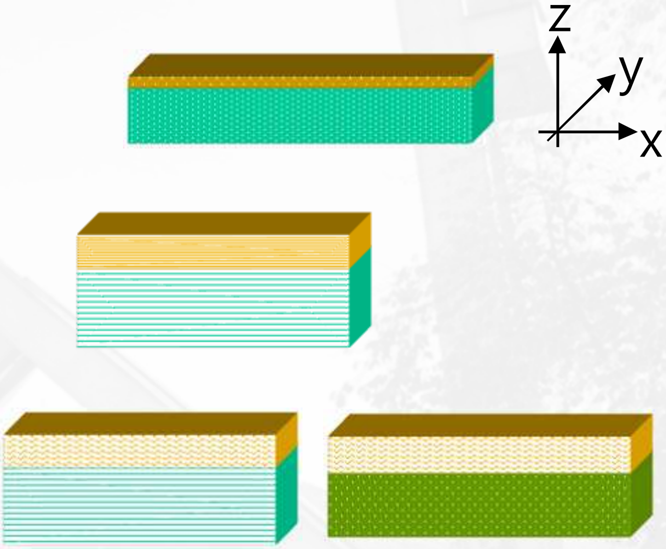
X-ray for characterization of thin films

Many slides from the ppt made by Bruker, Panalytical, Rigaku and Dr. Scott A. Speakman (prism.mit.edu/xray) were used.

Thin layer

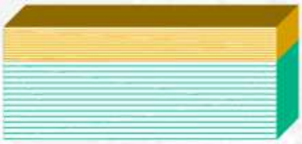
- Dimension in one direction is much smaller than those in other two directions.
- Epitaxial layer
- Polycrystalline layer
  - ✓ Non-single-crystal layer
- Amorphous layer
  - ✓ lack of long-range ordering of atoms

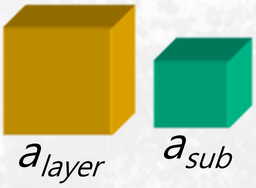


Prof. Elżbieta Dynowska

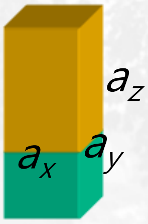
Epitaxial layer

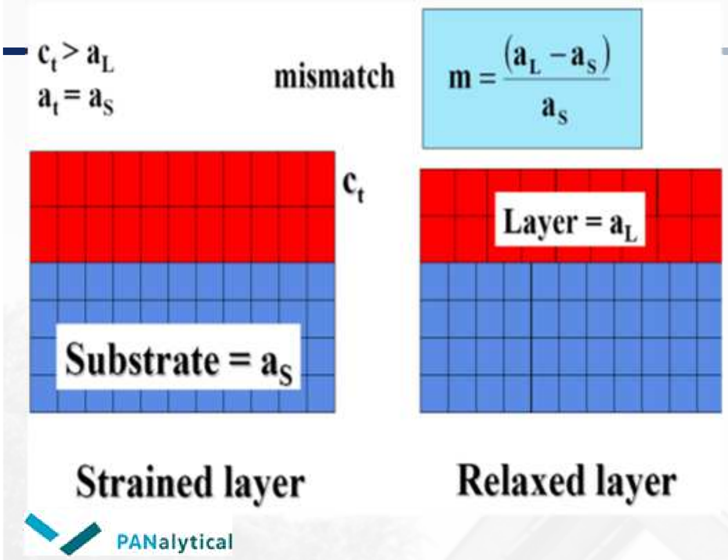
- Single crystal thin layer having crystal structure & orientation of substrate on which it was grown
  - ✓ Homoepitaxial layer – layer and substrate are same materials (same lattice parameters)
  - ✓ Heteroepitaxial layer – layer material is different from substrate (different lattice parameters)



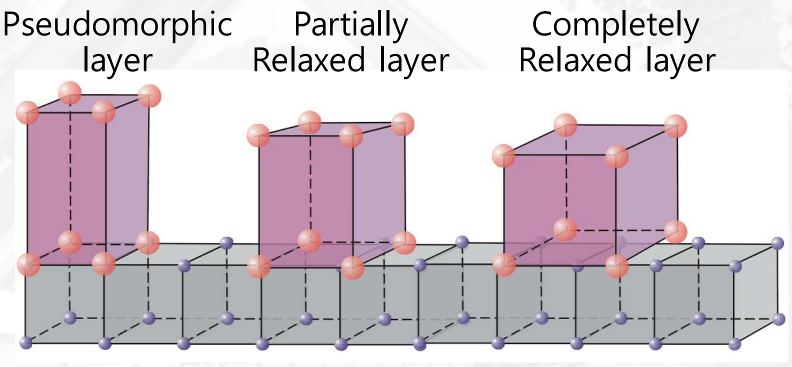


- Lattice mismatch $f = (a_{layer} - a_{subs})/\ a_{subs}$
- Critical thickness
  - ✓ thickness below which the layer grows pseudomorphically → the cubic unit cell of layer material is tetragonally distorted: $a_z \neq a_x = a_y = a_s$ (layer is strained).
  - ✓ decreases when f increases.
- Layer relaxation; $a_x, a_y \rightarrow a_z \rightarrow a_{l\ relax} = a_{bulk}$



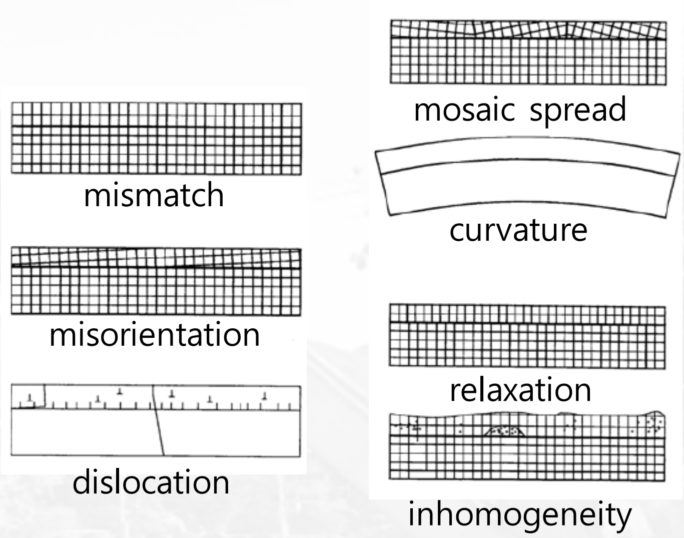


Epitaxial layer
Mismatch
Relaxation



What we want to know

- crystalline state of layer/layers - epi?; polycrystalline?; amorphous?
- crystal quality — chemical composition
- thickness — surface and interface roughness
- superlattice period
- mismatch
- relaxation
- misorientation
- dislocation density
- mosaic spread
- curvature
- inhomogeneity



www-ssrl.slac.stanford.edu/conferences/workshops/srxas2010/presentations/thinfilmscattering_epitaxiallayers_vailionis.pdf

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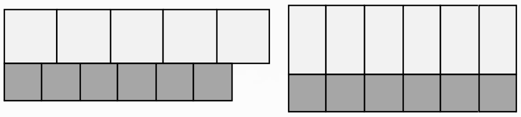
Relaxation (Lattice Strain)

Relaxation



Relaxed Film   Strained Film

- If the film is mismatched to the substrate → the film can be strained. → lattice parameters in the lateral direction (within the plane of the film) are forced to match those of the substrate. → distorts unit cell of the film.
- Determine the degree of relaxation.
  - ✓ No relaxation (fully strained)- the lateral lattice parameters of the film are strained and identical to those of the substrate.
  - ✓ Fully relaxed- the lateral lattice parameters of the film are equal to the bulk values – they have not been distorted at all.

Curvature

- The film and substrate may become slightly curved rather than perfectly flat. ← deposition process, thermal expansion mismatch between the film and substrate, etc

Dislocations

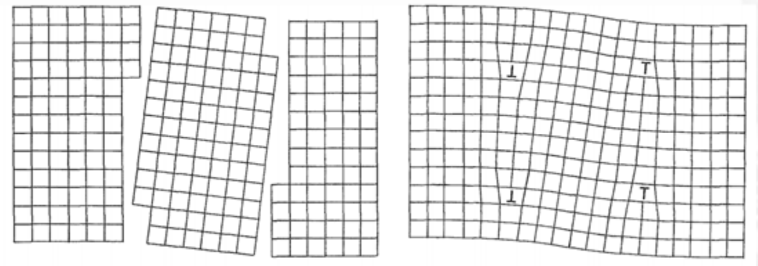
- Interface dislocations may form to relieve lattice strain between film and substrate with a large amount of mismatch.
- Slip dislocations are created by plastic deformation due to thermal or mechanical strain in the layer.

Scott A. Speakman

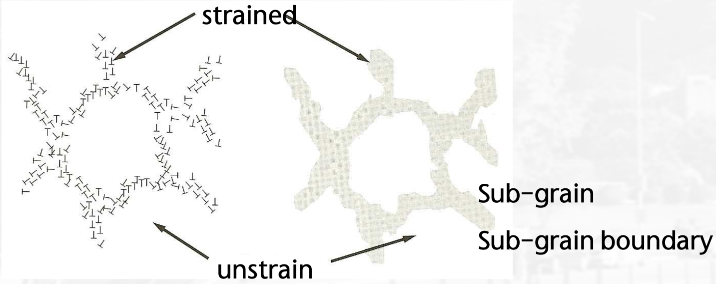
Mosaic structure, mosaic blocks

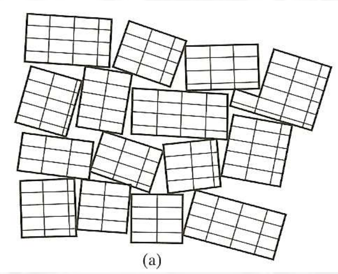
- Angle of disorientation between the tiny blocks is ε. → diffraction occurs at all angles between θ_B and $\theta_B \pm \varepsilon$.
- Increases the integrated intensity relative to that obtained (or calculated) for an ideally perfect crystal. ← strains & strain gradients associated with the groups of dislocations

A single xtal divided into 3 mosaic blocks



Boundaries are "walls" of edge dislocations.





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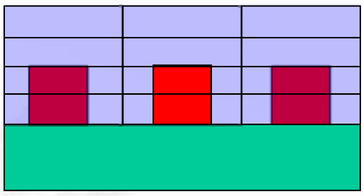
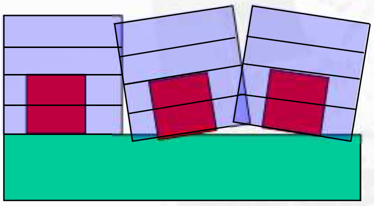
Mosaic spread

- Mosaicity is created by slight misorientations of different crystals as they nucleate and grow on the substrate. When the crystals join, they form boundaries.





In an ideal case, each nuclei (red) is perfectly oriented.
When the crystals grow and meet, there is perfect bounding between the crystallites → no boundary.

If the nuclei (red) are slightly misaligned, then boundaries will be formed.

Scott A Speakman

Thin film structure types

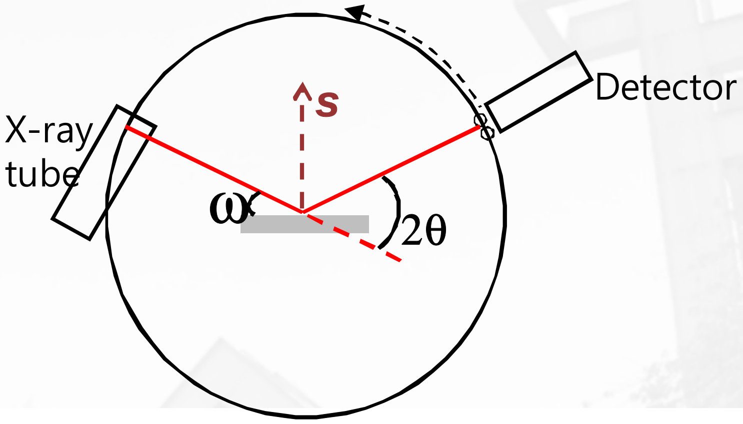
Perfect Epitaxy	Single crystal film in perfect registry with a substrate. There are no defects in the film or the substrate.
Nearly perfect Epitaxy	Single crystal film in nearly perfect registry with a substrate. Both film and substrate contain a low concentration of defects. Most defects are dislocations in the film.
Textured epitaxial	Film consists of mosaic domains in nearly perfect registry with the substrate. All domain boundaries are very low angle/low energy boundaries. There is nearly perfect bonding across domain boundaries.
Strongly textured polycrystalline	Film consists of grains with nearly perfect preferred orientation of all principle axes. This orientation is often strongly correlated to the substrate. Misorientation parameter for texture is small.
Textured polycrystalline	Film consists of grains with a preferred orientation for 3 principle axes or only along 1 axis out-of-plane.
Polycrystalline	Film consists of randomly oriented grains.
Amorphous	Film does not have long-range order.

Techniques ←→ type of information of film

	Thickness	Composition	Lattice Strain / Relaxation	Defects	Orientation	Residual Stress	Crystallite Size
Perfect Epitaxy	XRR HRXRD	HRXRD RC	Assume 100 %	Assume none	HRXRD	--	--
Nearly perfect Epitaxy	XRR HRXRD	HRXRD RC	HRXRD	RC	HRXRD	--	--
Textured epitaxial	XRR HRXRD	HRXRD	HRXRD IP-GIXD	RC	HRXRD	--	--
Strongly textured Polyxtalline	XRR	XRPD IP-GIXD	IP-GIXD	XRPD, IP-GIXD	IP-GIXD PF	IP-GIXD	XRPD, IP-GIXD
Textured Polyxtalline	XRR	XRPD, GIXD or IP-GIXD	--	XRPD, GIXD OR IP-GIXD	PF	Psi	XRPD GIXD
Polyxtalline	XRR	XRPD, GIXD	--	XRPD GIXD	PF	Psi	XRPD GIXD
Amorphous	XRR	--	--	--	--	--	--

HR- High Resolution XRD using coupled scan or RSM	PF- pole figure
IP-GIXD- in-plane grazing incidence XRD	XRR- X-Ray Reflectivity
RC- Rocking Curve	XRPD- X-ray powder diffraction
GIXD- grazing incidence XRD	Psi- sin^{2}psi using parallel beam

X-ray intensity as a function of omega and/or 2theta



- The incident angle w (omega) (X-ray source – sample)
- The diffraction angle 2θ (incident beam – detector)

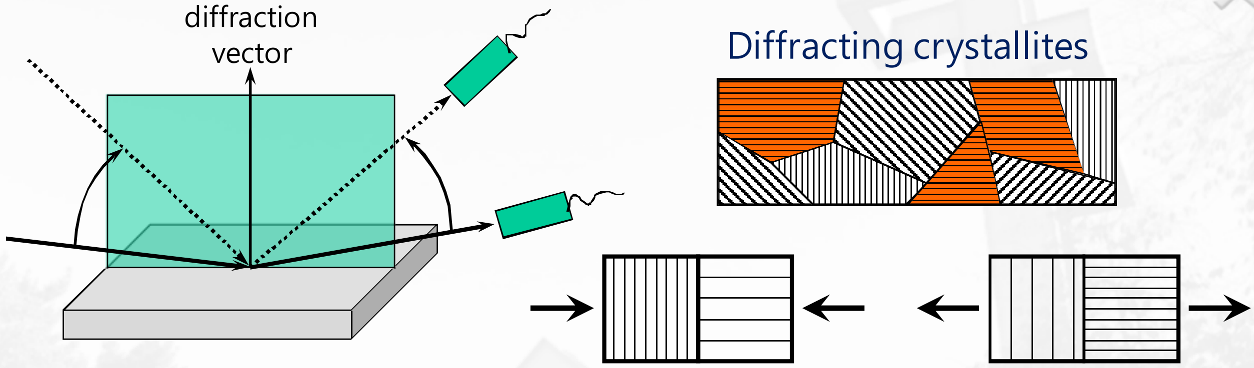
- **Rocking Curve;** X-ray intensity vs. Omega
- **Detector Scan;** X-ray intensity vs. 2θ without changing Omega
- **Coupled Scan;** X-ray intensity vs 2θ, but Omega also changes so that $\omega = \frac{1}{2} \times 2\theta + \text{offset}$.

Scott A. Speakman

X-ray technologies for thin films

- Grazing incident X-Ray diffraction (GID)
  - ✓ poly-crystalline thin films; phase ID, crystallite size, crystallinity
- In-plane grazing incident diffraction (IP-GID)
  - ✓ Textured film and epitaxial film; in-plane orientation, in-plane lattice parameter, crystallinity, depth analysis
- Rocking curves → dislocation density, mosaic spread, curvature, misorientation, inhomogeneity, layer thickness, superlattice period, strain and composition profile, lattice mismatch, ternary composition, relaxation
- Coupled scans → lattice mismatch, ternary composition, relaxation, thickness, superlattice period
- Reciprocal space map (RSM) → composition, thickness (> 50 nm), mismatch, mosacity, defects profile, etc. (most complete amount of information that are needed for the analysis of strained films)
- Reflectivity → composition, thickness (5-150 nm), interface/surface roughness; works with non-epitaxial and even non-crystalline thin films
- Grazing incident small-angle X-ray scattering (GISAXS)
  - ✓ pore structure (alignment), pore size distribution
- Pole figures → preferred orientation

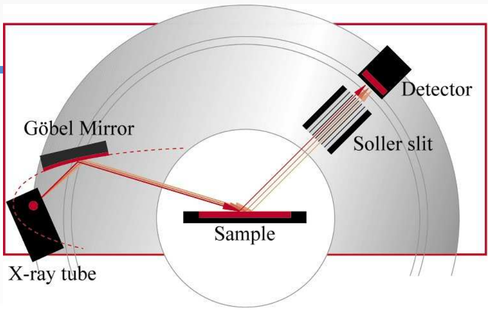
Conventional XRD

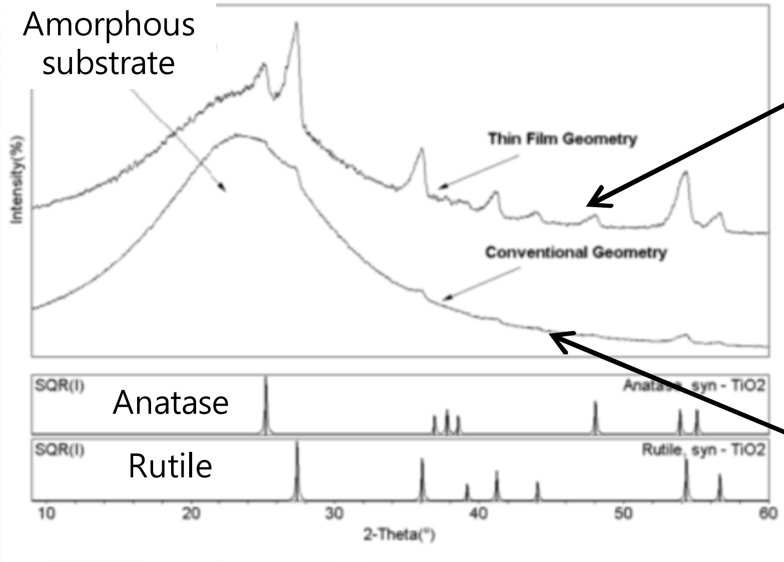


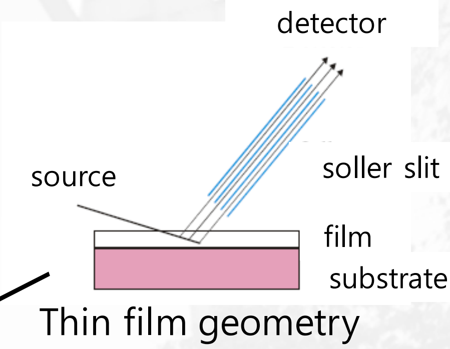
- Reliable information on
  - the preferred orientation of crystallites (out-of-plane orientation)
  - the crystallite size and lattice strain (in one direction)

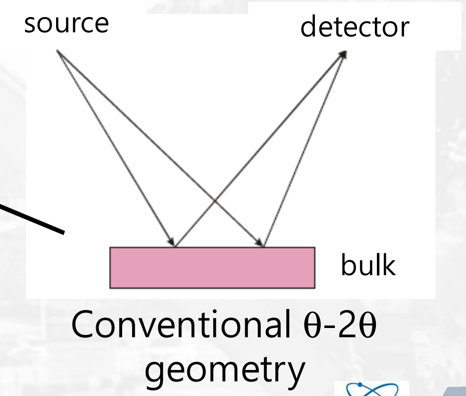
- No information on the residual stress (← constant direction of the diffraction vector)
- Low scattering from the layer (← large penetration depth)

GID

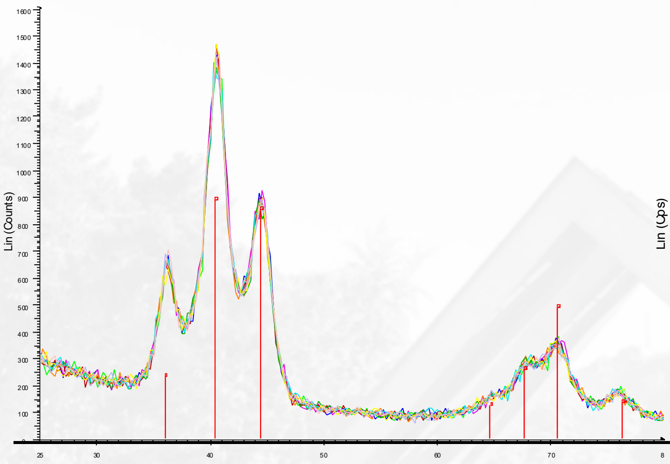




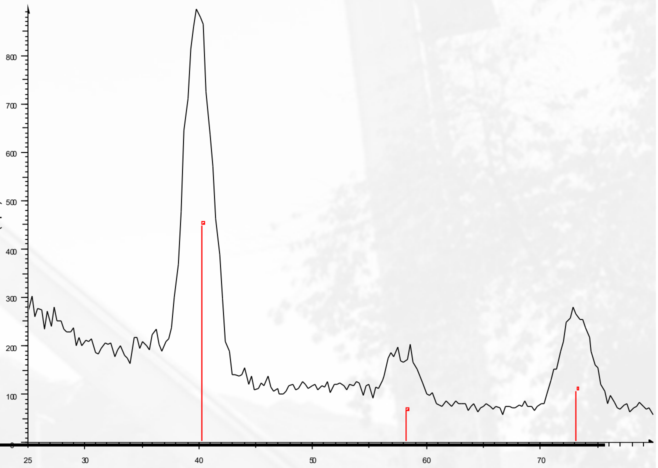




GID > phase analysis on tungsten films



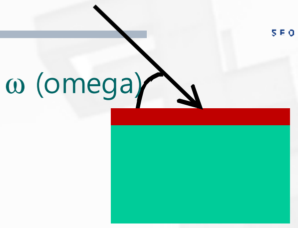
β-Tungsten
(10nm)

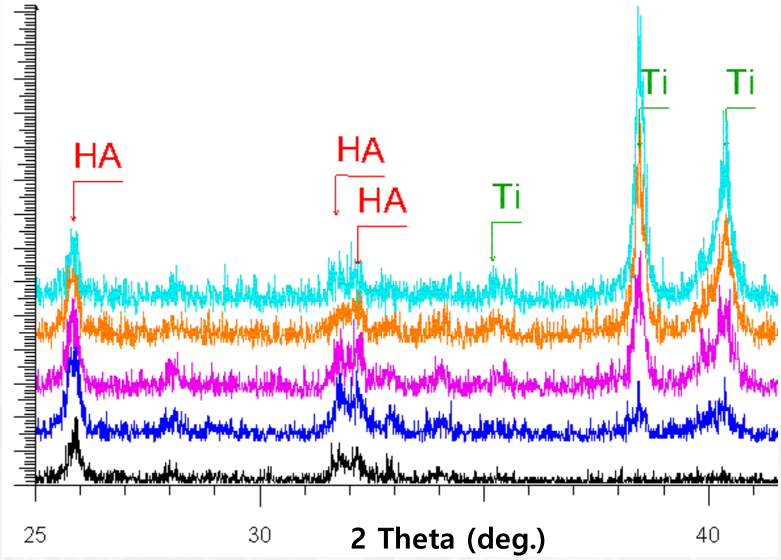


Tungsten, BCC phase (3nm)

GID > depth profile

Ti coated with hydroxyapatite (HA)





at progressively higher incidence angle, X-ray samples Ti substrate.

ω

at shallow angles, X-ray beam samples HA coating.

Parallel beam geometry must be used.

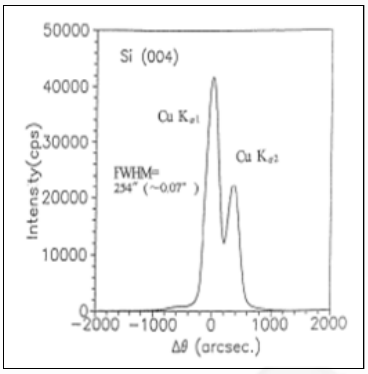
www.csec.ed.ac.uk/Instruments/D8_diffractometer/D8_GID.html

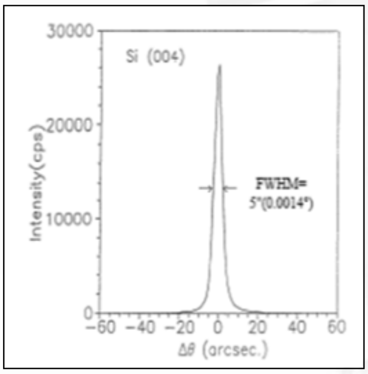
High-resolutuion X-ray diffraction (HRXRD)

normal XRD

~ 0.065 deg

(~ 230 arcsec)



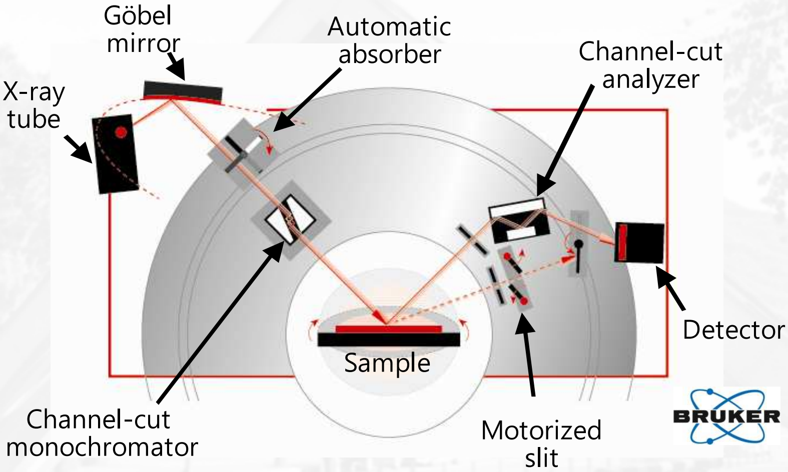


HR XRD

0.0015 ~ 0.008 deg

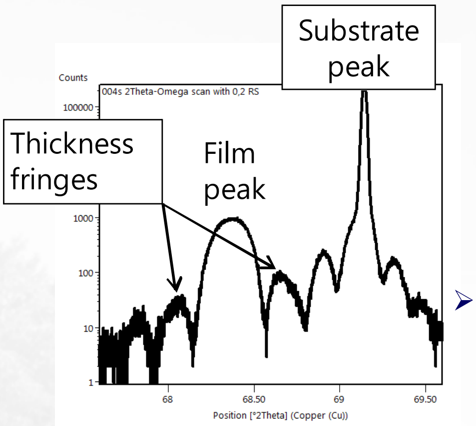
(5 ~ 30 arcsec)

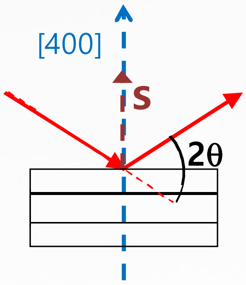
PANalytical

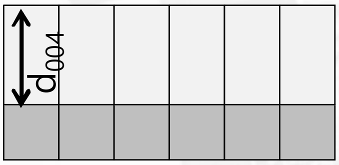


BRUKER

Coupled diffraction scan → d-spacing and thickness



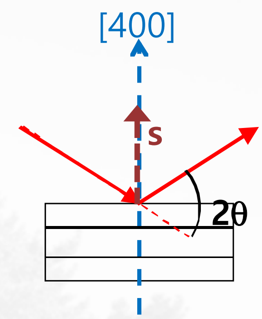




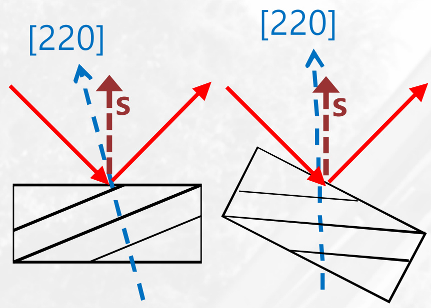
- ➢ Coupled scan: ω & 2θ change in coupled manner so the direction being measured (scattering vector, s) does not change.
- ➢ The peak position will give the d-spacing for the Bragg peak.
  - ✓This will provide information on anything that changes the lattice parameter of the unit cell, such as *composition* or *strain/relaxation.*
  - ✓This will only provide measurement of the **lattice parameter in one direction.**
- ➢ The width of film's Bragg peak can be used to quantify film thickness.
  - ✓ The thickness fringes can also be used to quantify the film thickness.

Scott A. Speakman

Sample tilt



- A symmetric scan requires that $\omega = \tfrac{1}{2}\,2\theta$, so that the scattering vector **s** will be $\perp$ to the sample surface.



- In order to measure different crystallographic directions in the sample, sample can be tilted. → asymmetric scan

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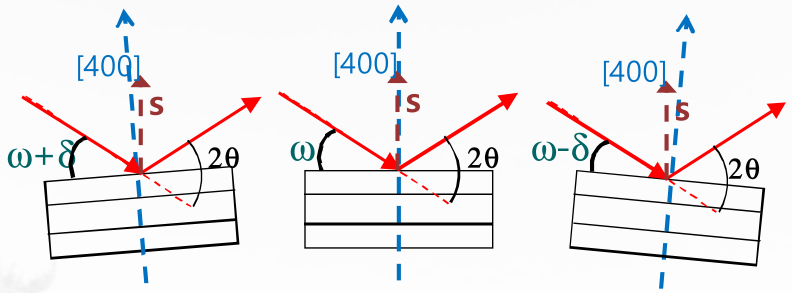
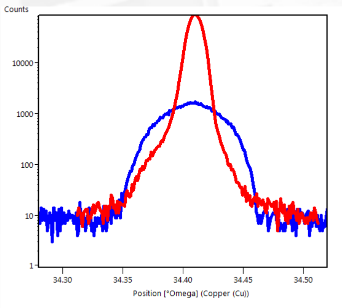
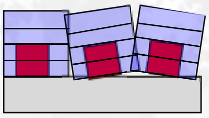
Rocking curve (ω scan)

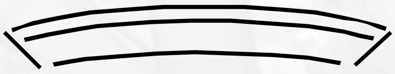




- The detector is set at a specific Bragg angle and the sample is tilted.
- A perfect crystal will produce a very sharp peak, observed only when the crystal is properly tilted so that the plane normal is // to the diffraction vector **s.**

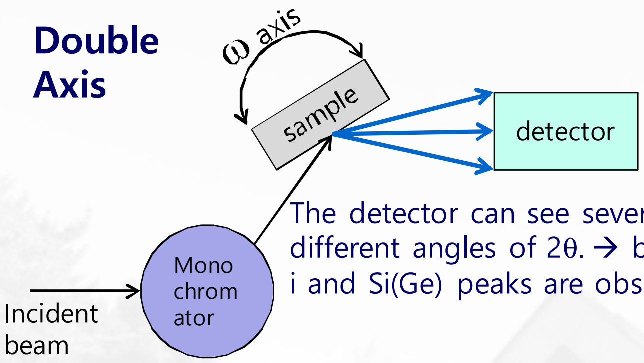
- Defects like mosaicity, dislocations, and curvature create disruptions in the perfect periodicity of atomic planes.
  - ✓ This is observed as broadening of the rocking curve.
  - ✓ The center of the rocking curve is determined by the d-spacing of the peaks.





Rocking curve > Double-axis vs. Triple-axis diffractometry

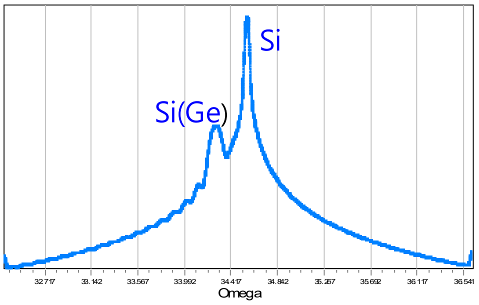
Double Axis



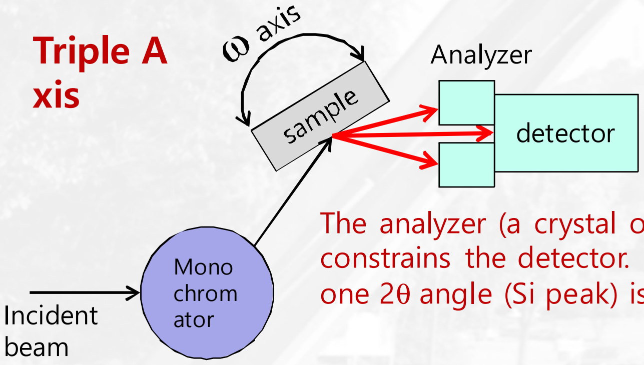
The detector can see several different angles of 2θ. → both the Si and Si(Ge) peaks are observed.

Si(Ge) film on Si

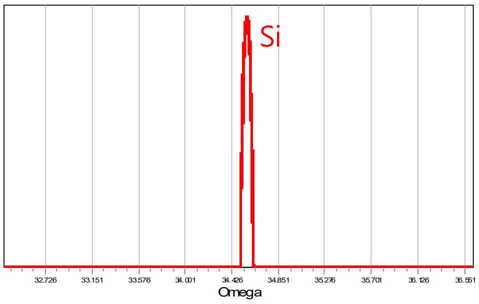
rotating omega while keeping the detector stationary



Triple Axis



The analyzer (a crystal or a slit) constrains the detector. → only one 2θ angle (Si peak) is observed.

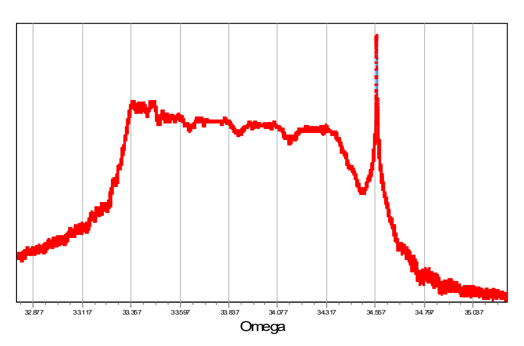


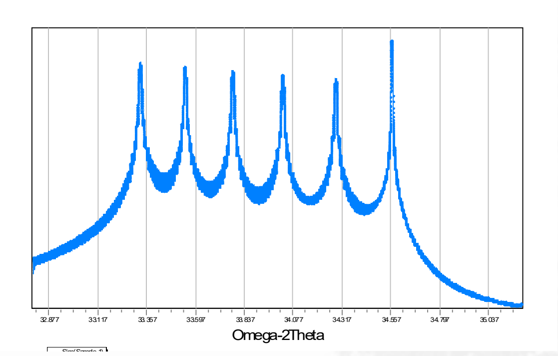
Double-axis vs. Triple-axis diffractometry

Two instrumental configurations for HRXRD

- ➢ Double-axis (double-crystal)
  - ✓ The detector does not discriminate between different diffraction angles 2θ.
  - ✓ All Bragg angles are measured simultaneously (over a limited range).
  - ✓ The sample is rotated about its ω axis (changing the incident angle) to produce a rocking curve (intensity vs ω).
- ➢ Triple-axis (triple-crystal)
  - ✓ A slit or analyzer crystal determines the angular acceptance of the detector.
  - ✓ The analyser crystal enables to distinguish between mosaic spread and strain contributions in the diffracted intensity distribution.
  - ✓ While a rocking curve (intensity vs ω) can be measured, it is more common to collect data by using a coupled scan.
  - ✓ As the sample is rotated about ω, the detector is rotated at twice the rate so that 2θ = 2ω, producing a coupled ω - 2θ scan.
  - ✓ **Reciprocal space maps** are collected by collecting coupled scans at different ω offsets, where 2θ = 2ω – offset.

Double-axis rocking curve vs. Triple-axis coupled scan





- The double-axis rocking curve
- A Si wafer coated with 5 slightly relaxed Si(Ge) layers of varying Ge concentration
- The Ge concentrations were 10, 20, 30, 40, and 50%.
- Each Ge layer was 500nm thick.

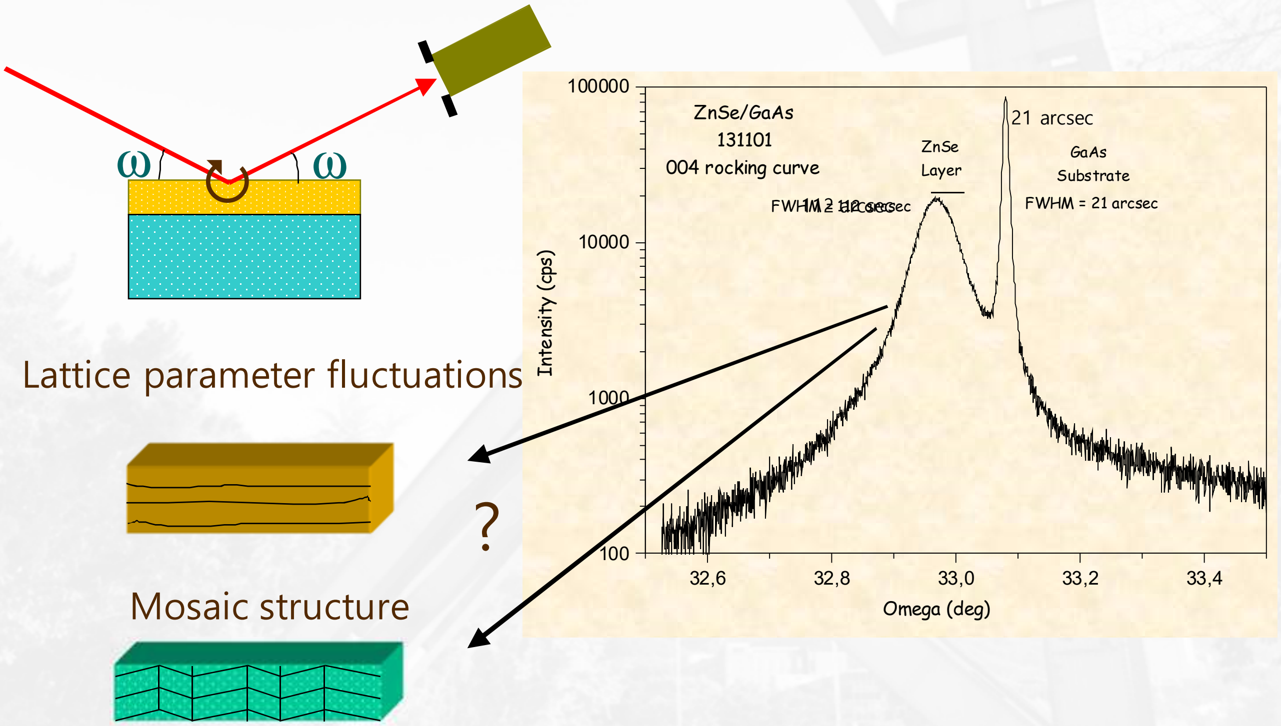
- The triple-axis coupled omega-2theta scan of the same Si wafer
- A rocking curve in triple-axis mode can be collected for each individual peak to determine the tilt variation of each individual Si(Ge) layer.

Triple-axis > coupled scans vs Reciprocal Space Map

- Coupled scan collects data as ω-2θ
  - ✓ 2θ is moved at twice the rate as the sample rotation about ω.
  - ✓ 2θ = 2ω + tilt
  - ✓ This will observe peaks with different Bragg angles, but only for one specific tilt.
  - ✓ If the epilayers are tilted w.r.t. the substrate, then a single coupled scan cannot observe both substrate and film peaks. → must collect coupled scans for a range of tilts: this is the **Reciprocal Space Map (RSM).**

- The **RSM** collects several ω-2θ coupled scans, but each coupled scan is collected with a slightly different tilt (offset) in the ω direction.
  - ✓ When the scan is collected, 2θ still moves at twice the rate as the sample rotation so that 2θ = 2ω + tilt.
  - ✓ The tilt value is slightly different for each coupled scan that is collected.
  - ✓ Complete map of ω-2θ vs tilt (ω).

Rocking curve > crystal quality

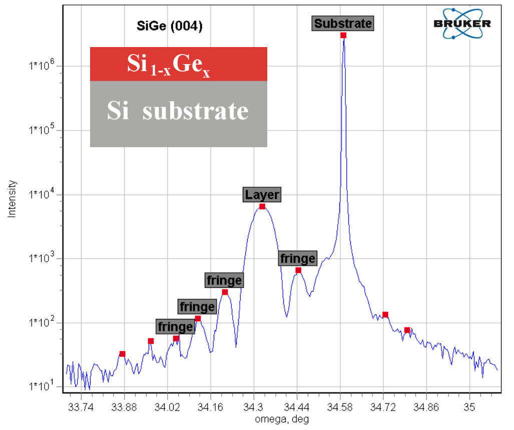


Lattice parameter fluctuations

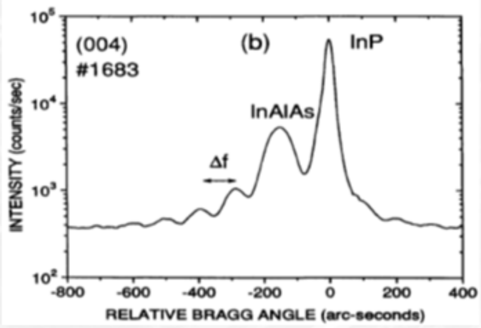
Mosaic structure

Prof. Elżbieta Dynowska

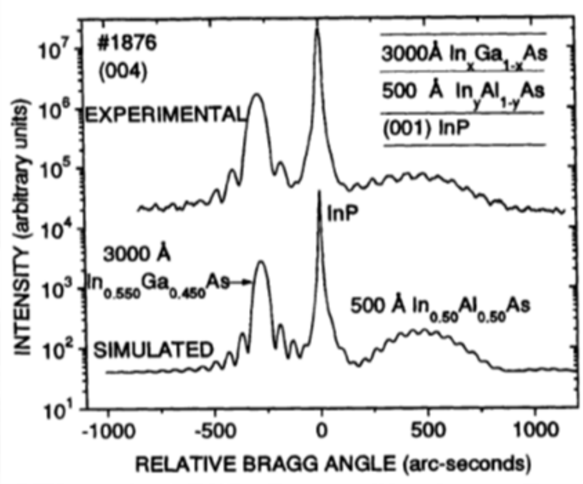
Rocking curve > thickness and composition



The best way to determine layer compositions & thicknesses is to compare the experimental rocking curve with simulated curves.



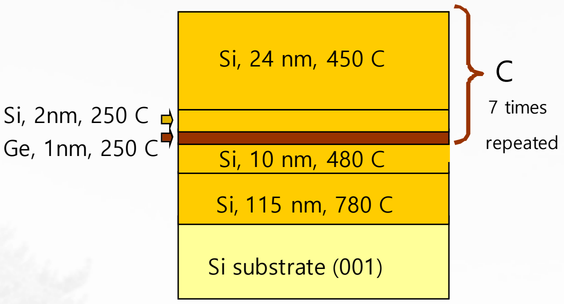
HRXRD (004) Rocking curve
for $In_{0.53}Al_{0.47}As$ on InP substrate

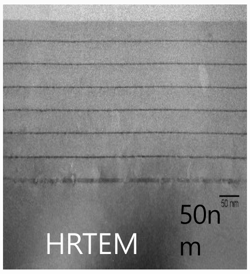


HRXRD (004) experimental and simulated rocking curves

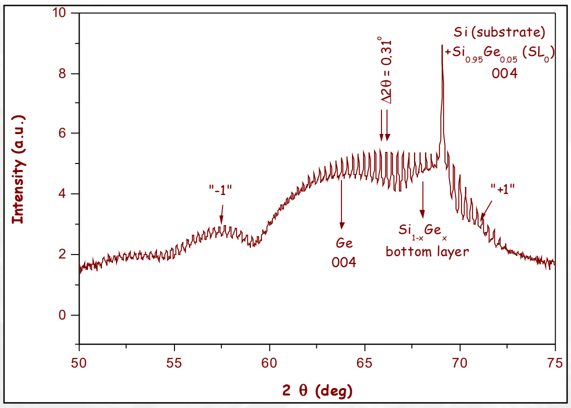
Dr. Ahmed El-Naggar

Rocking curve - superlattice of self-assembled ultra-small Ge quantum dots

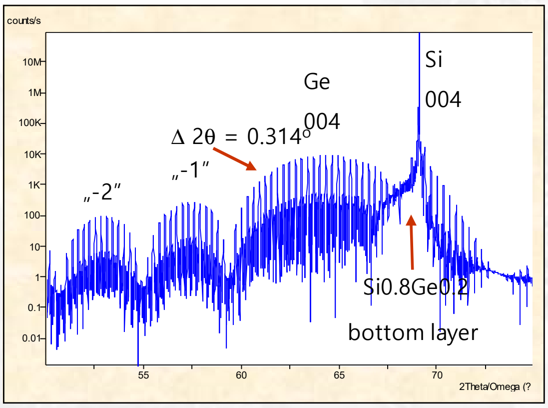




Results:	HREM	XRD
superlattice period C.....	≈ 33.5 nm	33 nm
thickness of Ge..............	≈ 1.8 nm	2.0 nm
thickness of SiGex bottom layer....................	≈ 6.7 nm	6.7 nm
Compositon......................	----	x ≈ 0.2



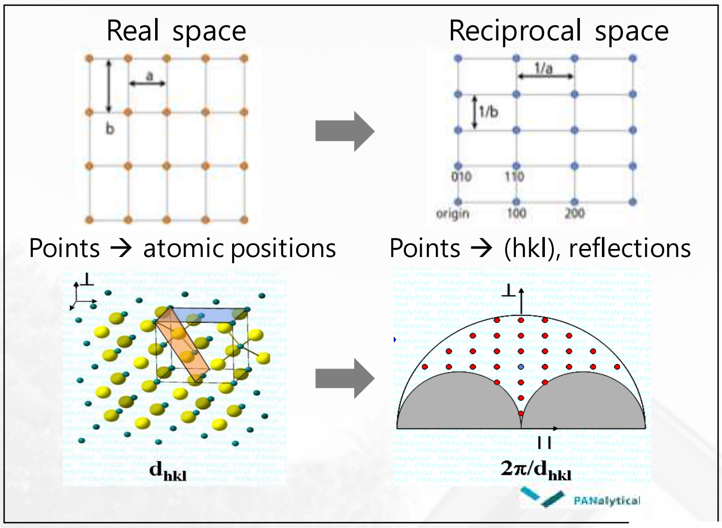
Experimental pattern, Hasylab (Hamburg)



Simulated pattern, X'Pert Epitaxy and Smoothfit software

Prof. Elżbieta Dynowska

Real vs. Reciprocal space

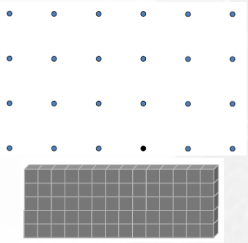


Real space

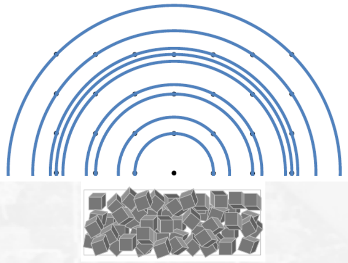
Reciprocal space

Points → atomic positions

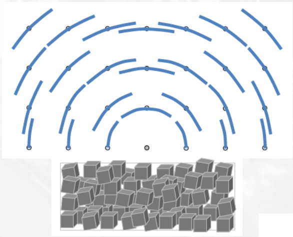
Points → (hkl), reflections



Single crystal



Polycrystalline random



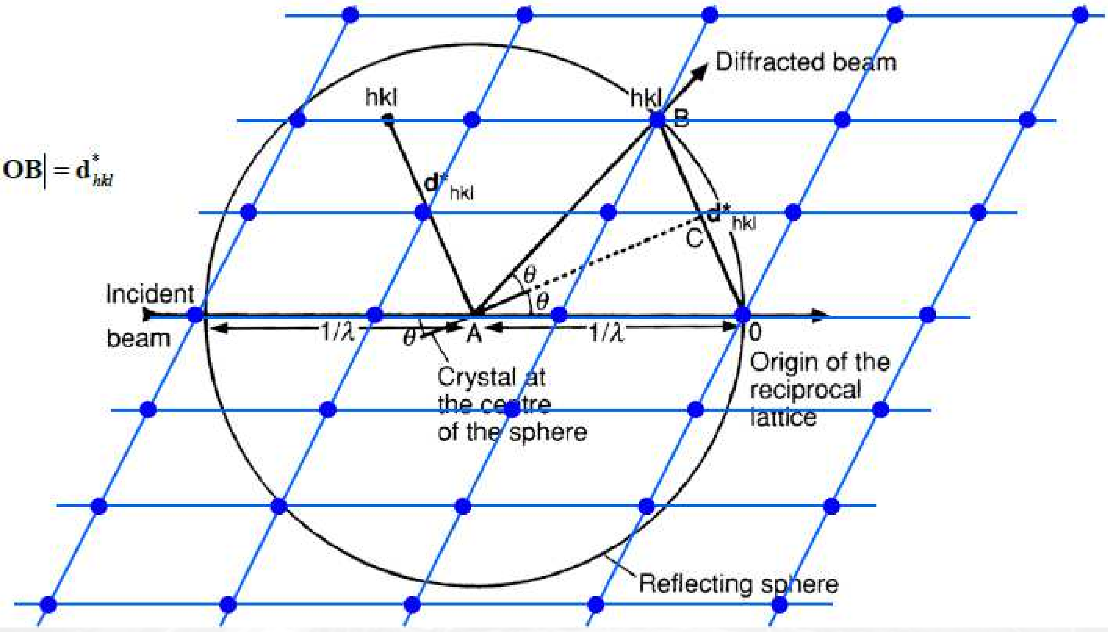
Polycrystalline textured

www-ssrl.slac.stanford.edu/conferences/workshops/srxas2010/presentations/thinfilmscattering_epitaxiallayers_vailionis.pdf

Reciprocal lattice > Ewald sphere

$$|\mathbf{OC}| = \frac{1}{\lambda}\sin\theta = \frac{1}{2}|\mathbf{d}^*_{hkl}| = \frac{1}{2d_{hkl}} \rightarrow \lambda = 2d_{hkl}\sin\theta$$

$$|\mathbf{OB}| = \mathbf{d}^*_{hkl}$$



www-ssrl.slac.stanford.edu/conferences/workshops/srxas2010/presentations/thinfilmscattering_epitaxiallayers_vailionis.pdf

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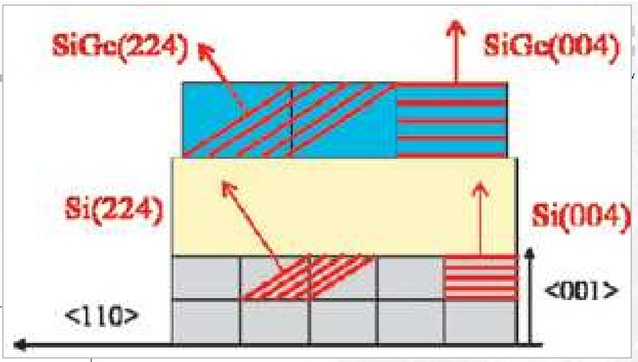
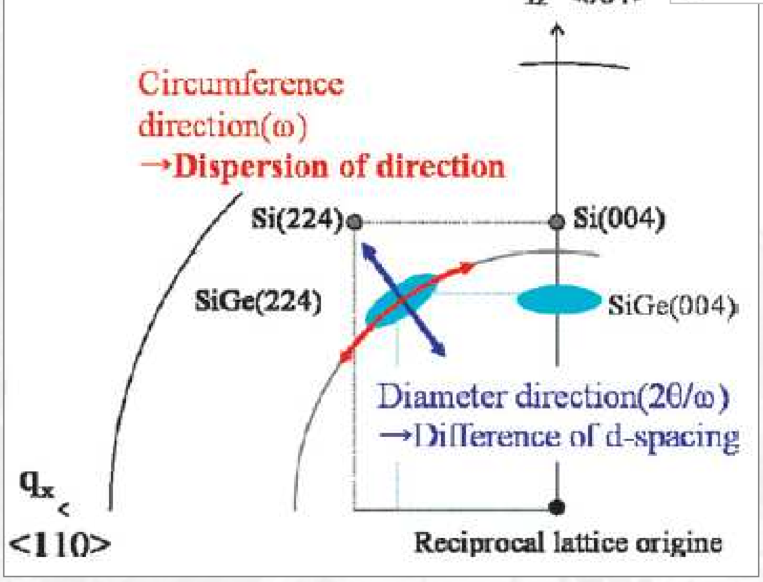
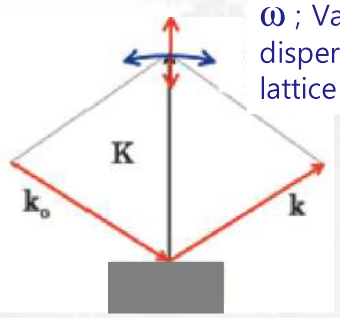
Reciprocal space map (RSM)





2θ/ω ; Change or spread in lattice constant (d-spacing)

ω ; Variation and dispersion of lattice direction

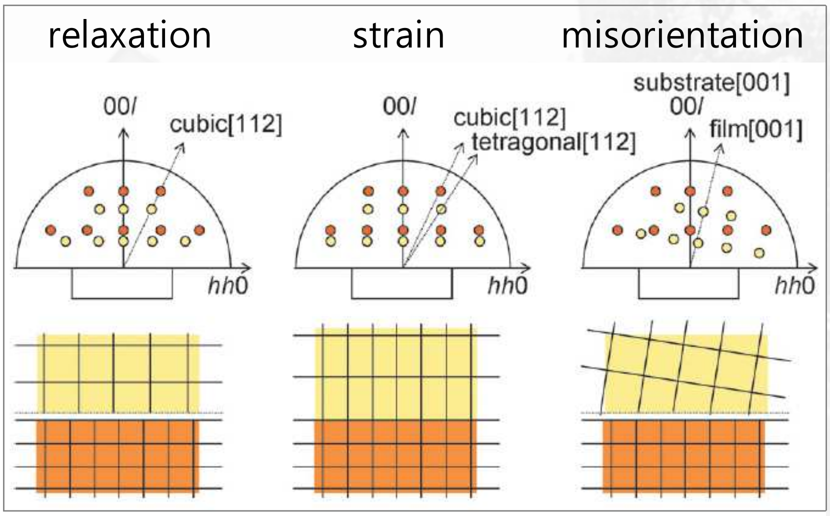


Rigaku Journal, 25(2), 2009, X-ray thin film measurement techniques

RSM

- RSM records diffraction intensity distributions by scanning both diffraction angle and sample rotation axes, and plots the result in the reciprocal space.
- RSM can provide <u>info on orientation relationships, composition, thickness, mismatch, relaxation, layer tilt, mosacity, defects profile, xtallinity, preferred orientation, etc.</u>

RSM of hetero-epitaxial layer



Rigaku Journal, 25(2), 2009, X-ray thin film measurement techniques

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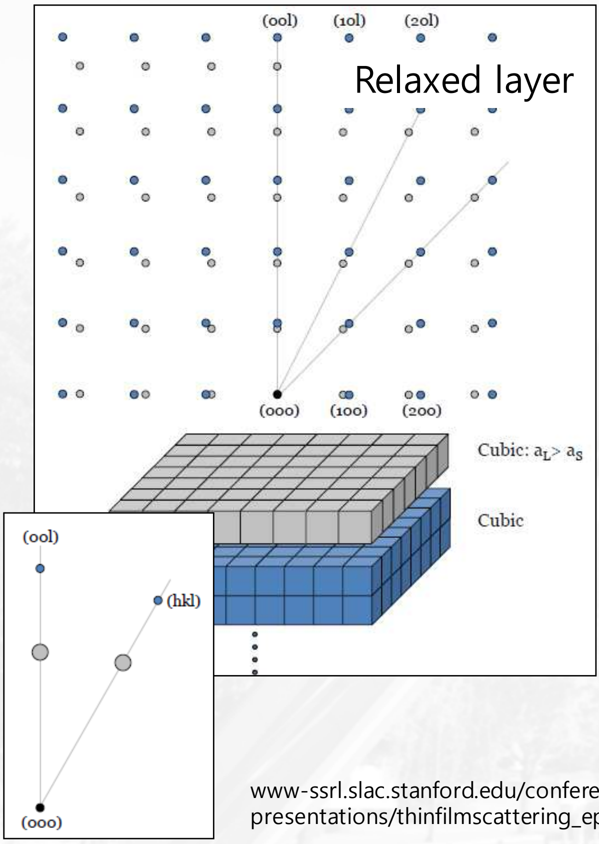
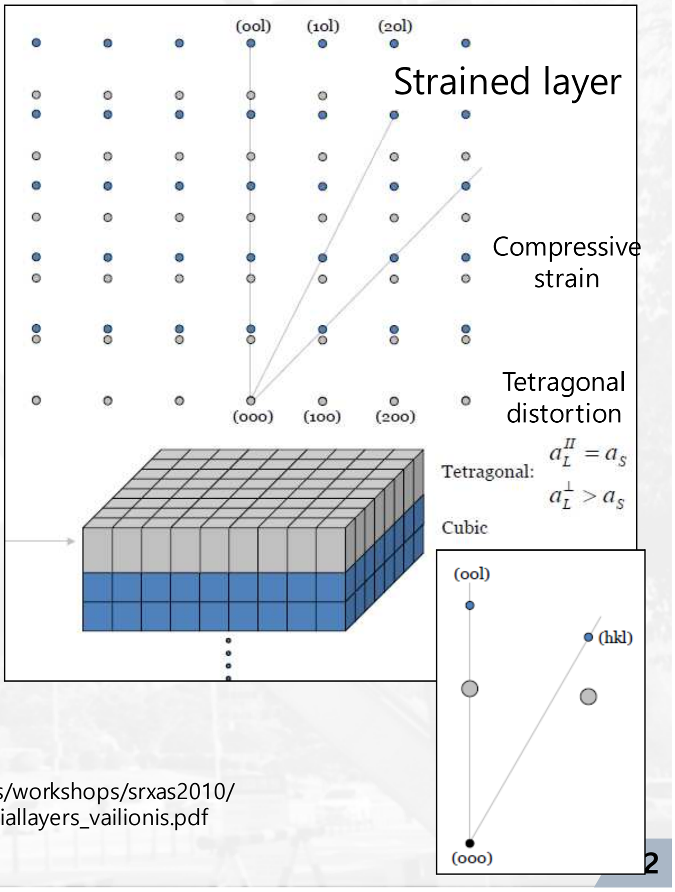
Relaxed layer vs. Strained layer





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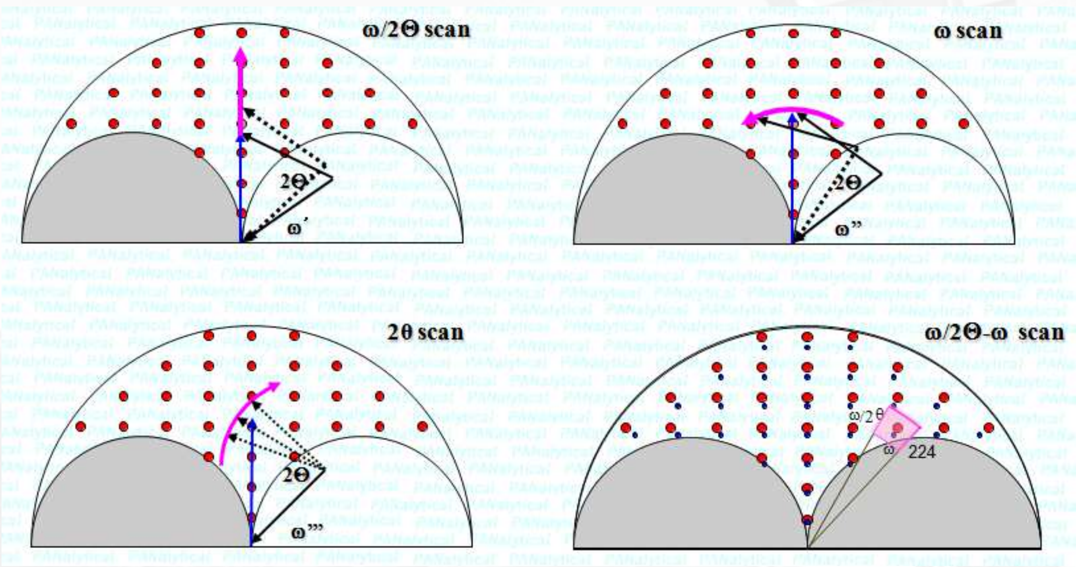
Scans in reciprocal space



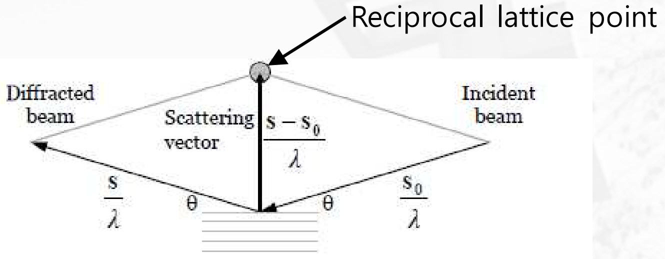
- Rocking curve (ω scan) - arc centered on the origin
- Detector scan (2θ scan) - arc along the Ewald sphere circumference
- Coupled scan (2θ-ω scan) - straight line pointing away from the origin

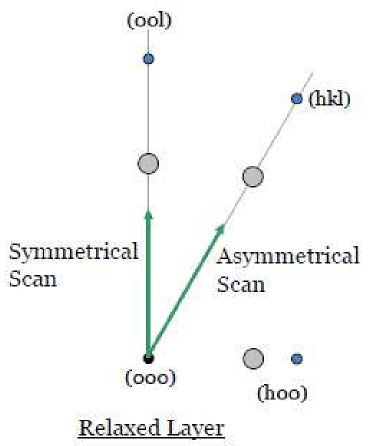
---

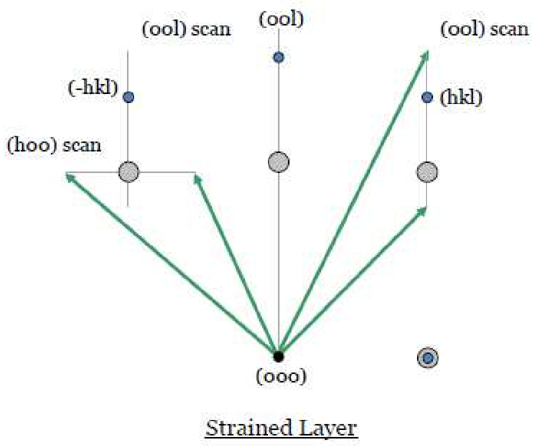
Reciprocal lattice – scattering vector

$$\left|\frac{\mathbf{s}-\mathbf{s}_0}{\lambda}\right| = \frac{2\sin\theta}{\lambda} = \left|\mathbf{d}^*_{hkl}\right| = \frac{1}{d_{hkl}}$$

$$\lambda = 2d_{hkl}\sin\theta$$







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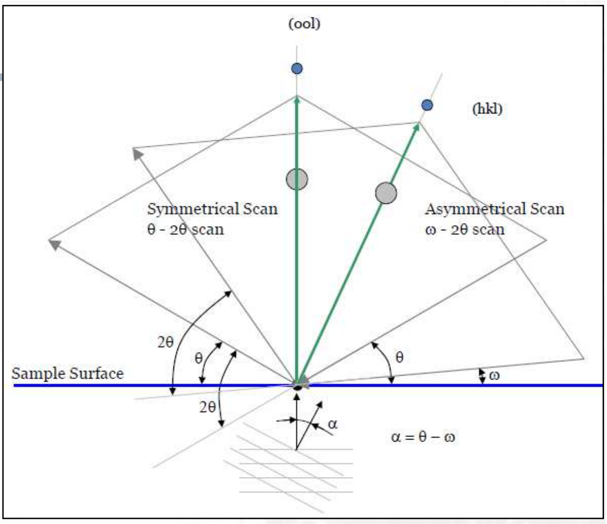
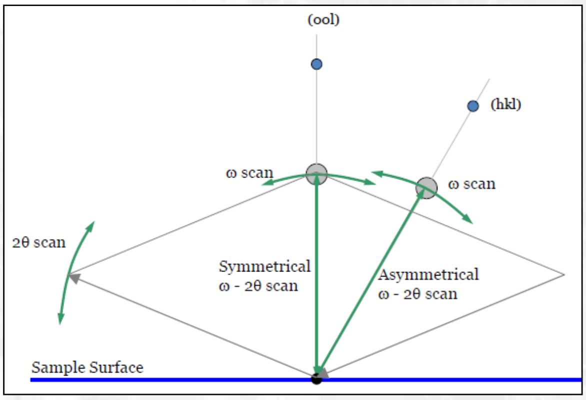
Scan directions

- One family of planes is // or nearly // to the surface of the sample.
  - ✓ These are the only planes examined in a symmetric scan.
  - ✓ The sample is not tilted. → 2θ = 2ω
- Other planes can only be observed by tilting the sample.
  - ✓ Asymmetric scans are used to collect peaks from these other planes by tilting the sample about ω. → 2θ = 2ω + tilt
- Several properties can only be determined by collecting both symmetric and asymmetric scans.





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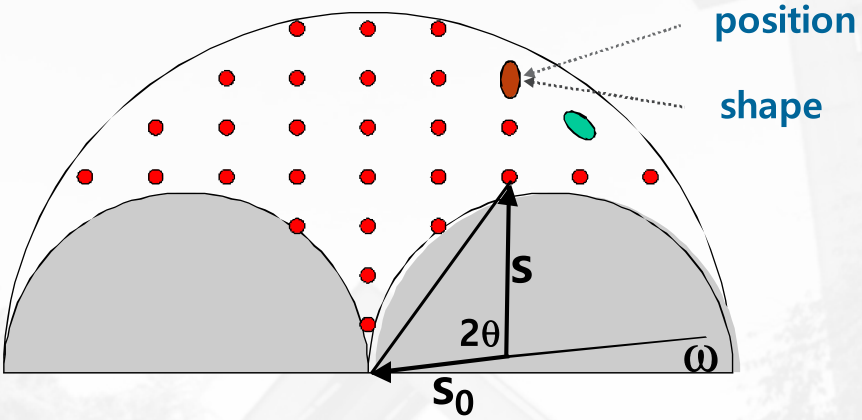
Scott A. Speakman

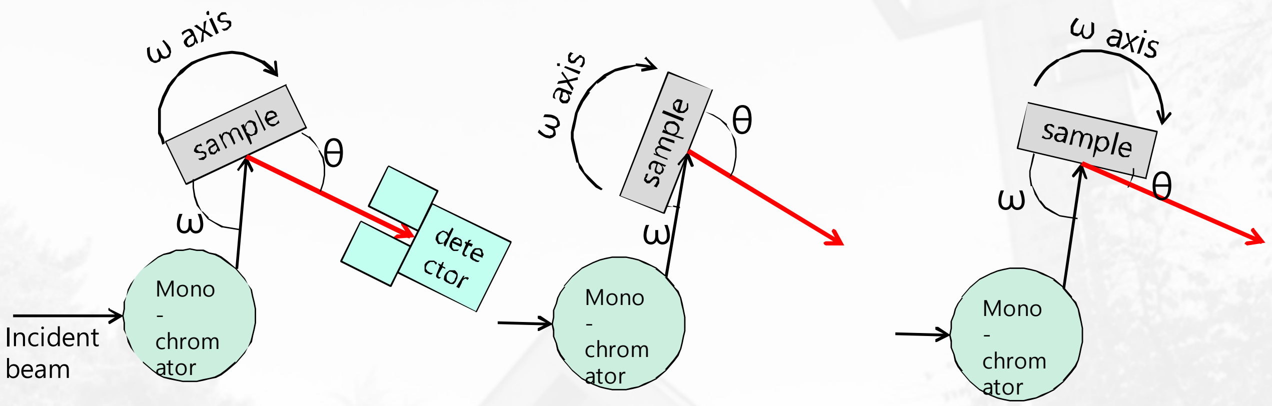
Symmetric vs Asymmetric



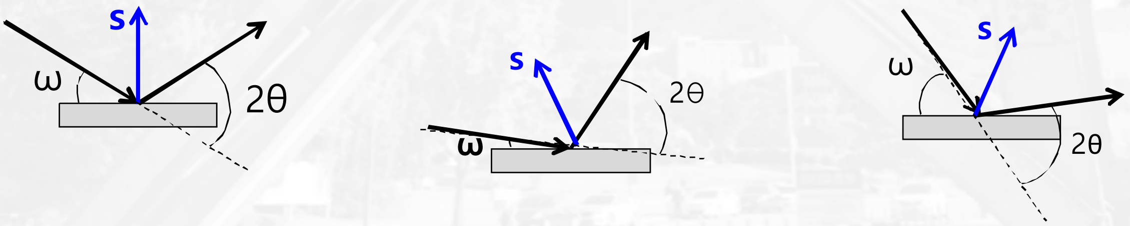
- Symmetrical reflection = planes parallel to surface
- Asymmetrical reflection = planes inclined to wafer surface
  - ✓ High angle of incidence or glancing exit = ω > 2θ/2
  - ✓ Glancing incidence = ω < 2θ/2

PANalytical

Symmetric vs Asymmetric



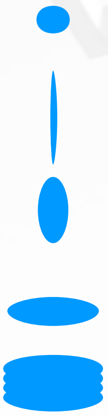
Symmetric Scan	Asymmetric Scan	Asymmetric Scan
	Grazing Incidence	Grazing Exit
ω = θ	**ω = θ *-Tilt***	**ω = θ *+Tilt***

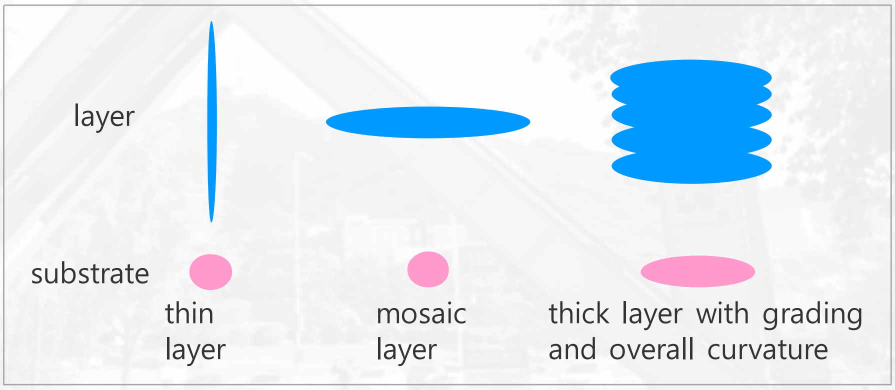


Scott A. Speakman

Shape of reciprocal lattice point

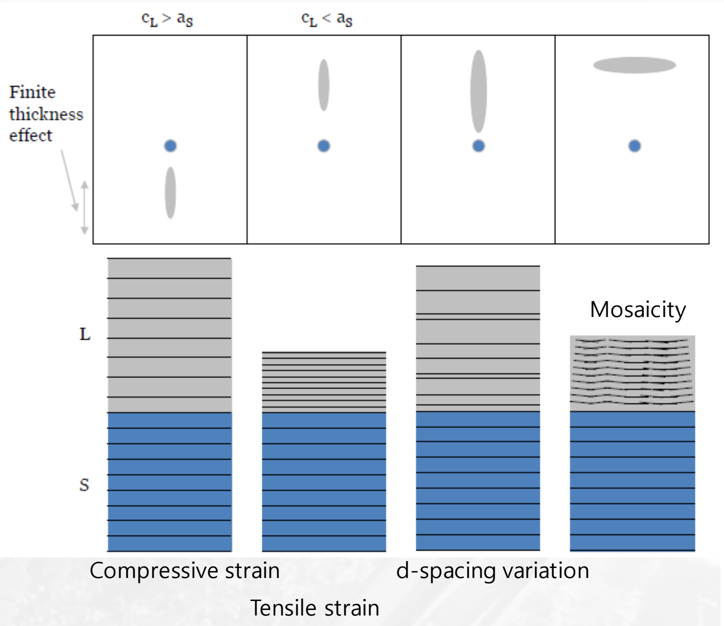
- high quality substrate - sharp peak
- broadening normal to sample surface
  - ✓ thin layers
  - ✓ d spacing variation with depth
- broadening parallel to surface
  - ✓ mosaic structure
  - ✓ variable tilts (curvature or dislocations)

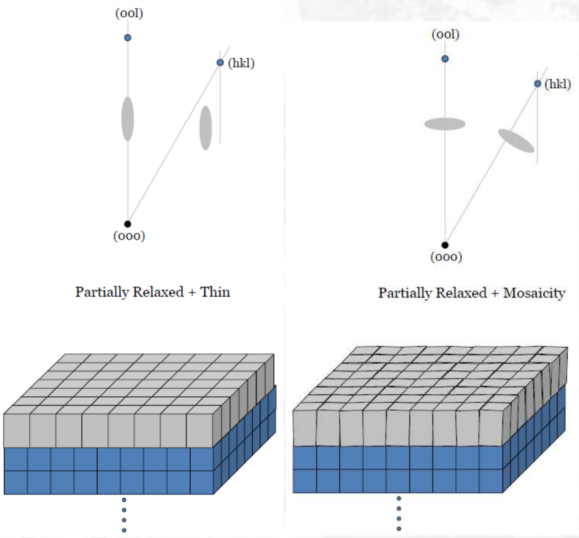




PANalytical

Shape of reciprocal lattice point





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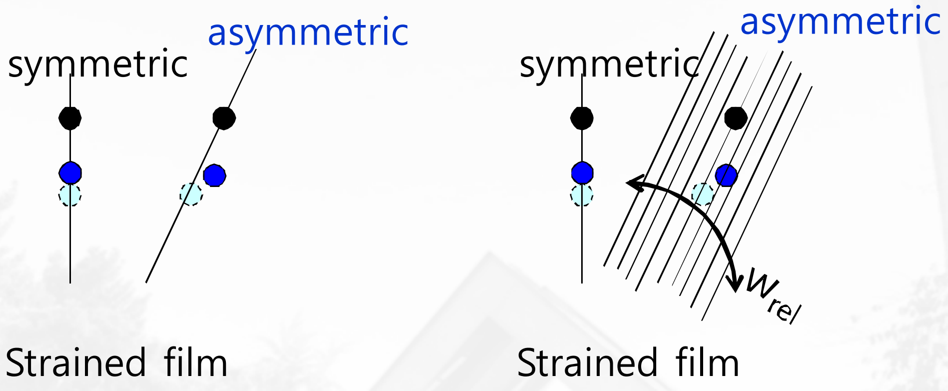
Highly strained film

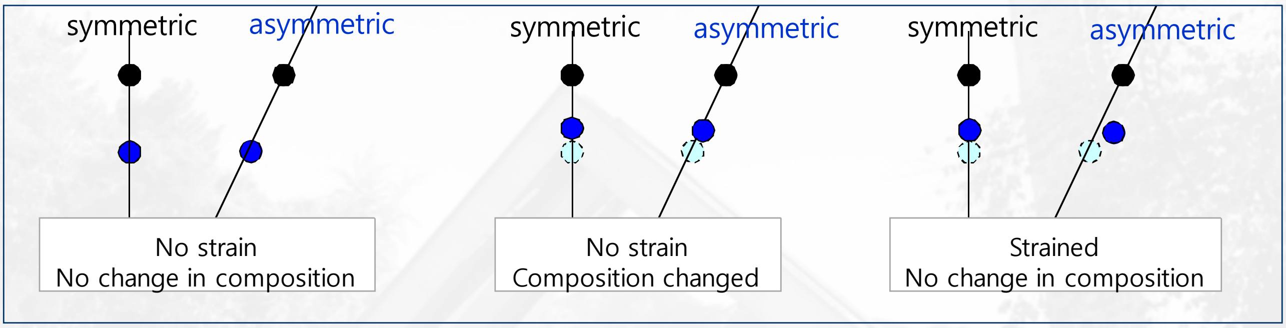


- The typical way to collect reciprocal space maps is to vary relative ω and collect multiple 2θ/ω coupled scans.

Scott A. Speakman

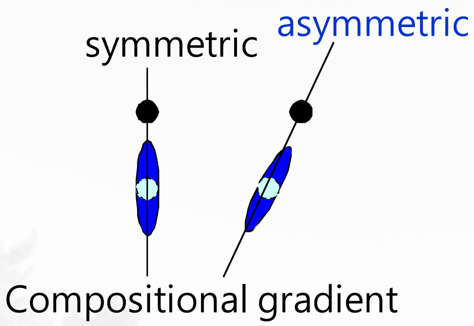
Change of Strain and Composition

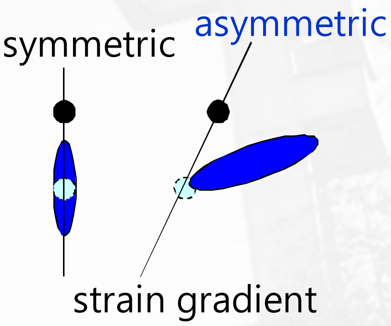
- In substitutional solid solutions, the composition can vary.
- Changes in the composition will change the lattice parameters, which will change d_{hkl} and therefore the Bragg peak positions.
  - ✓ Unlike relaxation, changes in composition will not change lattice tilts.

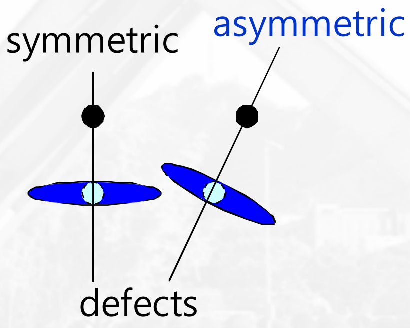


- Symmetric scans cannot distinguish between strain & compositional changes.
- In the symmetric scan, strain and compositional changes produce similar peak shifts.
- In order to quantify both strain and composition, must combine a symmetric scan with an asymmetric scan.

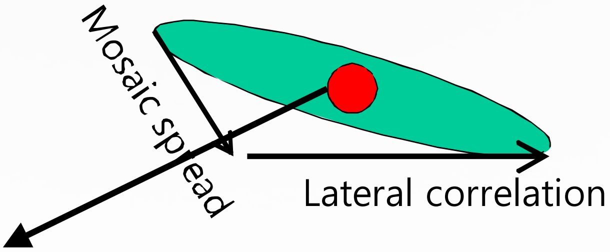
Defects & gradients can produce spreading of RLP







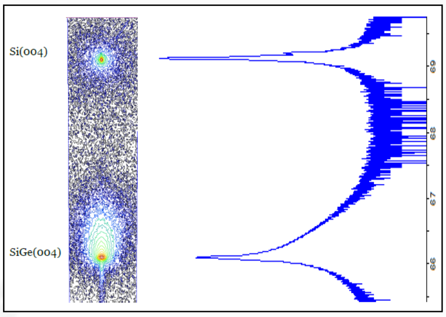
Mosaic spread ← broadening of the RLP

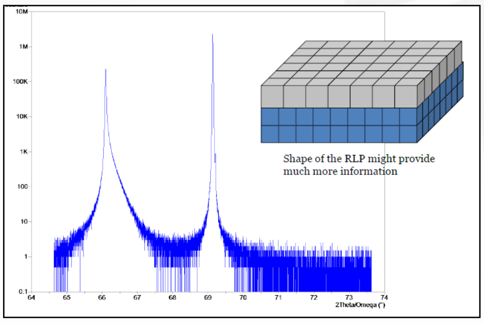


- The amount of broadening of the reciprocal lattice point that is ⊥ to the reflecting plane normal can be attributed to mosaic spread.
- The peak broadening // to the interface can be attributed to lateral correlation length.

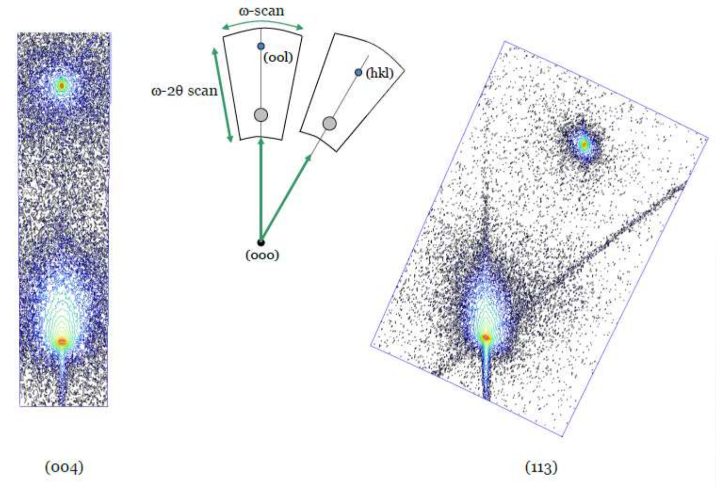
Scott A. Speakman

Relaxed SiGe on Si(001)





Shape of the RLP might provide much more information



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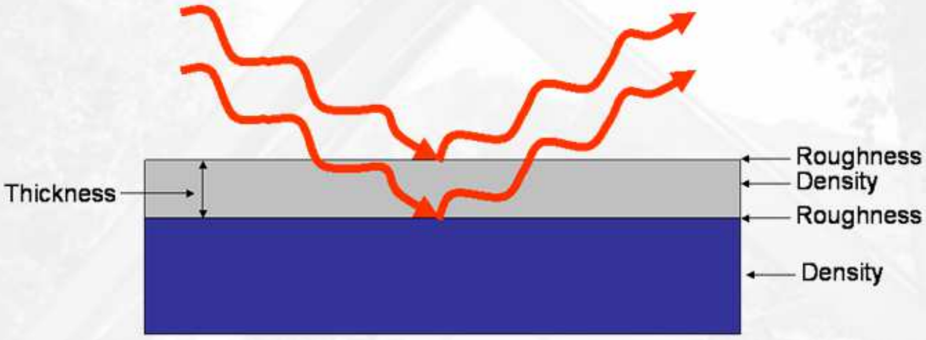
X-Ray Reflectivity (XRR)

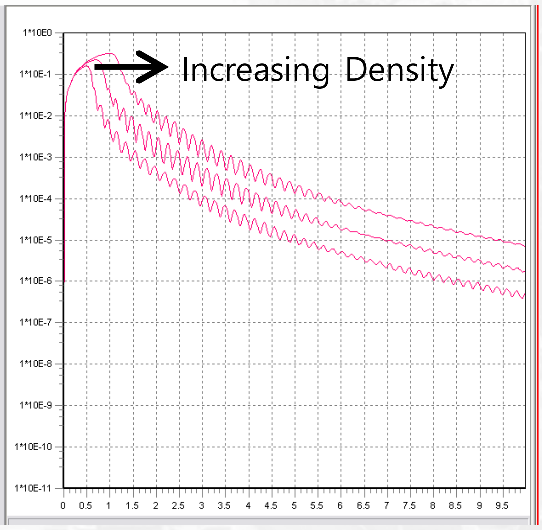
- The same equipment that is optimized for HRXRD can also be used for XRR analysis of thin films.
- X-ray waves reflecting from each different surfaces in a multilayer thin film.
  - ✓ The multiple reflected waves interfere with each other. → reflectivity curve
  - ✓ The XRR scan can be used to determine the density, thickness, and roughness of each layer in a multilayer thin film.



XRR > critical angle

- The critical angle is a function of the density & composition of the layer.
- Below the critical angle, θ_C, the X-ray beam is completely reflected (total external reflection).

- The critical angle for a layer is a function of its electron density.
  - ✓ This is a convolution of density and composition.
  - ✓ If one is known, the other can be determined using XRR.
  - ✓ For example, for a given composition, as the density of the film ↑, the critical angle θ_C often ↑.

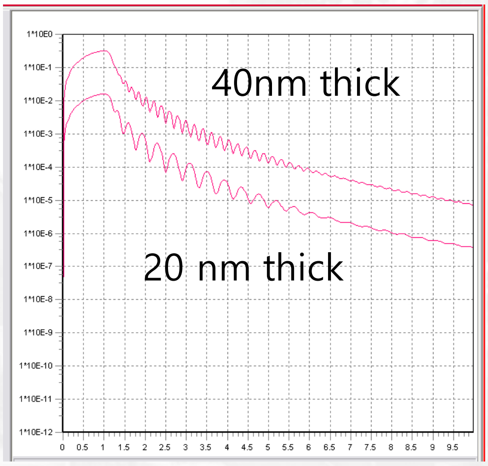


Scott A Speakman

XRR > distance between interference fringes

- The distance between interference fringes is a function of the thickness of the layers.
- Interference fringes are created by the phase difference between X-rays reflected from different surfaces.

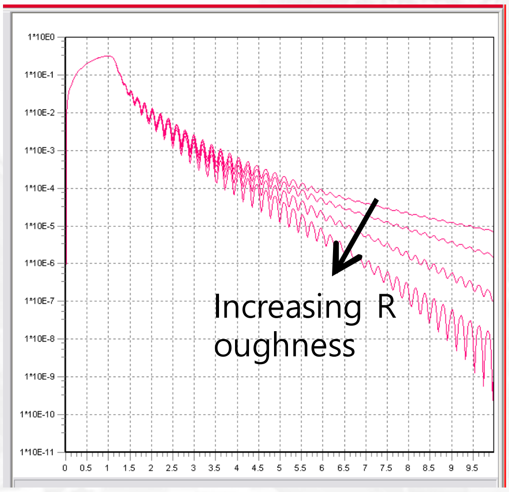
- The distance between the fringes is inversely proportional to the thickness of the layer.
  - ✓ Because of this, thicker films need better resolution (use a monochromator) and thinner films need more intensity (use only the mirror).



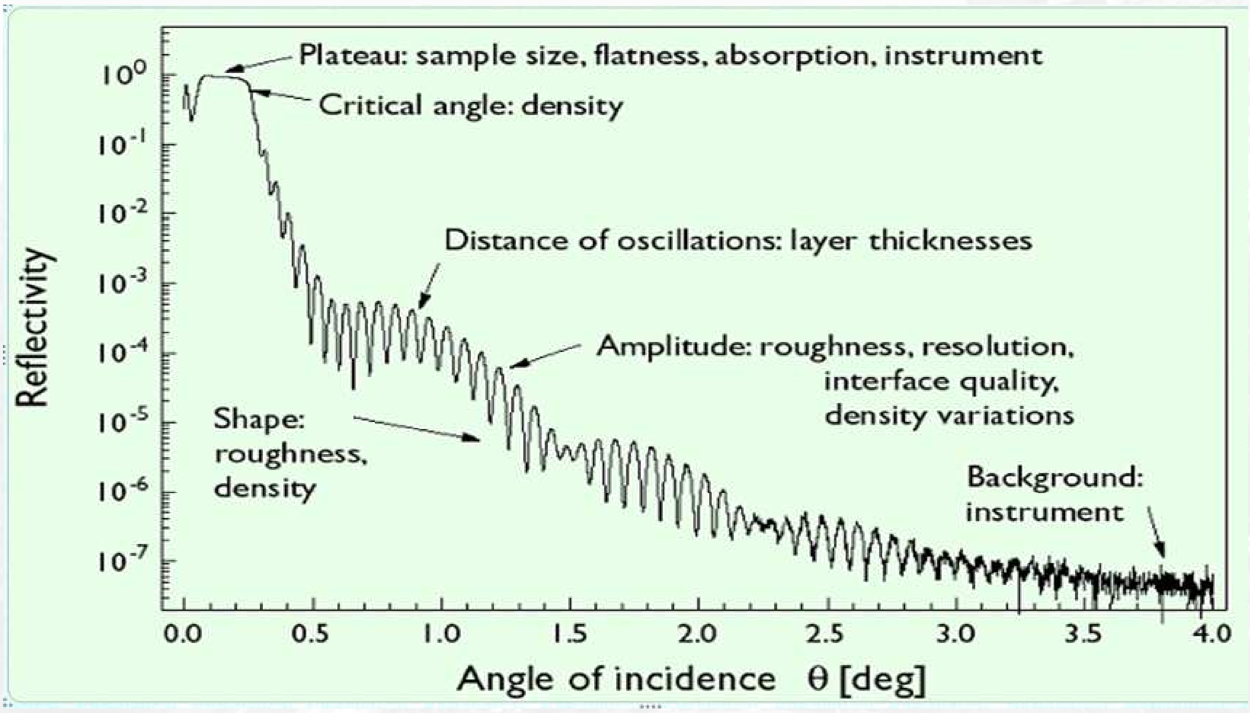
XRR > how quickly the reflected signal decays

- Roughness determines how quickly the reflected signal decays.
- Roughness causes X-rays to be scattered rather than reflected.
  - ✓ This produces a decay in the reflected beam intensity.
  - ✓ The loss of beam intensity ↑ with θ.

- A rougher surface produces more diffuse scatter, causing the reflected beam intensity to decay more with θ.
  - ✓ The diffuse scatter can be measured to look for order in the roughness of the film.



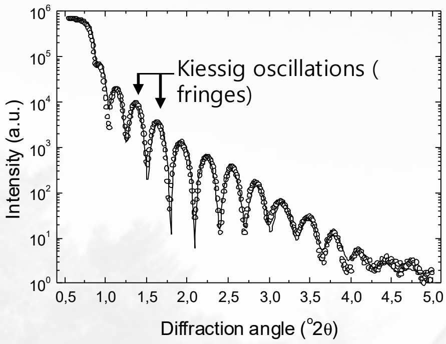
XRR



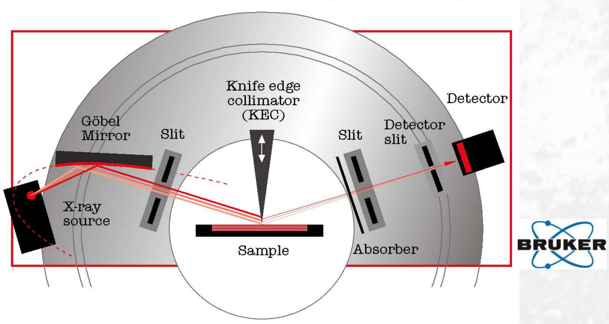
PANalytical

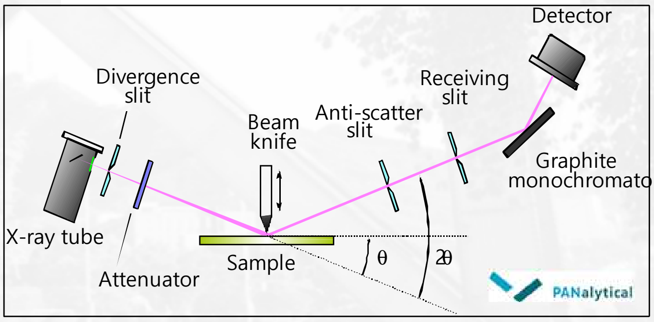
XRR

- density, thickness and interface roughness for each layer ← multi-layer thin film



	ρ	t [Å]	σ [Å]
Mo	0.68	19.6	5.8
Mo	0.93	236.5	34.0
Mo	1.09	14.1	2.7
W	1.00	5.0	2.7
Si	1.00		2.8

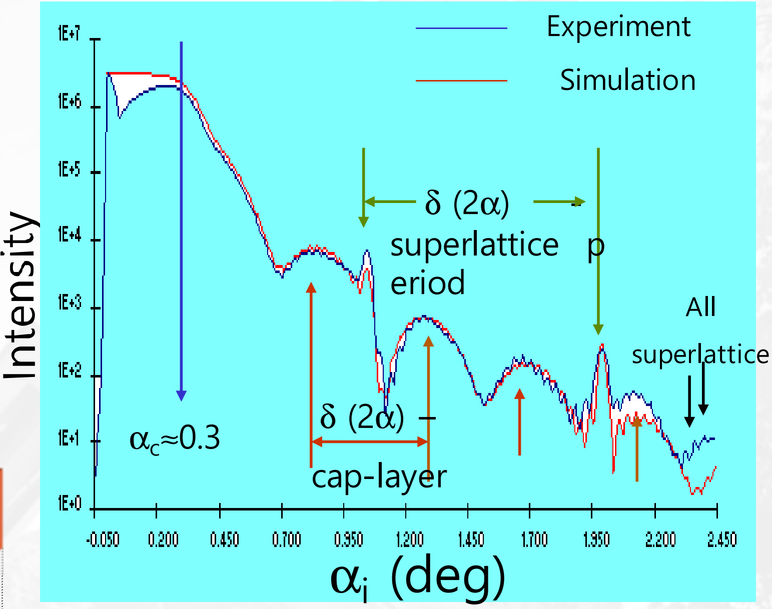




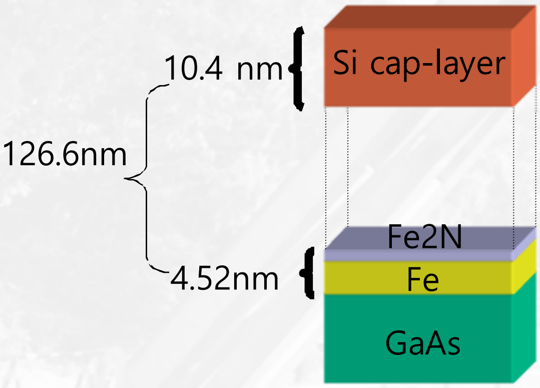
<u>The surface must be smooth (mirror-like).</u>

Schichten

XRR > Si/{Fe/Fe2N}x28/GaAs(001) superlattice



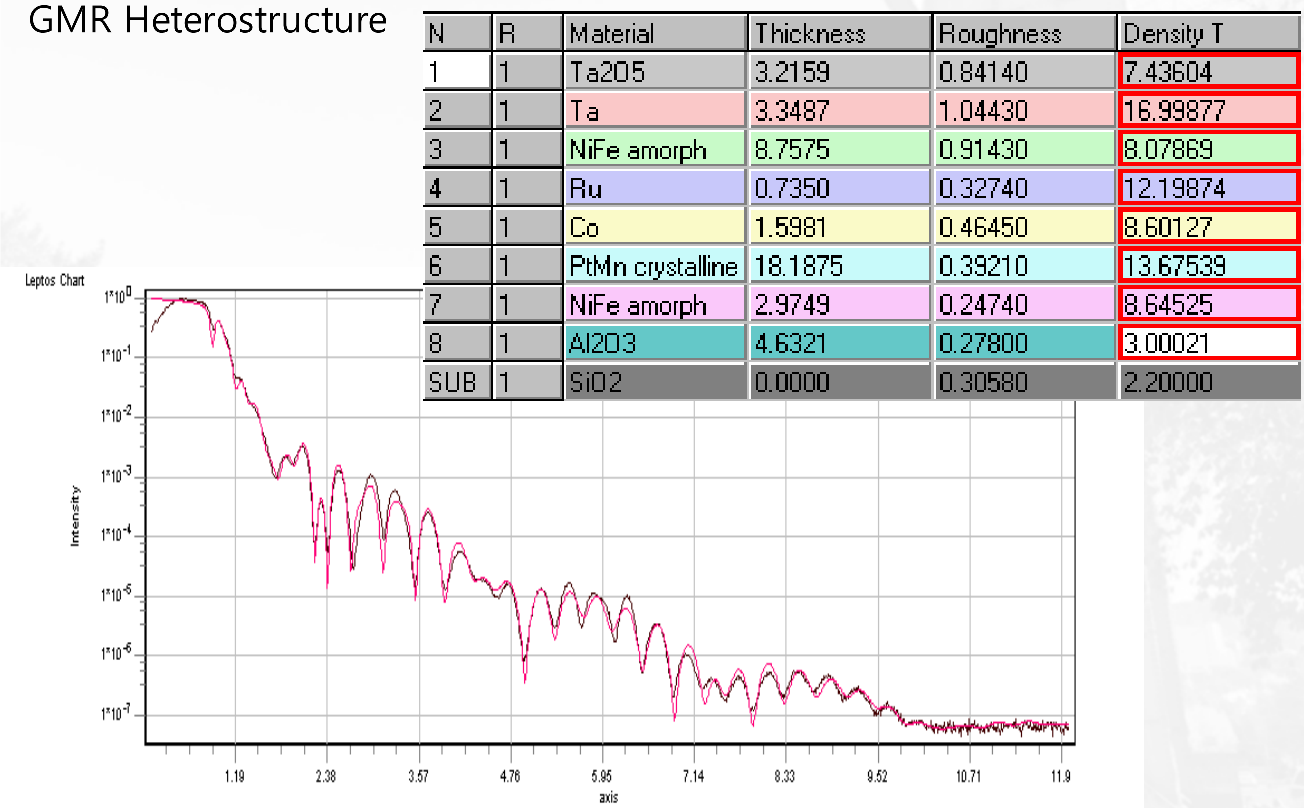
Results of simulation



Prof. Elżbieta Dynowska

XRR

GMR Heterostructure



N	R	Material	Thickness	Roughness	Density T
1	1	Ta2O5	3.2159	0.84140	7.43604
2	1	Ta	3.3487	1.04430	16.99877
3	1	NiFe amorph	8.7575	0.91430	8.07869
4	1	Ru	0.7350	0.32740	12.19874
5	1	Co	1.5981	0.46450	8.60127
6	1	PtMn crystalline	18.1875	0.39210	13.67539
7	1	NiFe amorph	2.9749	0.24740	8.64525
8	1	Al2O3	4.6321	0.27800	3.00021
SUB	1	SiO2	0.0000	0.30580	2.20000

Dr, Schug, IBM Mainz