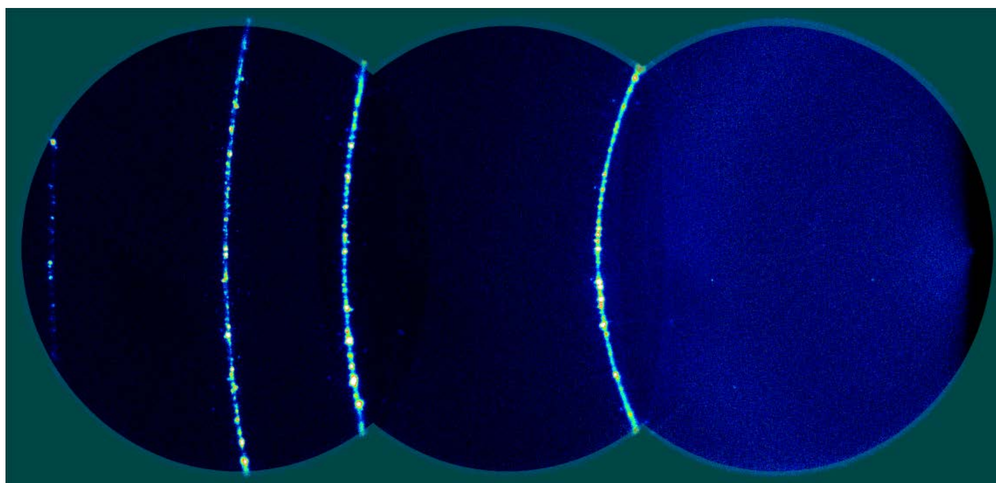
Instrument Effects on XRD² Resolution

Primary Optic Divergence

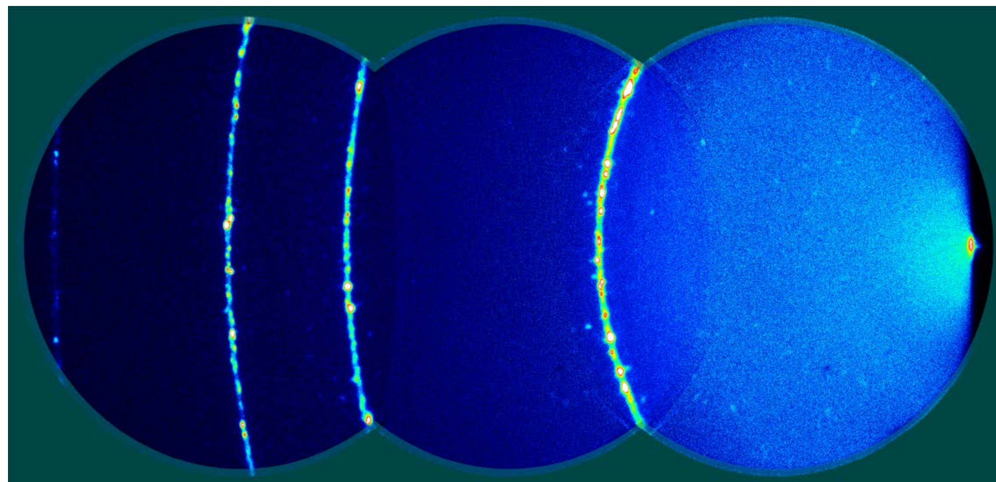


Configuration:

- Si Powder in a Capillary
- 0.5 mm Collimator
- 3 Frames, 10 min each



Montel



PolyCap

Instrument Effects on XRD² Resolution

Coverage versus Detector Distance

Angular Coverage (2 Theta)

140
120
100
80
60
40
20
0

50 100 150 200 250 300 350 400

Detector Distance (mm)

Corundum

AgBh

Instrument Effects on XRD² Resolution

Resolution versus Detector Distance

0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00

FWHM of First AgBh Peak

50 100 150 200 250 300 350 400

Detector Distance (mm)

500 micron beam size

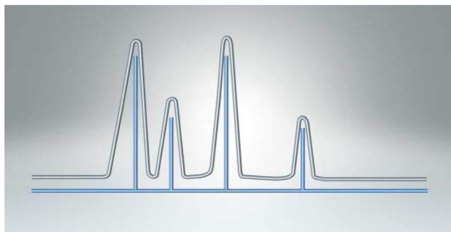
AgBh
500 µm Collimator
Detector Distance

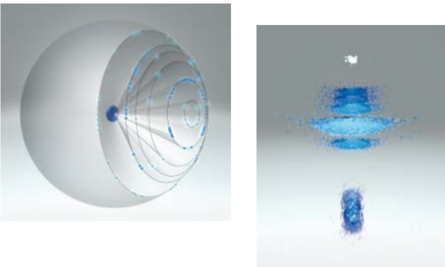
Instrument Effects on XRD² Resolution

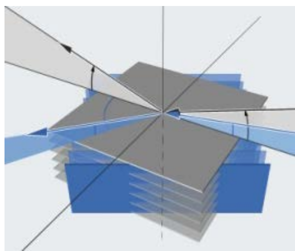
For the best results, the **whole system** should be optimized for the application!

- **Primary Optic**
  - Intensity vs Resolution
  - Monochromaticity vs Intensity vs Resolution
- **Detector**
  - Coverage vs Resolution

Topics to be discussed







Introduction to XRD^2

- What is XRD^2
- Instrument Effects on XRD^2 Resolution

Traditional XRD^2 Techniques

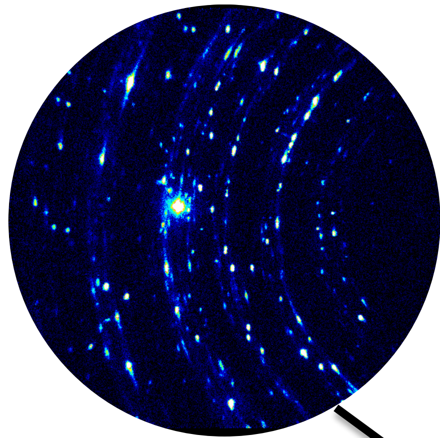
- Enhanced Phase Identification
- Residual Stress
- Texture

Innovative XRD^2 Techniques

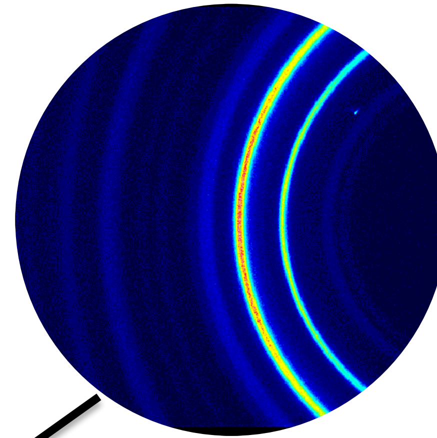
- Quantitative Phase Analysis with XRD^2 (Retained Austenite)
- Gamma Profile Analysis for Crystallite Size
- Single Crystal Orientation Analysis via Laue Diffraction
- Rapid X-ray Reflectometry with XRD^2
- Surface Diffraction with XRD^2
- Large Scale Rapid Reciprocal Space Mapping

Traditional XRD❷ Techniques

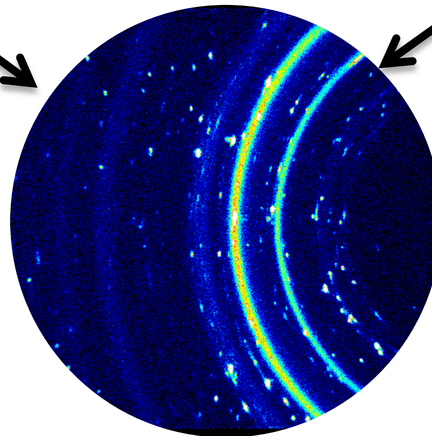
Enhanced Phase Identification



Inactive Filler



Active Ingredient

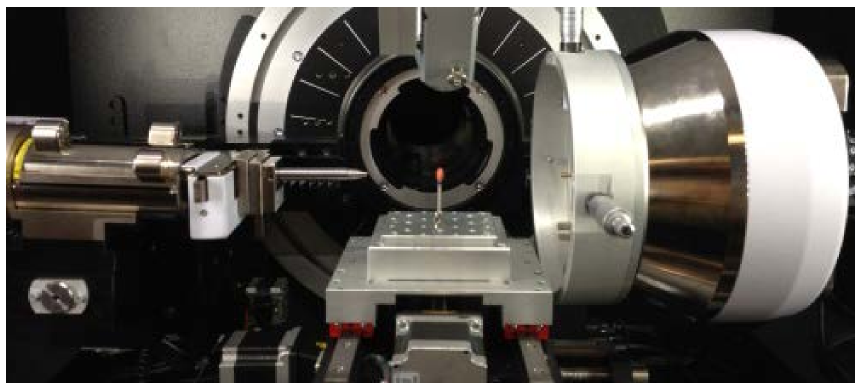


Mixed Product

Peaks can be associated with Debye Ring morphology!

Traditional XRD² Techniques

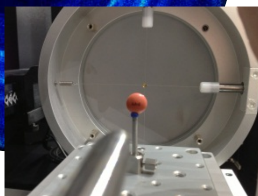
Phase Identification of Unconventional Samples



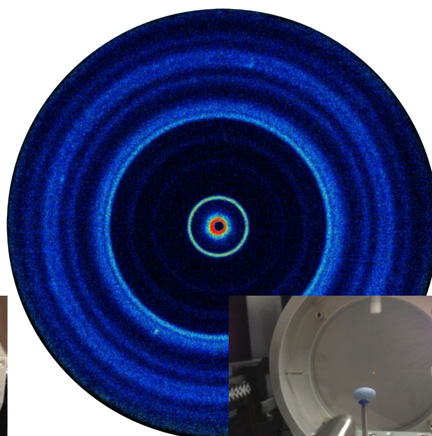
Non-Destructive Product Screening

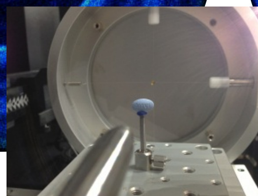
- IµS with 500-micron UBC and Beam Stop
- Phase ID in EVA or Refinement in TOPAS
- Can be measured in Blister Package also

Ibuprofen

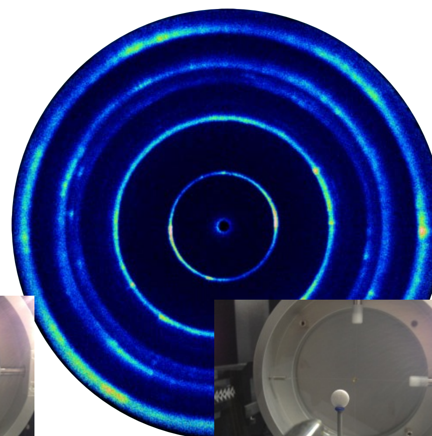


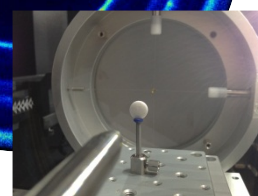
Naproxen Sodium



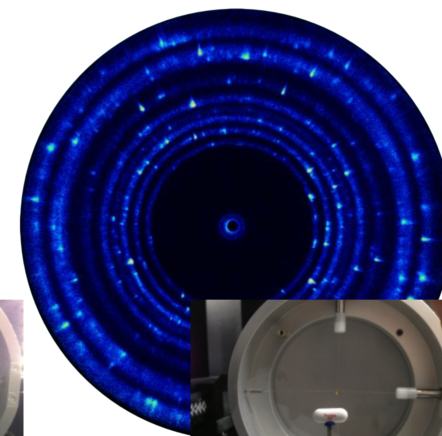


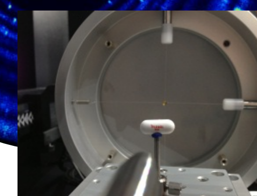
Aspirin





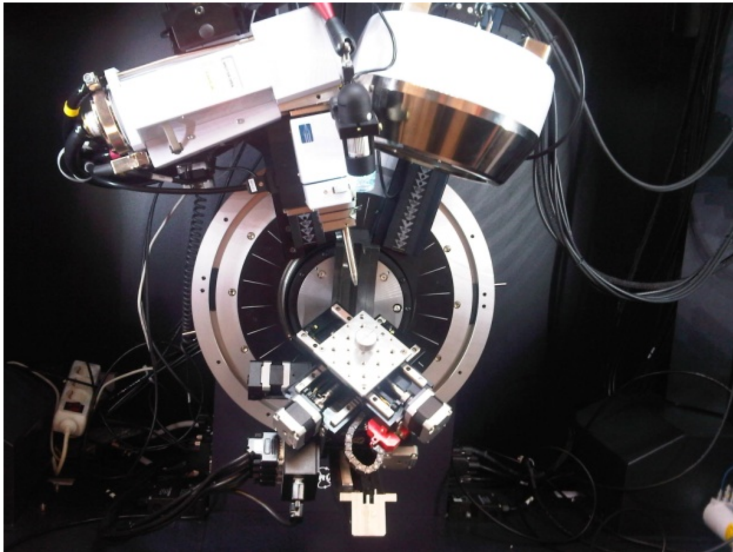
Acetaminophen





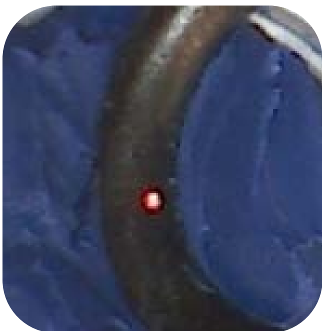
Traditional XRD² Techniques

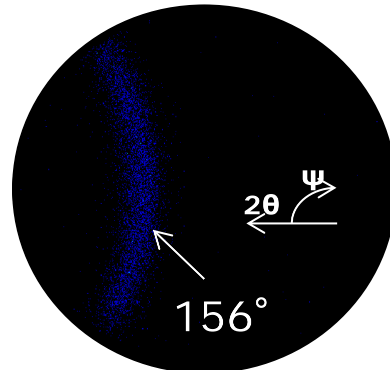
Residual Stress Analysis with DIFFRAC.LEPTOS
Measurement of a Curved Surface

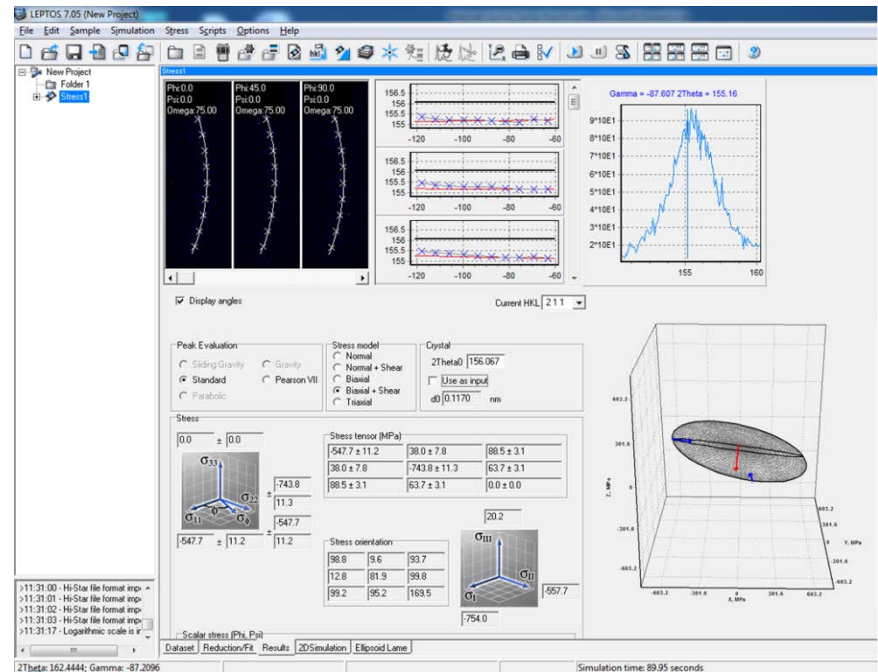


Residual Stress with DIFFRAC.LEPTOS

- 100 µm Beam Size to minimize sample curvature effects
- >156° can be obtained with the standard setup
- Modern Software applications reduce full Debye ring fitting to push-button operation

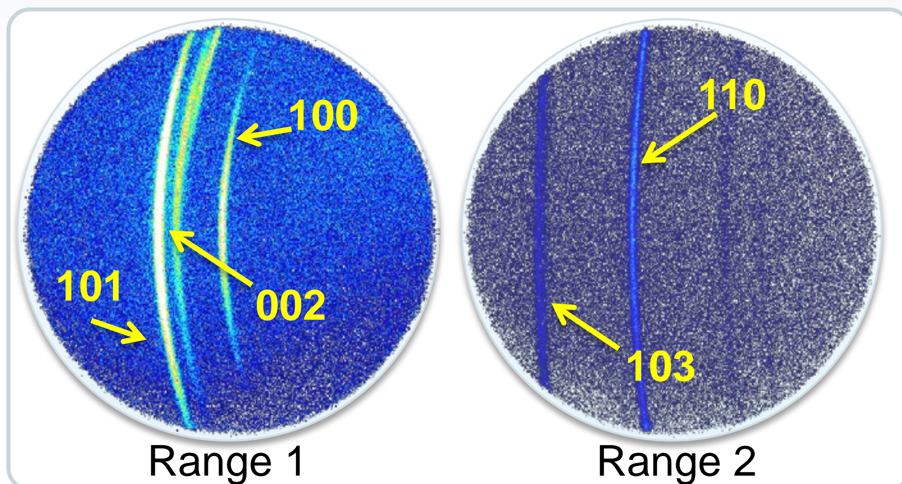






Traditional XRD² Techniques

Texture Analysis with DIFFRAC.MULTEX

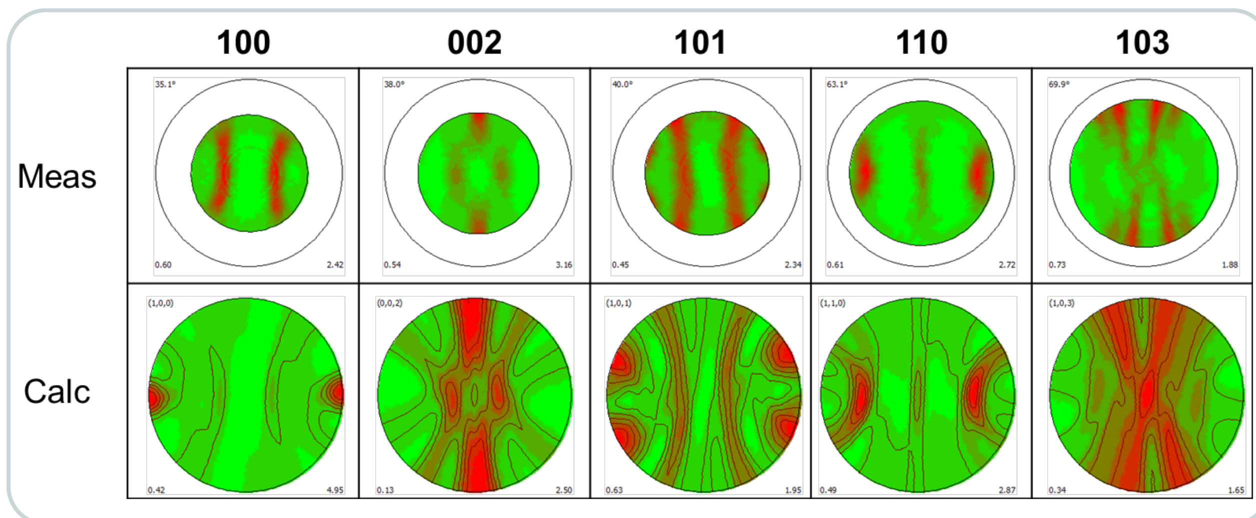


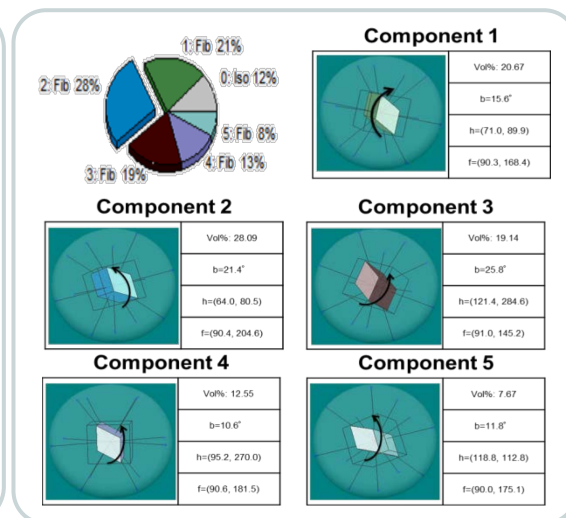
Simultaneous Multiple HKL Acquisition

- 5 pole figures in 2 frame sets

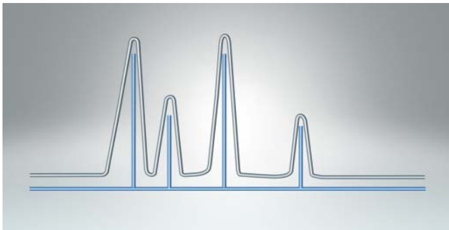
Texture Component Fit in DIFFRAC.MULTEX

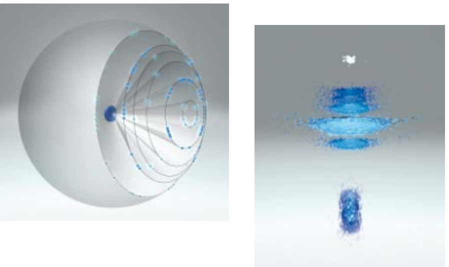
- 0D, 1D and 2D data support
- Calculated pole figures are refined against measured pole figures
- Volume %, Euler coordinates, ODF and inverse pole figures are created

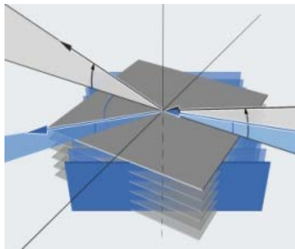




Topics to be discussed







Introduction to XRD²

- What is XRD²
- Instrument Effects on XRD² Resolution

Traditional XRD² Techniques

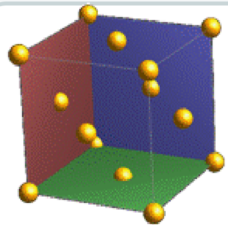
- Enhanced Phase Identification
- Residual Stress
- Texture

Innovative XRD² Techniques

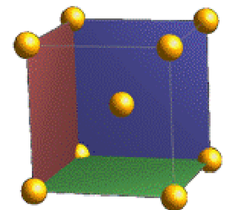
- Quantitative Phase Analysis with XRD² (Retained Austenite)
- Gamma Profile Analysis for Crystallite Size
- Single Crystal Orientation Analysis via Laue Diffraction
- Rapid X-ray Reflectometry with XRD²
- Surface Diffraction with XRD²
- Large Scale Rapid Reciprocal Space Mapping

Innovative XRD² Techniques

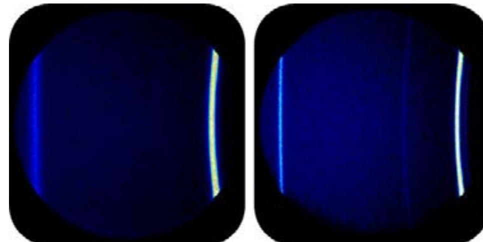
Quantitative Phase Analysis
Retained Austenite Determination



Austenite

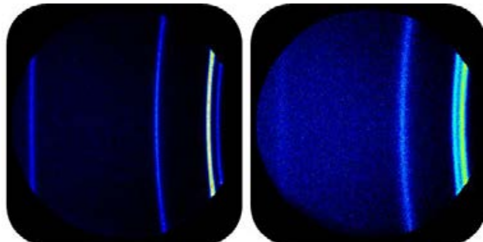


Martensite



0% Austenite

5% Austenite



30% Austenite

70% Austenite

Why XRD²?

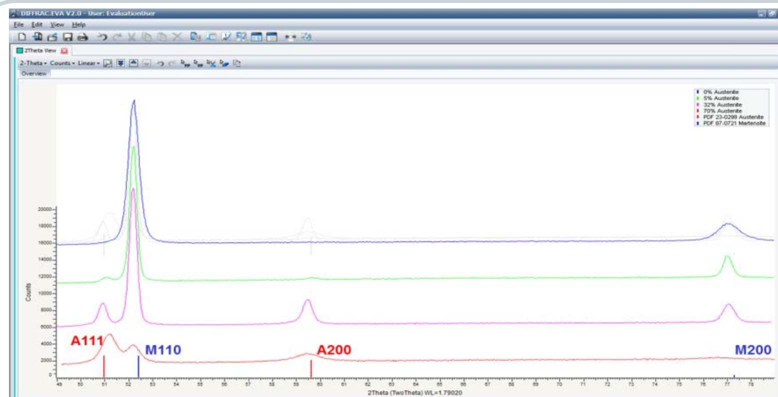
- All peaks can be captured in a single frame with Co radiation
- 15 minute total analysis time!

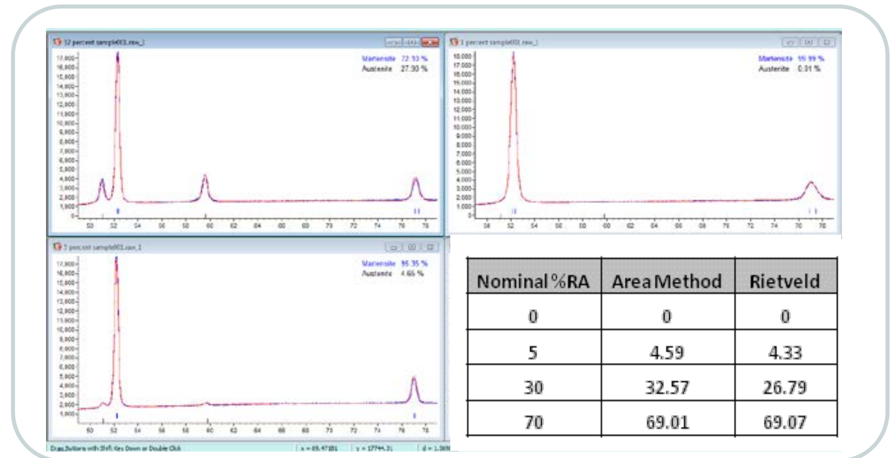
Conventional Analysis Method

- Multiple Austenite and Martensite peaks areas are measured

Rietveld Analysis Method

- Fundamental Parameters are used
- Standardless

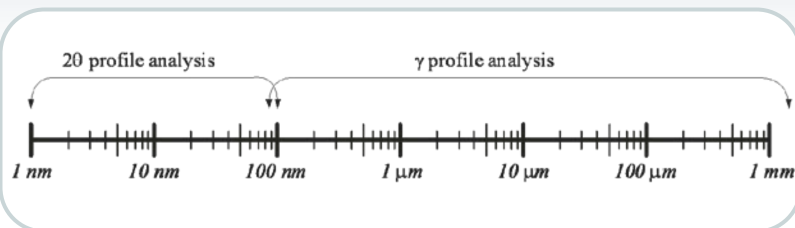


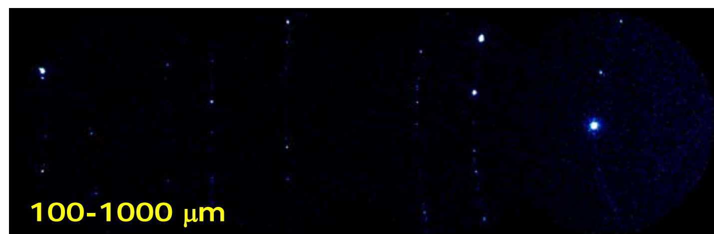


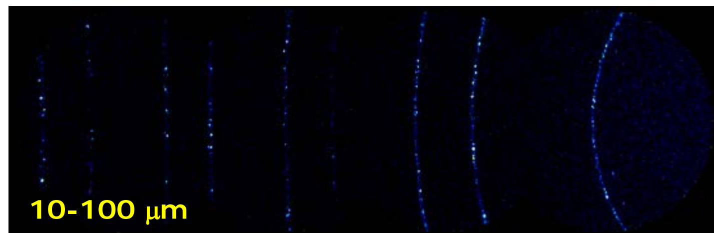
Nominal %RA	Area Method	Rietveld
0	0	0
5	4.59	4.33
30	32.57	26.79
70	69.01	69.07

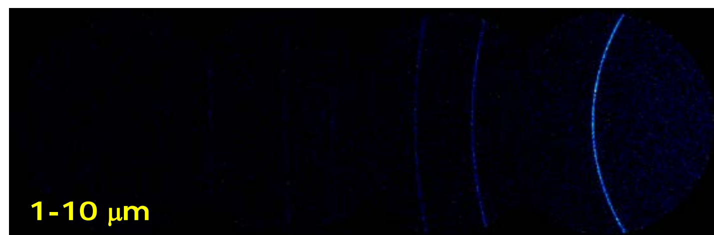
Innovative XRD❷ Techniques

Crystallite Size Analysis with XRD❷



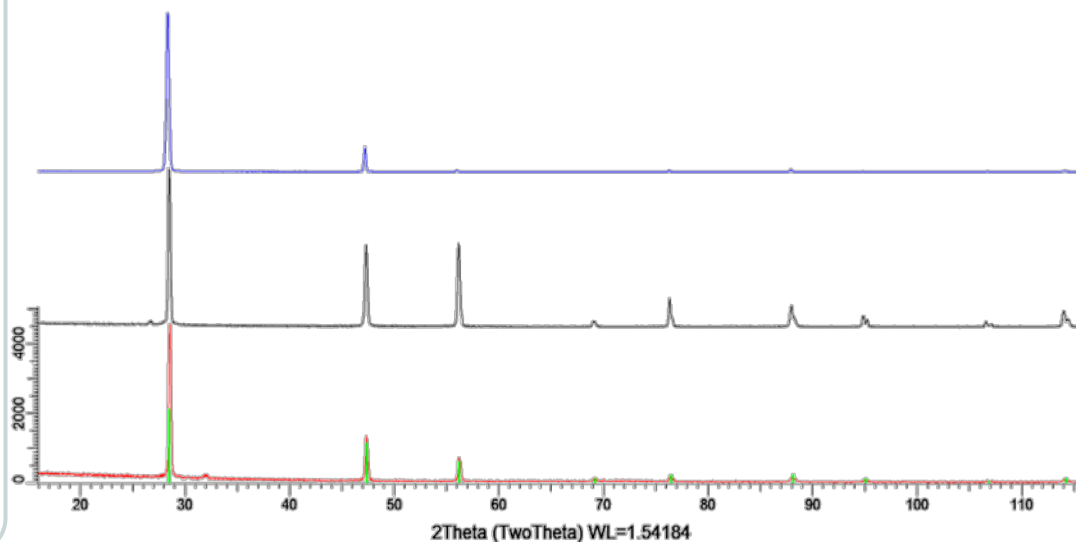






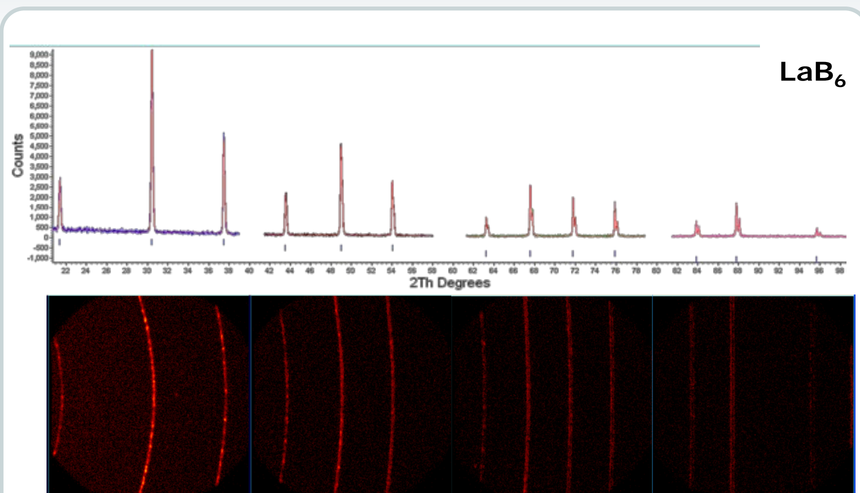
How is crystallite size determined?

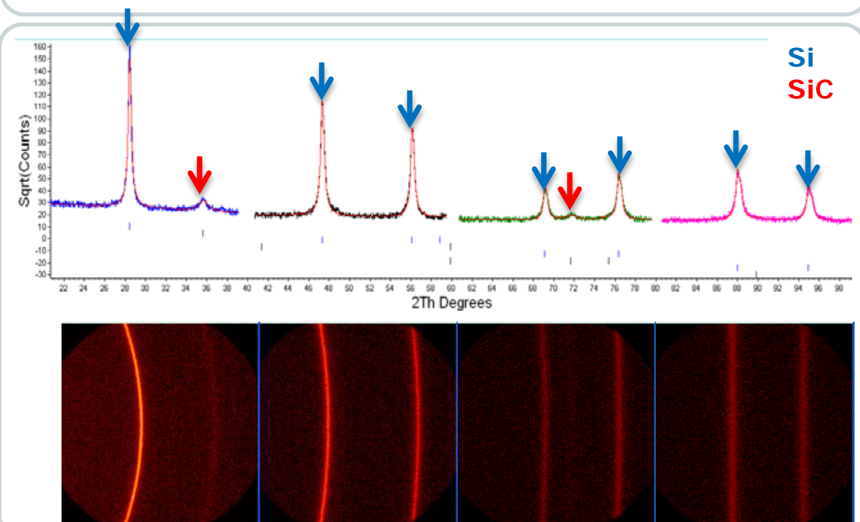
- 2θ profile analysis
  - Conventional approach
  - Particle size below 100 nm
- γ profile analysis
  - Unique to XRD❷
  - Particle size from <1 µm to mm's



Innovative XRD❷ Techniques

Crystallite Size Analysis with XRD❷
Conventional 2 Theta Profile Analysis





2θ profile analysis

- Nano-Crystallites → Broad Peaks
- Micro-Crystallites → Sharp Peaks

Standard is Measured

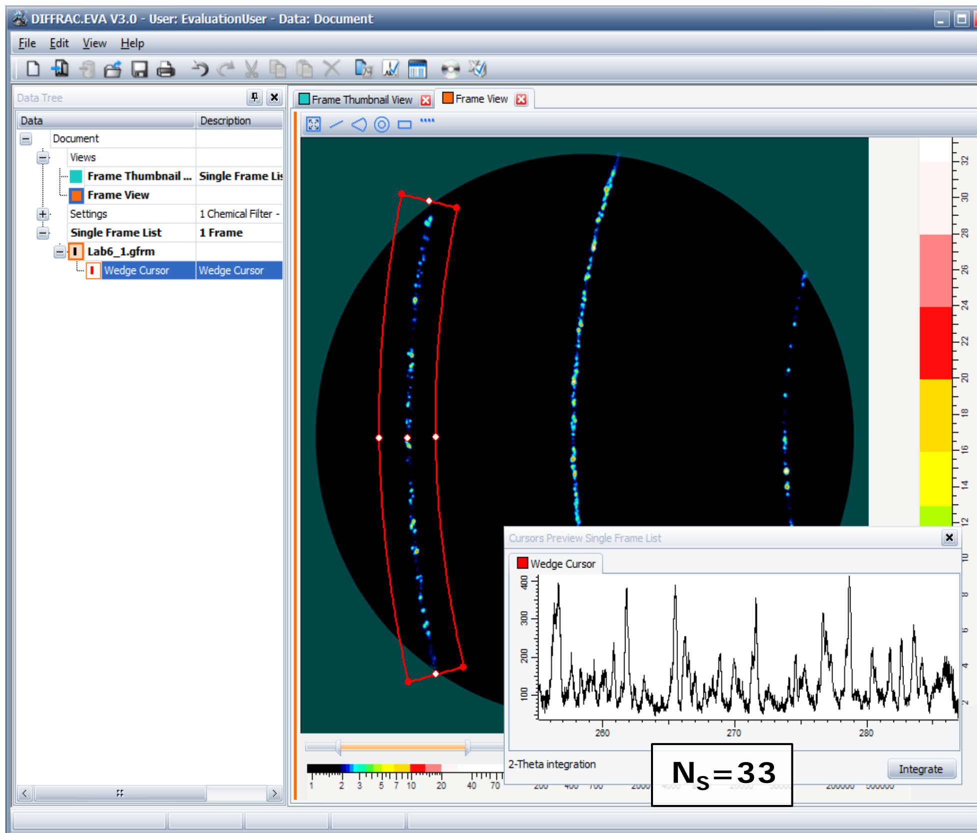
- TOPAS parameters are determined with fixed sample parameters

Unknown Sample is Measured

- Sample parameters are determined with fixed TOPAS parameters
- Si
  - Crys size (nm) = 57.2
  - a (Å) = 5.432315(44)
- SiC
  - Crys size (nm) = 10.4
  - a (Å) = 4.3641(12)

Innovative XRD❷ Techniques

Crystallite Size Analysis with XRD❷
Gamma Profile Analysis



Gamma Crystallite Size Analysis

- Many Sharp Gamma Peaks → Micro-Crystallites
- Few Broad Gamma Peaks → Milli-Crystallites

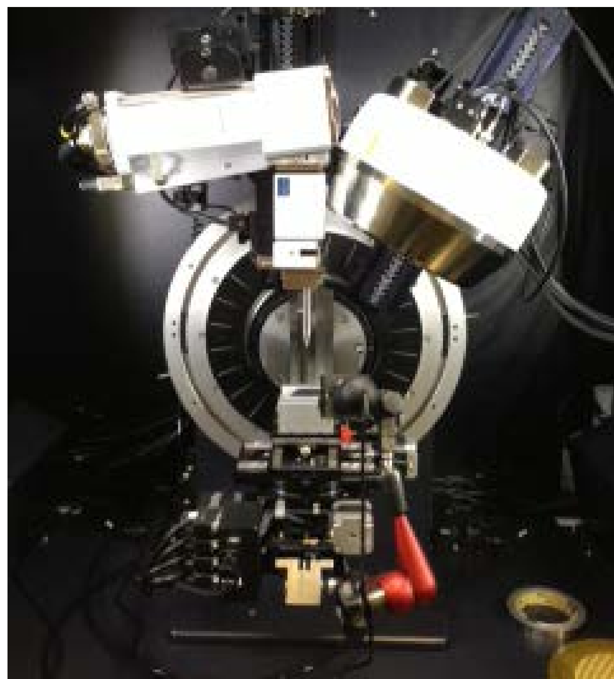
$$d = k\left\{\frac{p_{hkl} b^2 \arcsin[\cos\theta \sin(\Delta\gamma/2)]}{2\mu N_s}\right\}^{1/3}$$

$$k = \left(\frac{3\beta}{4\pi}\right)^{1/3}$$

$$\#\,\text{of peaks} = 33 \rightarrow t_{CrystSize} \approx 0.8\mu m$$

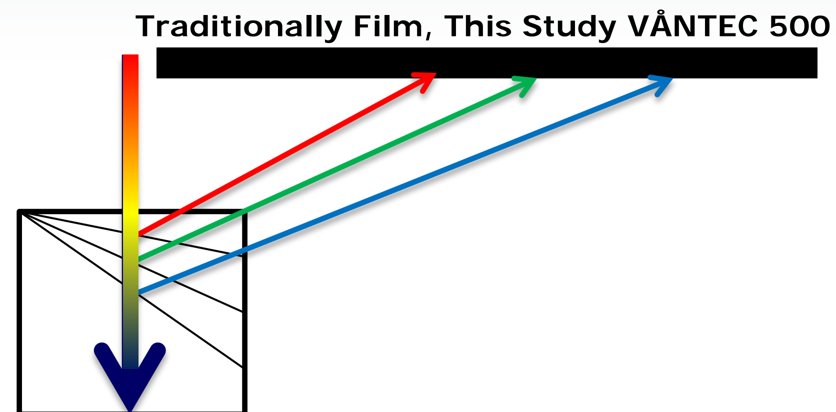
Innovative XRD❷ Techniques

Laue Diffraction with XRD❷ Instrument Configuration



Instrument Setup

- Sealed Cu Tube
- PolyCap Optic
- VÅNTEC 500

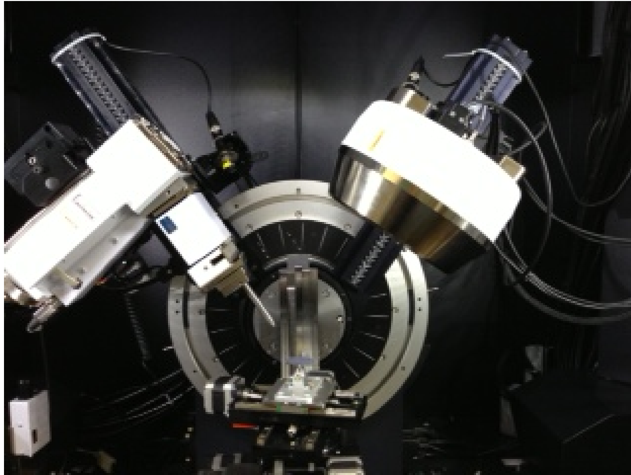


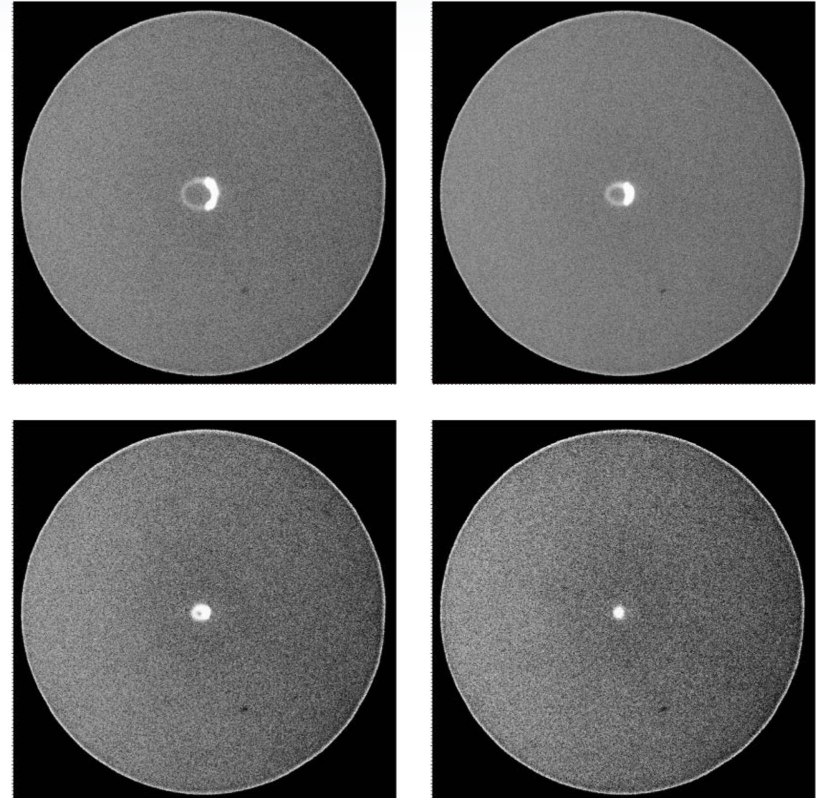
$$\lambda = 2d\sin\theta$$

Conventional Diffraction (Monochromatic)	Laue Diffraction (Polychromatic)
$\Delta\theta \rightarrow d$	$\Delta\lambda \rightarrow d$

Innovative XRD❷ Techniques

Laue Diffraction with XRD❷
Miscut Determination and Zone Axis Alignment





Simple Single Crystal Alignment

- Drives set to the bisector for the Zone Axis
  - Si 00L → 69.132/2 = 34.566
- Sample is rotated in Phi
- Width and Height of the procession are proportional to the miscut/ misalignment
- Can be corrected with a eucentric tilt stage

Innovative XRD^2 Techniques

Laue Diffraction with XRD^2
Raw Data

Phi = 0

Phi = 45

Phi = 90

Phi = 135

Phi = 180

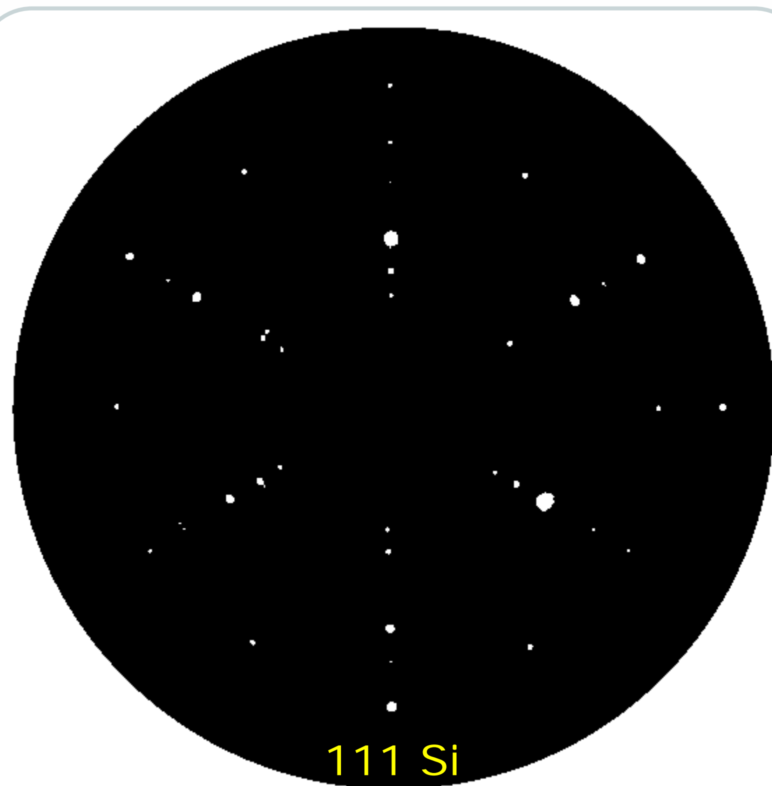
Phi = 225

Phi = 270

Phi = 315

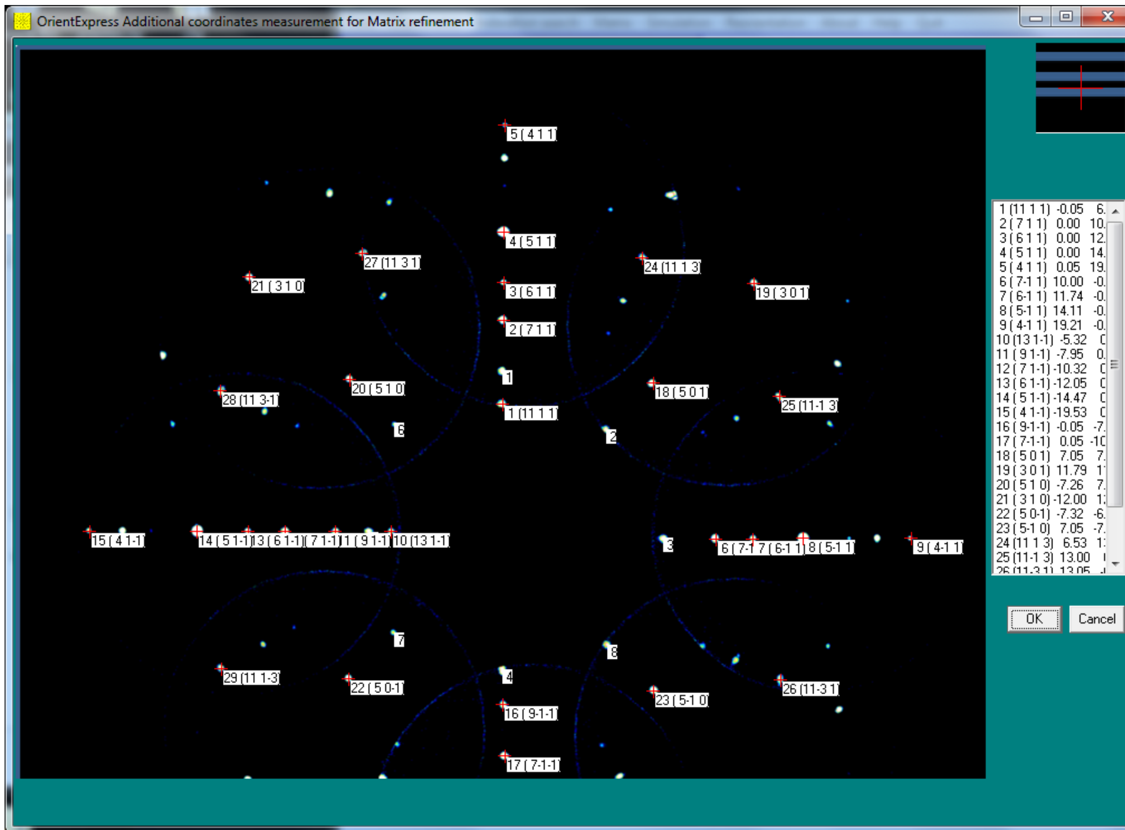
Innovative XRD❷ Techniques

Laue Diffraction with XRD❷
Assembled Laue Images



Innovative XRD❷ Techniques

Laue Diffraction with XRD❷
Fitting the Laue Pattern



Indexing

- 2 to 6 reflections are chosen
- HKL can be set for 2 or HKL can be determined
- More reflections can then be chosen for further refinement

Innovative XRD❷ Techniques

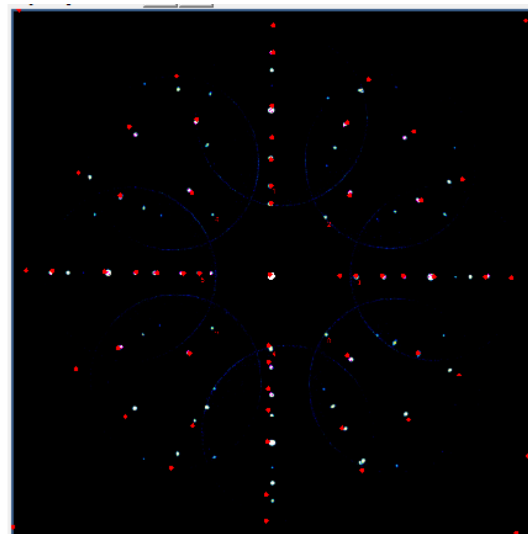
Laue Diffraction with XRD❷
Fitting the Laue Pattern

Matrix orientation refinement
Before matrix refinement
Distance: 23.73
Mean error: 0.0547 computed with 37 reflections

h	k	l	xobs	xcalc	yobs	ycalc	dist.
11	1	1	-0.05	-0.02	6.26	6.34	0.086
9	1	1	-0.05	0	7.84	7.79	0.073
7	1	1	0	0.03	10.21	10.15	0.07
6	1	1	0	0.06	12	12.01	0.061
5	1	1	0	0.1	14.37	14.77	0.414
4	1	1	0.05	0.17	19.42	19.39	0.117
13	1	-1	-5.32	-5.35	0.26	0.21	0.058
11	1	-1	-6.37	-6.33	0.21	0.23	0.044
9	1	-1	-7.95	-7.78	0.26	0.25	0.172
7	1	-1	-10.32	-10.13	0.26	0.29	0.184
6	1	-1	-12.05	-11.99	0.26	0.32	0.087
5	1	-1	-14.47	-14.75	0.26	0.37	0.299
4	1	-1	-19.53	-19.37	0.26	0.45	0.243
9	-1	1	7.53	7.52	-0.05	0.01	0.068
7	-1	1	10	9.86	-0.11	-0.02	0.167
6	-1	1	11.74	11.7	-0.11	-0.05	0.072
5	-1	1	14.11	14.43	-0.05	-0.09	0.324
4	-1	1	19.21	18.98	-0.05	-0.15	0.25
11	-1	-1	-0.05	-0.22	-6.26	-6.06	0.258
9	-1	-1	-0.05	-0.24	-7.89	-7.5	0.436
7	-1	-1	0.05	-0.28	-10.32	-9.84	0.578
7	0	1	4.84	4.85	5.05	4.95	0.102
5	0	1	7.05	6.98	7.26	7.02	0.256
3	0	1	11.79	12.65	11.95	12.54	1.043
7	1	0	-5.16	-4.95	5.37	5.11	0.333
5	1	0	-7.26	-7.02	7.42	7.25	0.295
3	1	0	-12	-12.57	12.26	12.98	0.921
7	0	-1	-5.16	-5.09	-4.53	-4.68	0.171
5	0	-1	-7.32	-7.22	-6.68	-6.74	0.112
7	-1	0	4.89	4.69	-5.11	-4.83	0.345
5	-1	0	7.05	6.74	-7.26	-6.95	0.442
11	1	3	6.53	6.74	13.16	13.36	0.291
11	1	-3	-13.32	-13.55	-6.21	-6.31	0.25
11	-1	3	13	13.26	6.63	6.58	0.269
11	3	1	-6.68	-6.59	13.37	13.59	0.244
11	3	-1	-13.37	-13.37	6.89	7.02	0.13
11	-3	1	13.05	13.03	-6.74	-6.69	0.051

Refinement

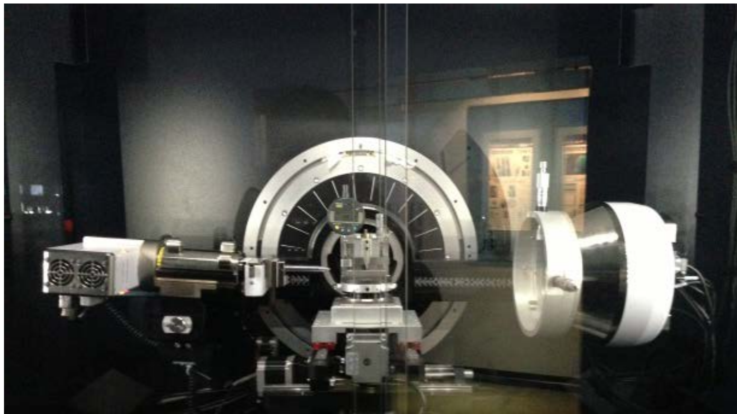
- 37 reflections were used
- Distance, Lattice parameter and Orientation are refined

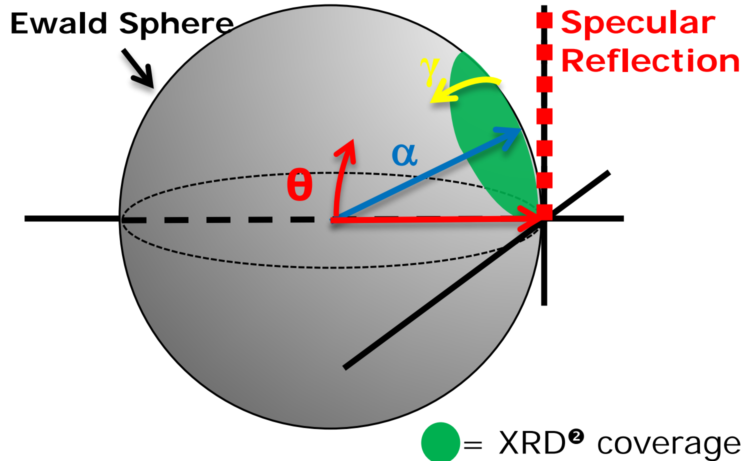


Crystal axis // to the beam axis (OX) :	5.430971	-0.0181	-0.00165
(OY) :	0.011513	3.806823	-3.87347
Crystal axis // to the camera axis (OZ) :	0.014051	3.87344	3.806832
Magnitude of Vector:	5.431001	5.431001	5.431
In Plane Orientation:	---	44.50304	-45.4971

Innovative XRD❷ Techniques

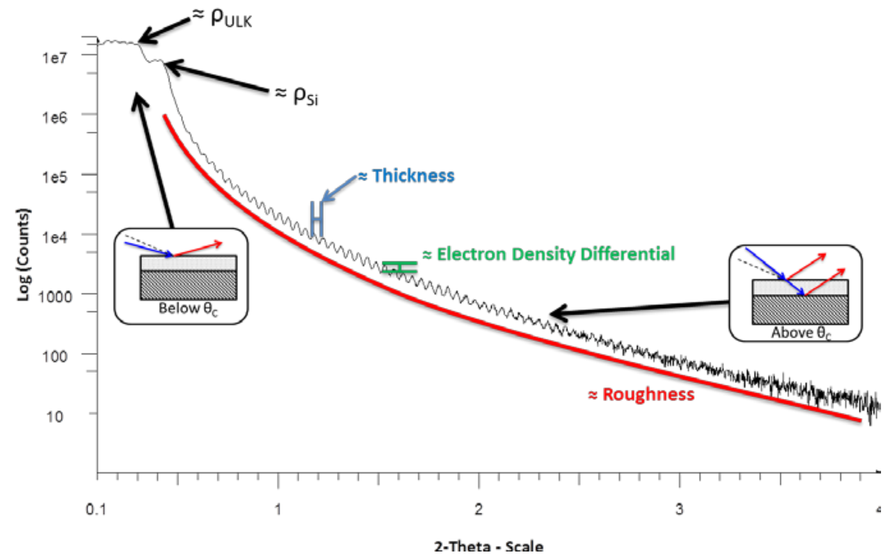
Rapid X-ray Reflectometry with XRD❷





Instrument Setup

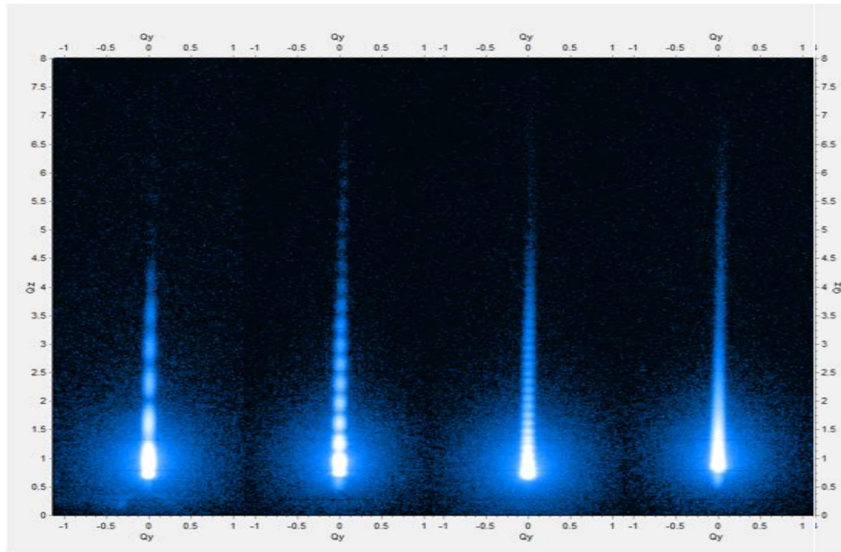
- IμS microfocus Cu Tube
- Montel Optic
- 0.5 mm Collimator
- Knife Edge
- VÅNTEC 500

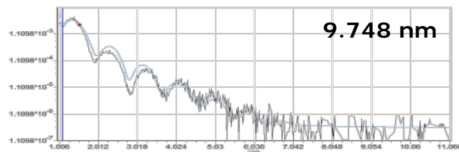


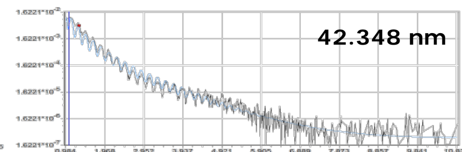
Innovative XRD² Techniques

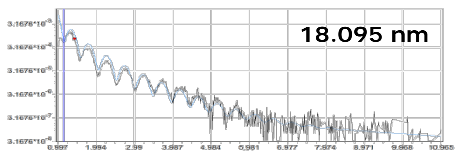
Rapid X-ray Reflectometry with XRD²

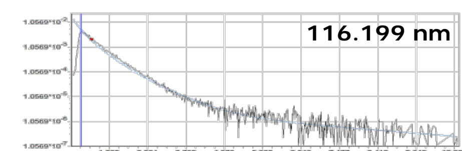
Layers of Various Thicknesses



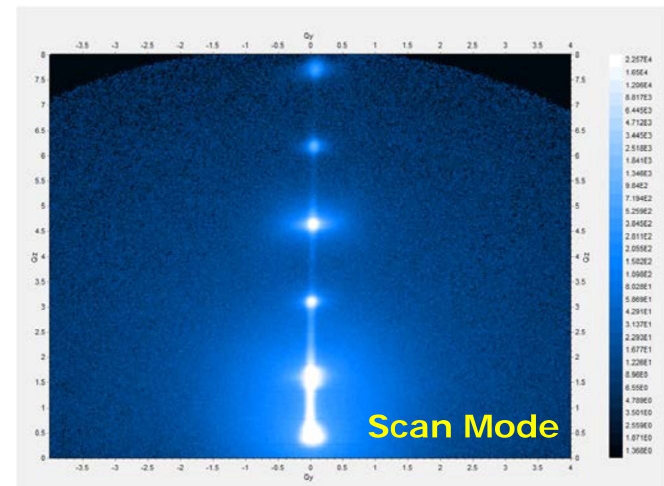


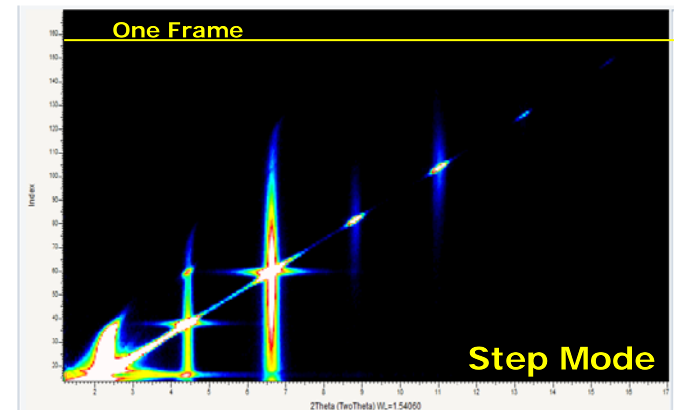






Superlattice with 4nm period





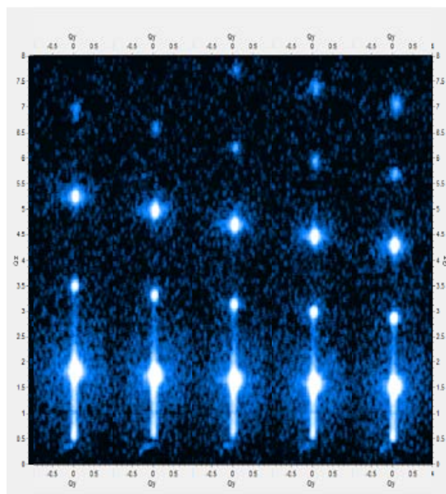
Innovative XRD❷ Techniques

Rapid X-ray Reflectometry with XRD❷ Superlattice Period Mapping

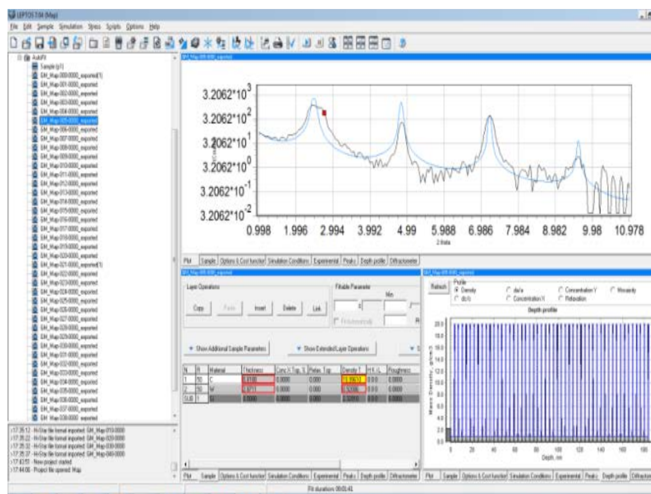
Pico-scopic Control for Online Applications

- IμS with 500 micron UBC and Beam Stop
- 40 mm total, 1 mm step, 10 sec per frame
- DIFFRAC.LEPTOS Auto fit used to refine data
- **Less than 10 min** from mounting to refinement for 41 measurement points

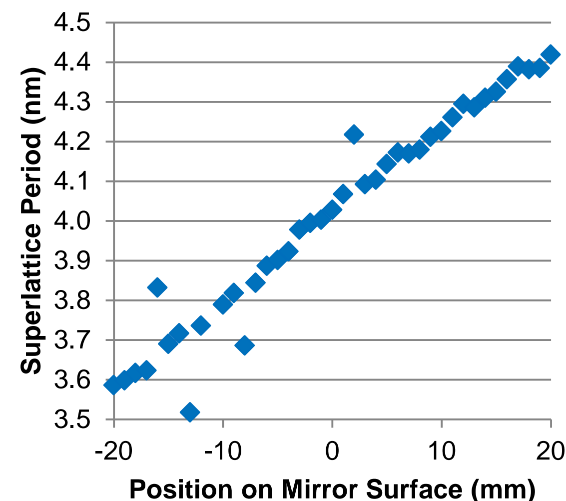
Raw Data



Refinement



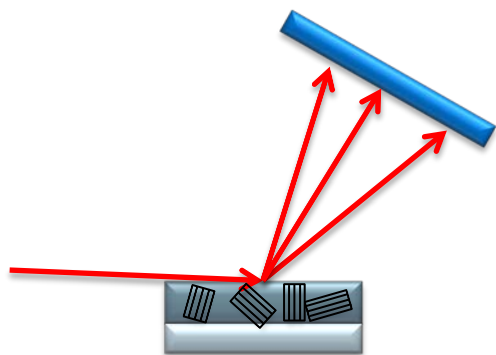
Result



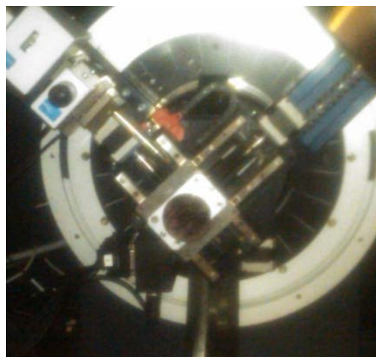
Innovative XRD² Techniques

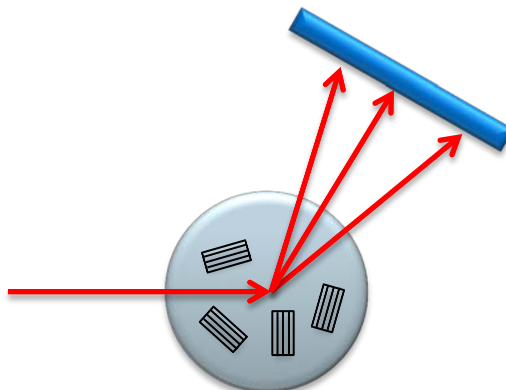
In-Plane Grazing Incidence Diffraction with XRD²

Standard GID (Polycrystalline Film)

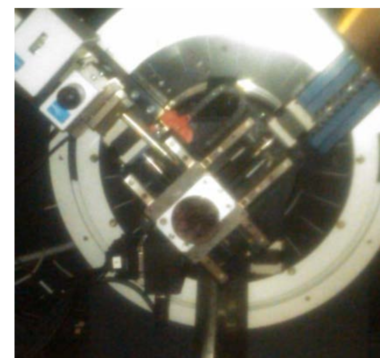


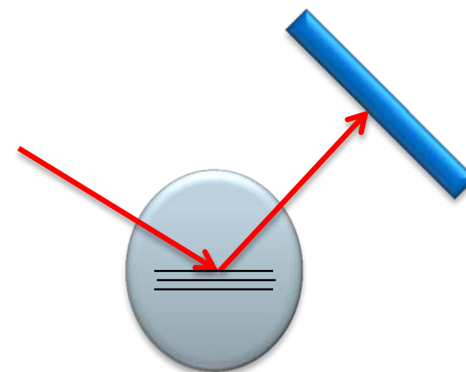
In-Plane GID (Polycrystalline Film)





In-Plane GID (Epitaxial Film)

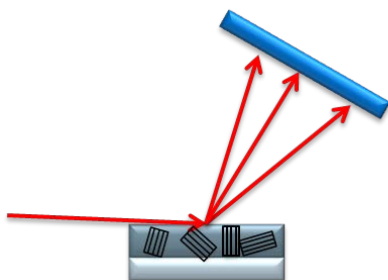


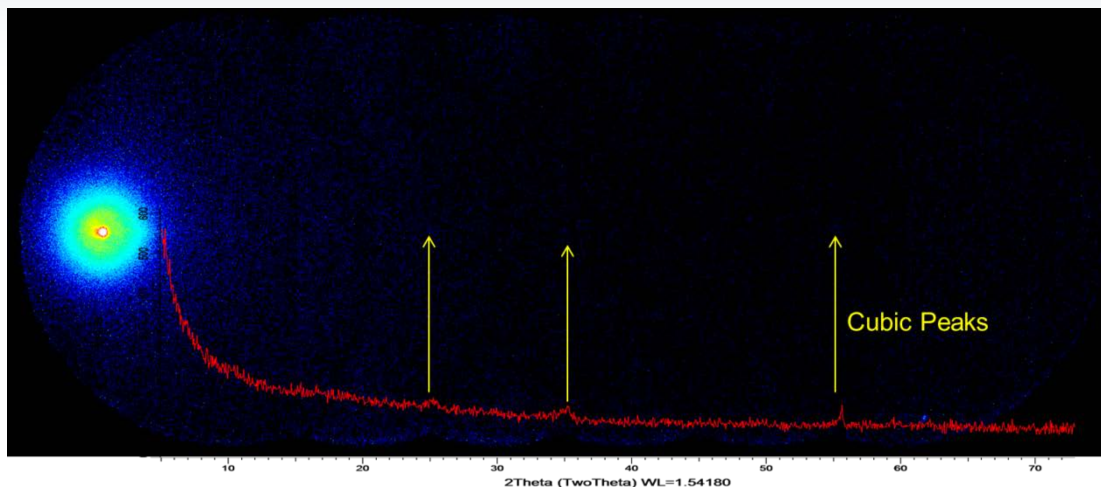


Innovative XRD❷ Techniques

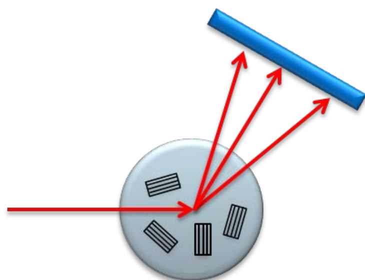
In-Plane Grazing Incidence Diffraction with XRD❷
10 nm PolyCrystalline Film on Si – Conventional GID

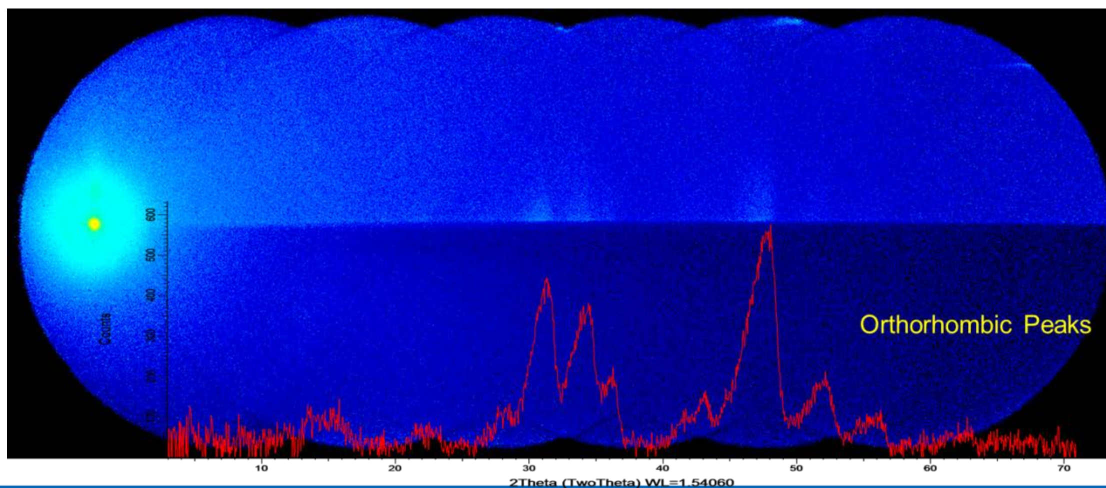
GID





In-Plane GID





Innovative XRD² Techniques

In-Plane Grazing Incidence Diffraction with XRD²

Comparison of Conventional and XRD²

12 hour Conventional Scan
3 10 min frames

Counts

0
100
200
300
400
500

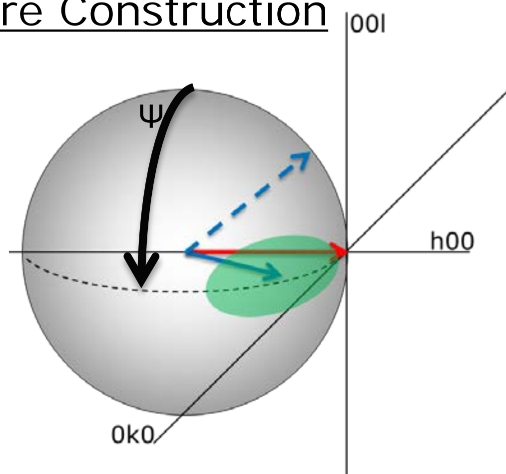
30
40
50
60
70

2Theta (TwoTheta) WL=1.54060

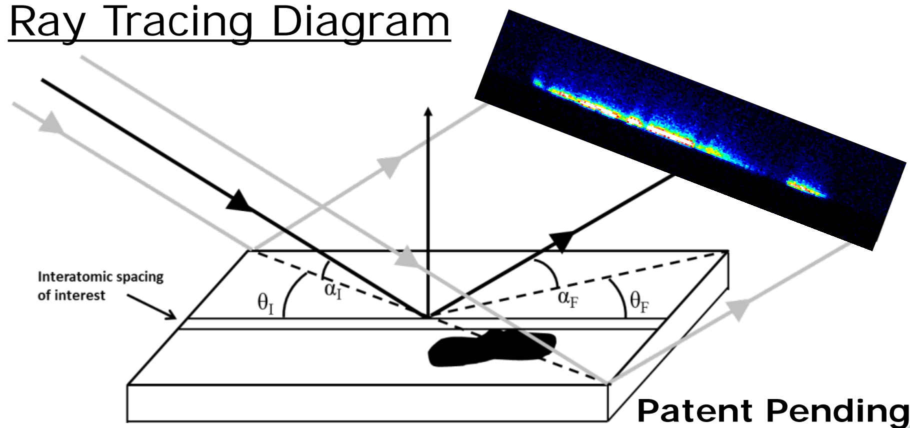
Innovative XRD❷ Techniques

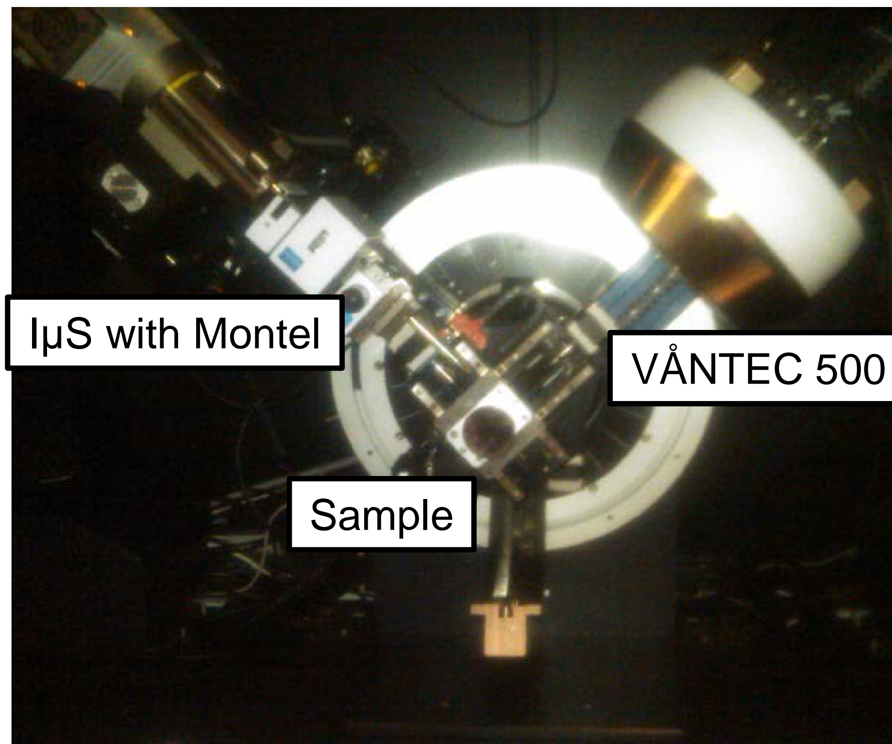
In-Plane Grazing Incidence Diffraction with XRD❷

Ewald Sphere Construction



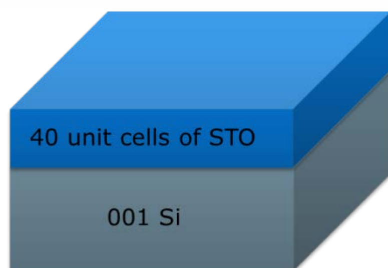
Ray Tracing Diagram

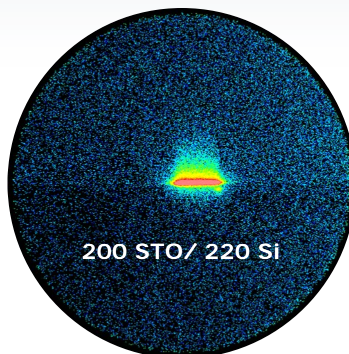


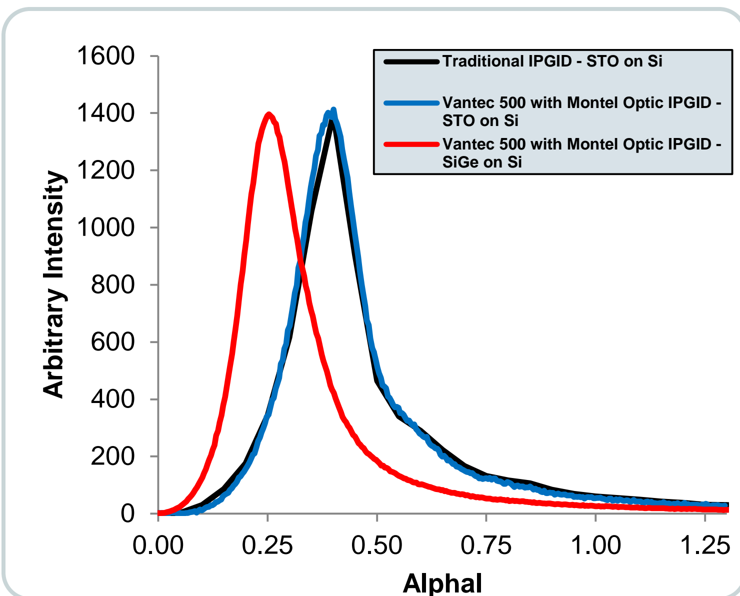


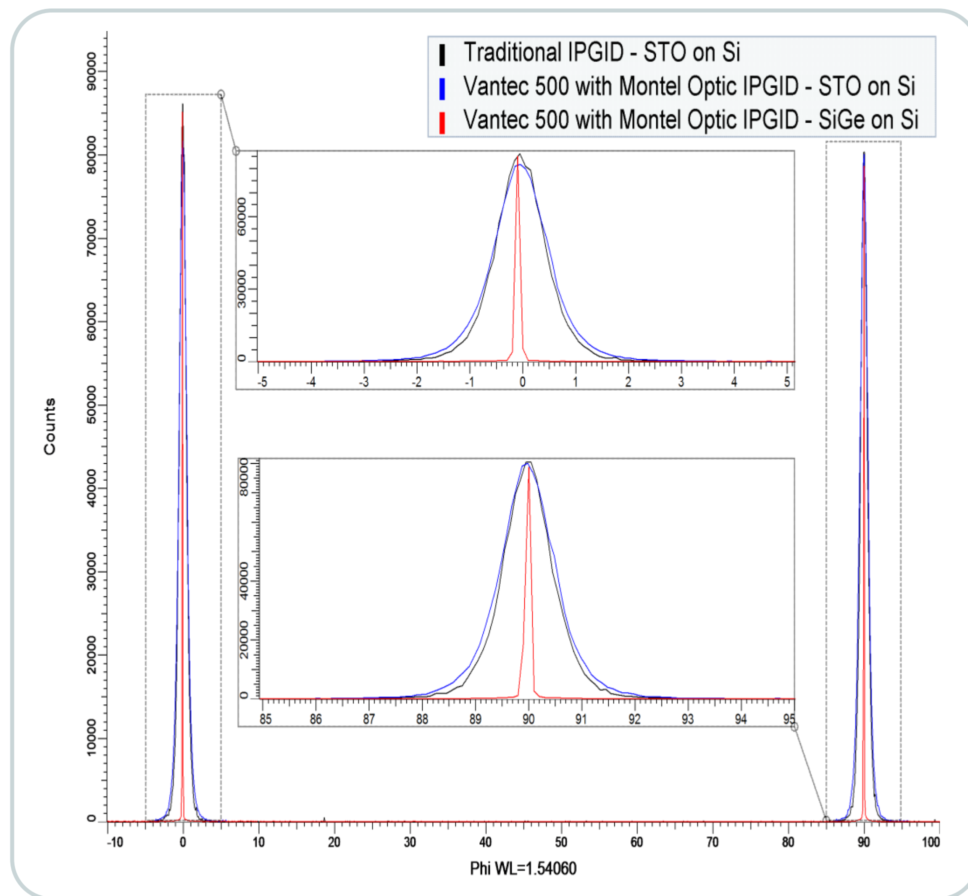
Innovative XRD² Techniques

In-Plane Grazing Incidence Diffraction with XRD²
20 nm STO on Si and 50 nm SiGe on Si



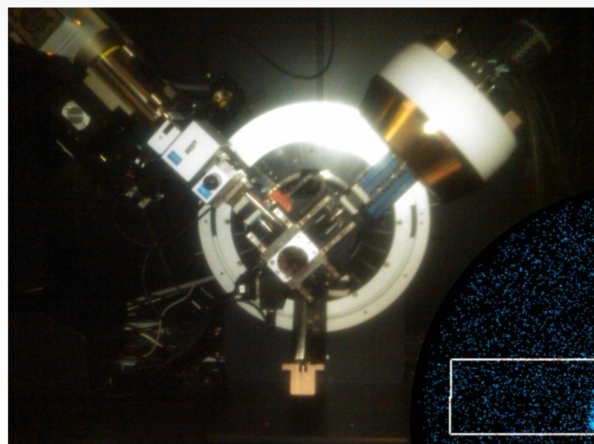


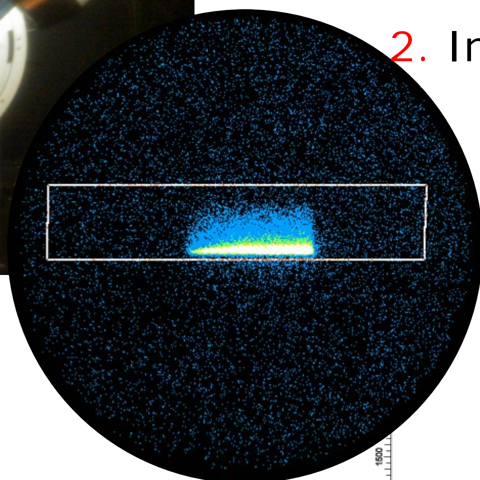




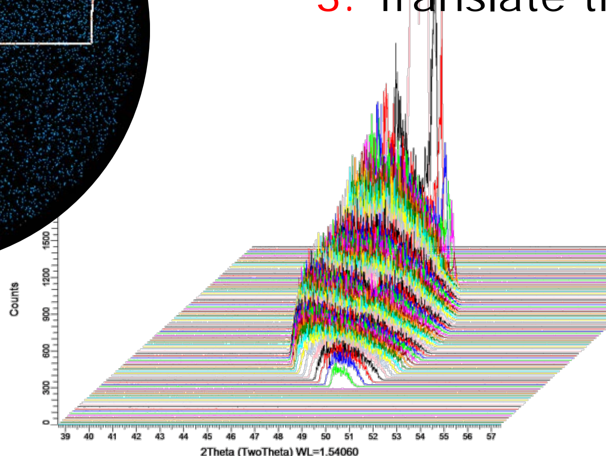
Innovative XRD❷ Techniques

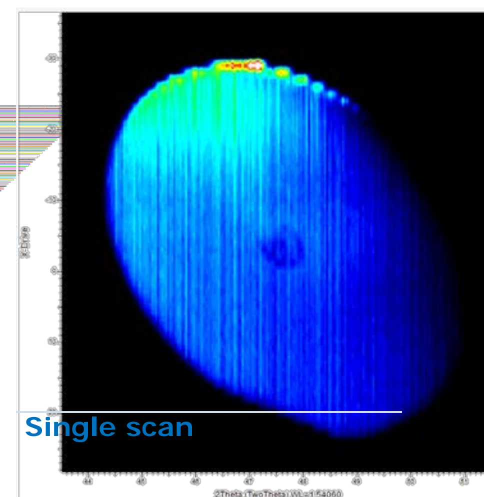
In-Plane Grazing Incidence Diffraction with XRD❷
Wafer Flat Determination





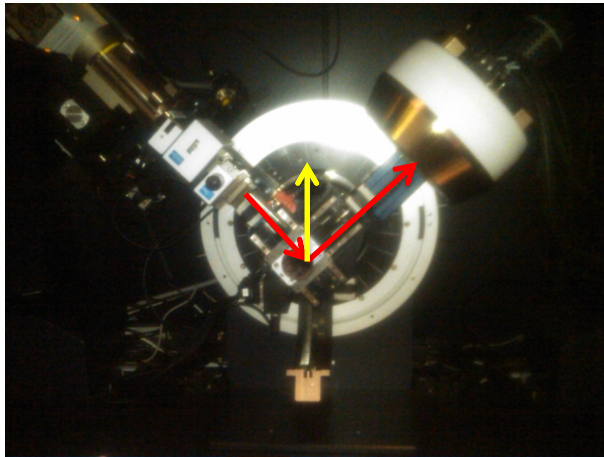
1. Set the Goniometer for In-Plane Scattering
2. Integrate the frame along the Surface Direction
3. Translate the sample and repeat

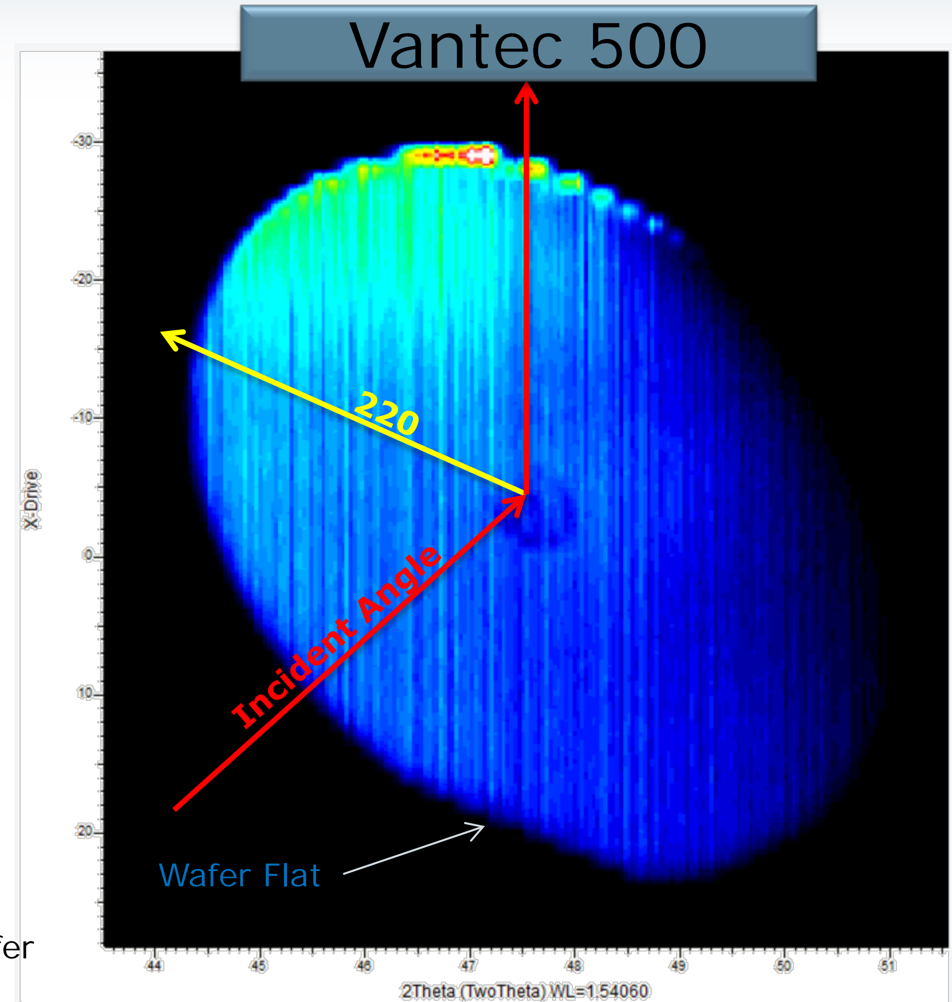




Innovative XRD² Techniques

In-Plane Grazing Incidence Diffraction with XRD²
Wafer Flat Determination



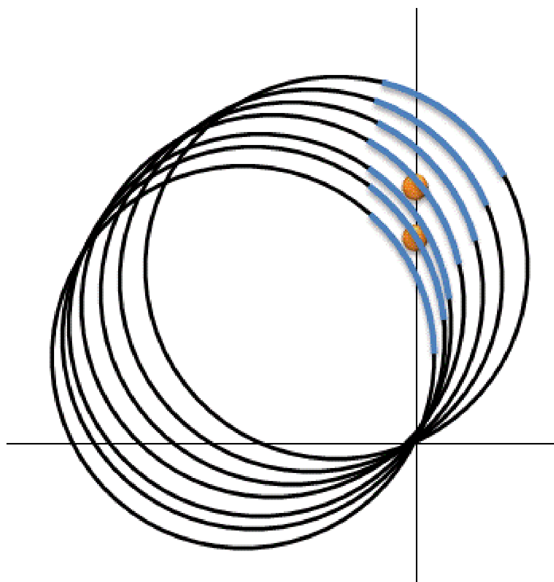


Wafer Flat Direction Determination

- 220 is the plane of interest
- VÅNTEC 500 is parallel to the scan axis
- Incident Angle is 180 – 2 Theta of peak
    - 180-47 = 133
- Plane Normal is the Bisector
- This corresponds perfectly to the flat of the wafer

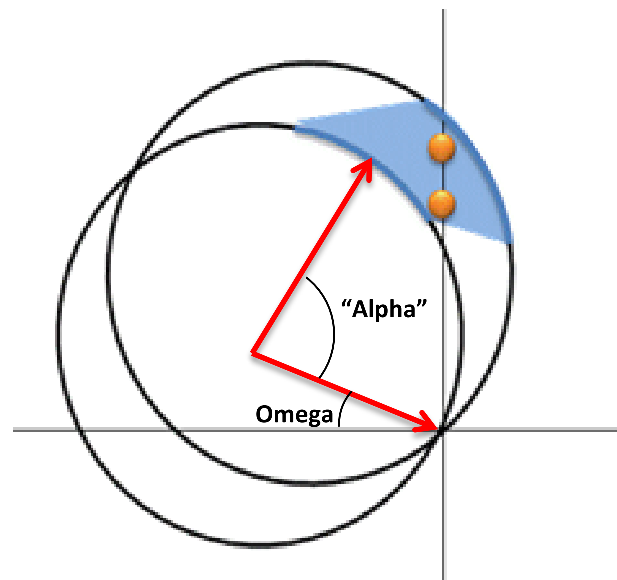
Innovative XRD❷ Techniques

Reciprocal Space Mapping with XRD❷



Step Mode

- Volumetric Reciprocal Space Data
- Non-coplanar substrate peak referencing
- Multi-dimension mosaic spread

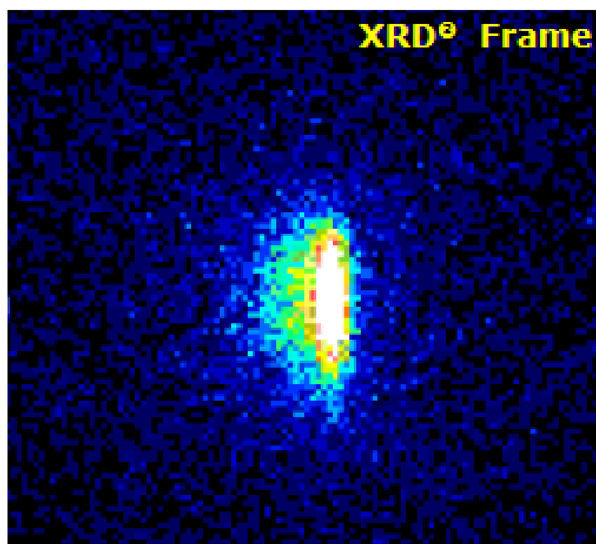


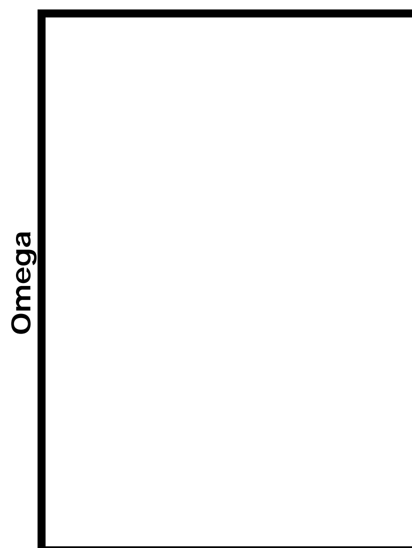
Scanning Mode

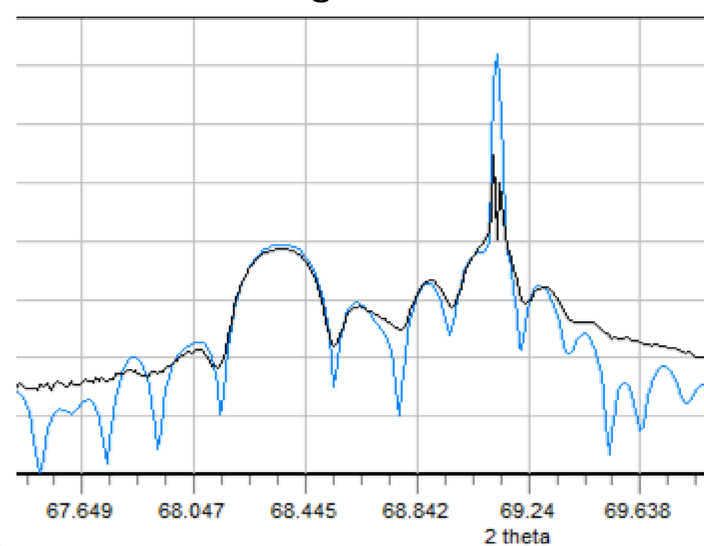
- Simplest way to locate secondary phases with preferred orientation
- Convenient for finding on and off axis reflections

Innovative XRD² Techniques

Reciprocal Space Mapping with XRD²
Step Mode

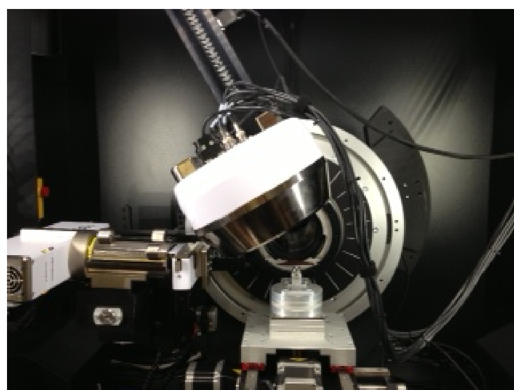


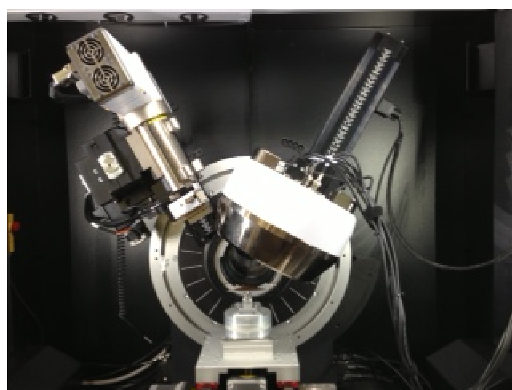


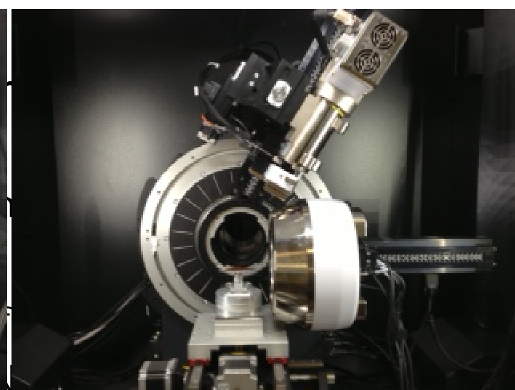


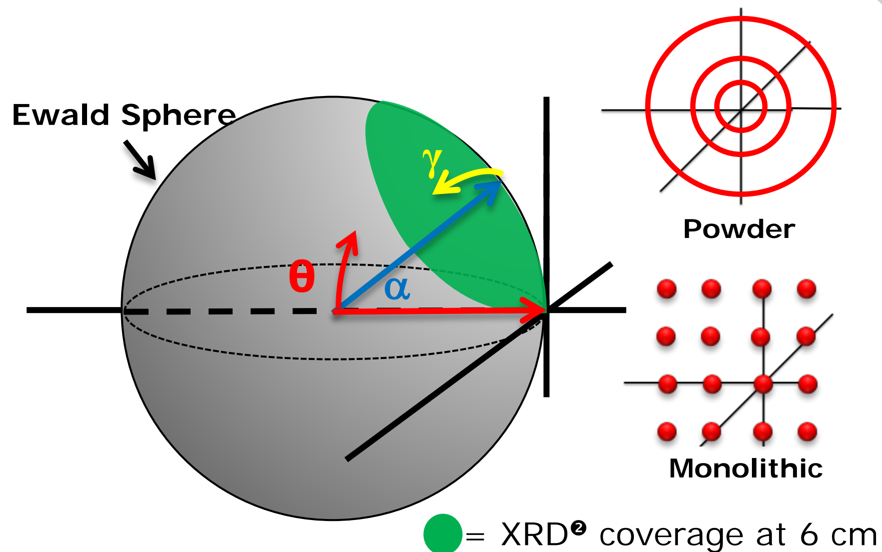
Innovative XRD❷ Techniques

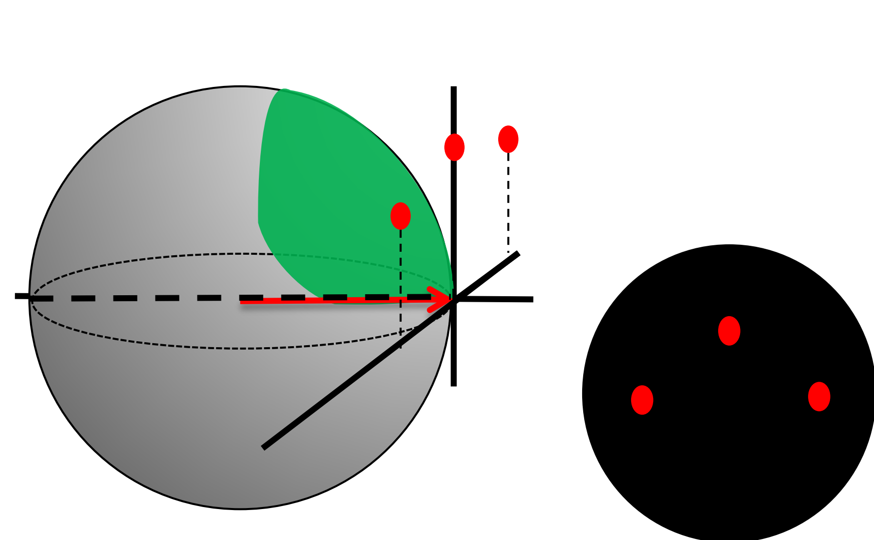
Reciprocal Space Mapping with XRD❷ Scan Mode











Innovative XRD❷ Techniques

Reciprocal Space Mapping with XRD❷
Scanning Mode – Si Powder

335
206
135
404
115
224
133
004
113
202
111

q(y(0 0 L))

q(x(H 0 0))

Innovative XRD❷ Techniques

Reciprocal Space Mapping with XRD❷
Scanning Mode – 001 Si Wafer

206
135
404
135
115
115
206
206
004
113
113
q(y(0 0 L))
q(x(H 0 0))

444
335
206
206
115
335
335
135
135
115
224
115
115
004
113
113
113
q(y(0 0 L))
q(x(H=K 0))

Innovative XRD² Techniques

Reciprocal Space Mapping with XRD²
Scanning Mode – Textured Cu film on 001 Si Wafer

024
133
206
004
135
404
135
222
113
115
115
206
206
022
004
113
113
002
111

q(y(0 0 L))

q(x(H 0 0))

444
024
335
133
004
206
206
335
115
222
335
135
135
113
224
115
115
022
004
113
113
002
113
111

q(y(0 0 L))

q(x(H=K 0))

Yellow = Si peaks
Green = Cu peaks

Innovative XRD❷ Techniques

Reciprocal Space Mapping with XRD❷
Scanning Mode – Epitaxial $SrTiO_3$ on 001 Si Wafer

224
206
114
404
233
135
233
135
204
115
115
204
206
206
103
103
004
202
113
102
002
113
102
202
112
112
001
q(y(0 0 L))
q(x(H 0 0))

444
335
204
114
004
115
206
135
335
206
135
335
115
224
115
103
103
004
103
112
113
113
112
113
002
101
101
q(y(0 0 L))
q(x(H=K 0))

Yellow = Si peaks
Green = STO peaks

Innovative XRD² Techniques

Reciprocal Space Mapping with XRD²
Comparison of RSM with XRD² and 1D LYNXEYE

BRUKER

1D Detector

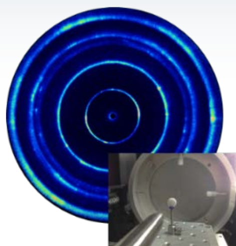
444
335
204
114
004
206
335
135
115
224
135
206
335
115
115
103
103
004
103
112
113
113
112
113
002
101
101

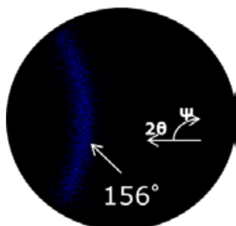
1D Detector

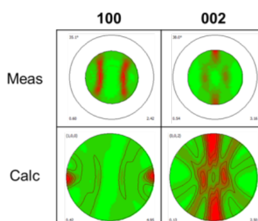
Total Time for XRD² RSM (27 peaks): 15 minutes

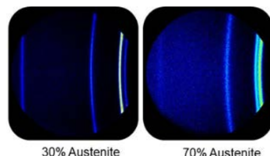
Total Time for 1D RSMs (4 peaks): 1.5 hours

Summary
Audience Poll





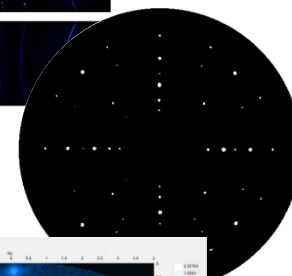


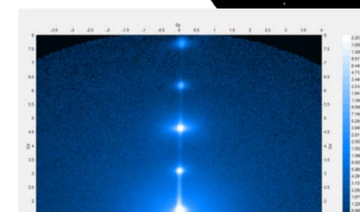


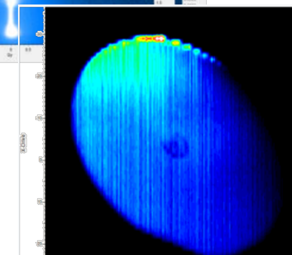
Please use your mouse to answer the question in the poll window on your screen.

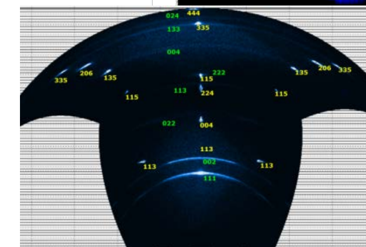
Which of the XRD² applications presented in this webinar are most relevant to your work? (Select all that apply.)

- ❑ Enhanced phase identification
- ❑ Residual stress measurement
- ❑ Texture analysis
- ❑ Quantitative phase analysis (retained austenite)
- ❑ Gamma profile analysis for crystallite size
- ❑ Single-crystal orientation analysis via Laue diffraction
- ❑ Rapid X-ray reflectometry
- ❑ Surface diffraction
- ❑ Large-scale, rapid reciprocal space mapping









Questions?

Any questions?

Please type any questions you may have for our speakers in the Q&A panel and click Send.

How did we do?

When you exit the webinar, please fill out our evaluation survey to let us know. We appreciate your feedback.

Thank you!

Past and Future XRD Webinars

Industries Products Service News Events About us

Globally interacting with experts

Related links

- News
- Events

Contact

Home • Service • Education & Training • Webinars • XRF

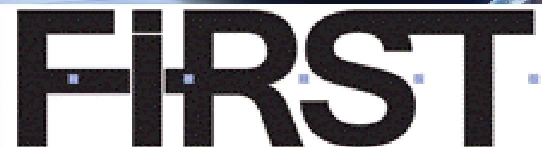
XRD Webinars

Live and On-Demand

Available at www.bruker.com/service/education-training/webinars/xrd.html

Webinar	Content
Jun 4, 2013 **Good Diffraction Practice VIII: Innovative 2D XRD Applications in Materials Science**	This 1-hour educational webinar will give you an overview of 2D X-ray diffraction geometry and present-day applications that highlight XRD²s unique capabilities. Application examples will include crystallite size by gamma -profiling, characterization of ultra-thin epitaxial films and superlattices, single-crystal orientation by Laue diffraction, miscut angle determination of single-crystal substrates, and retained Austenite analysis with 2D XRD. 2 sessions, Register now

Webinar	Content
Sep 30, 2010 **Good Diffraction Practice III: Powder XRD Instrumentation and Data Quality**	Join Dr. Lutz Bruegemann as he explains important aspects of X-ray powder diffraction workflow: from mechanical setup of the goniometer to data collection and evaluation of data quality. View recording Download slides
Aug 11, 2010	X-ray diffraction analysis with a two-dimensional detector is fast and accurate for many applications because a 2-D pattern covers a large solid ange



FRONTIERS IN RESEARCH SCIENCE & TECHNOLOGY

newsletter

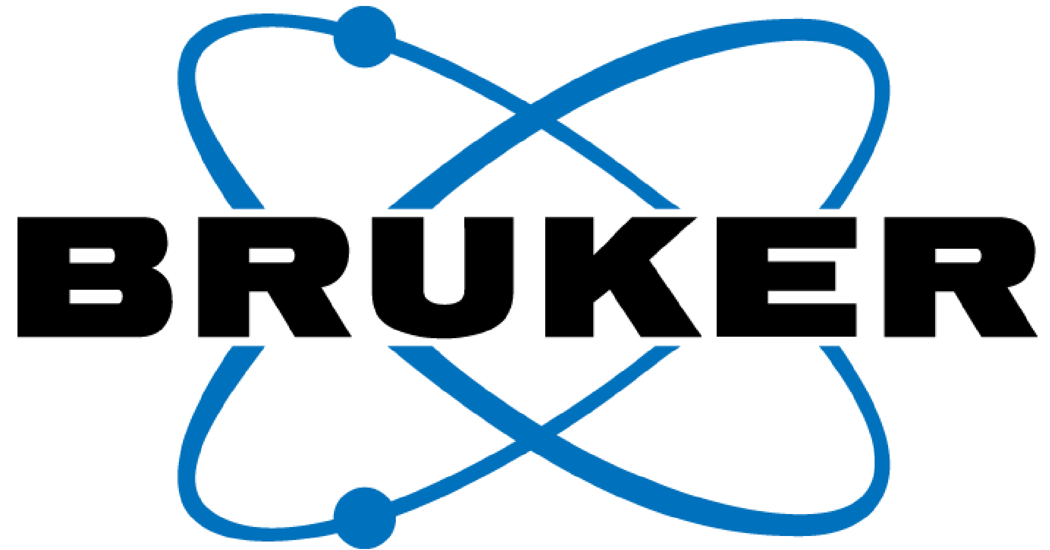
ISSUE

Like what you learned in this webinar?

Subscribe to Bruker's ***FIRST Newsletter*** to get webinar announcements, fascinating articles, and analytical X-ray news delivered right to your inbox.

Subscribe at:

https://www.bruker.com/about-us/register.html



www.bruker.com

© Copyright Bruker Corporation. All rights reserved.