SCHEDULE

	Date	Topic
1.	Tue 14.09.	Lec-1: Introduction
2.	Fri 17.09.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Fri 17.09.	EXERCISE 1
4.	Tue 21.09.	Lec-3: Crystal chemistry & BVS
5.	Fri 24.09.	Lec-4: Molecular Symmetry & Point Groups
6.	Fri 24.09.	EXERCISE 2
7.	Tue 28.10.	Lec-5: Crystallography & Space Groups
8.	Fri 01.10.	Lec-6: XRD & Reciprocal Lattice
9.	Fri 01.10.	EXERCISE 3
10.	Tue 05.10.	Lec-7: ND
11.	Fri 08.10.	Lec-8: Rietveld
12.	Fri 08.10	EXERCISE 4: Rietveld
13.	Tue 12.10.	Lec-9: Synchrotron rad. & XAS & RIXS
14.	Fri 15.10.	Lec-10: EXAFS & Mössbauer
15.	Fri 15.10.	EXERCISE 5
16.	Tue 19.10.	Seminars: XPS, SEM
17.	Fri 22.10.	Lec-11: GI-XRD & XRR (10.00-11.30)
18.	Fri 22.10.	EXERCISE 6: XRR (12.00 → ca. 14) by Ramin Ghiyasi

EXAM: Wednesday, Oct. 27th, 2021, at 10.00 – 13.00, in Zoom

LECTURE 11:

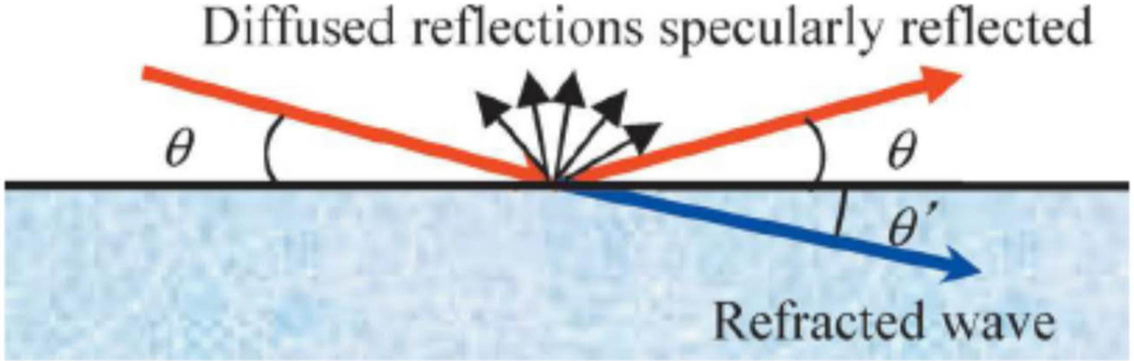
XRR (X-ray reflection) & GI-XRD (grazing incidence)

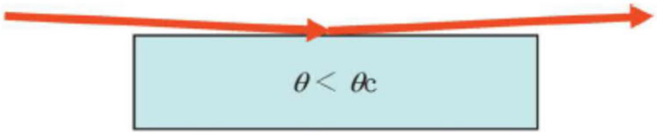
- Thin-film characterization techniques
- GI-XRD: Crystal structure, phase composition, orientation (!)
- XRR: thickness, density, roughness & superstructures
- KEYWORDS: diffraction, reflection & refraction, total reflection, critical angle, incident angle

- **DIFFRACTION:** Bulk phenomenon, takes place at the surface and also within the material, but only at certain angles.
  Bragg Equation: conditions and positions of interference peaks.
- **REFLECTION (Heijastuminen):** Surface phenomenon.
  X-rays strike a surface and bounce back (reflect off it).
  Law of Reflection: reflection angle = incidence angle
- **REFRACTION (Taittuminen):** X-rays enter a different medium of different optical density and change direction or bend.
  Snell's Law: degree of refraction.

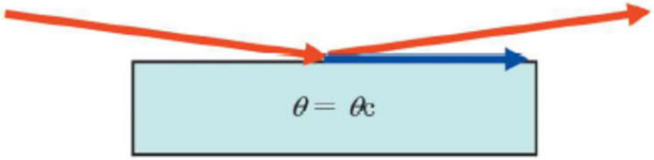
TOTAL INTERNAL REFLECTION
in a wine glass

TOTAL INTERNAL REFLECTION by the water's surface at the shallow end of a swimming pool. The broad bubble-like apparition between the swimmer and her reflection is merely a disturbance of the reflecting surface. Some of the space above the water level can be seen through "Snell's window" at the top of the frame.

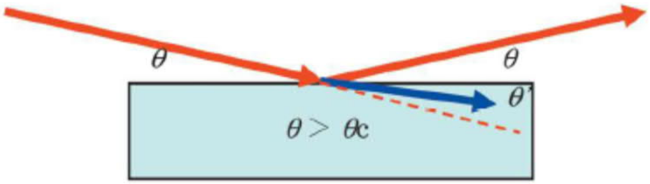




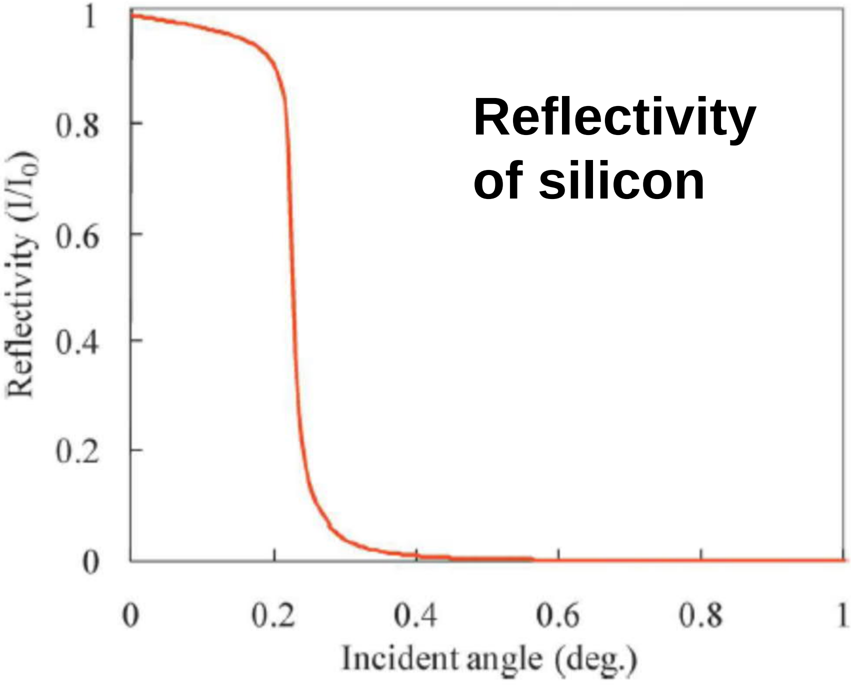
A) Incident angle < Total reflection critical angle
All incident X-rays are reflected.



B) Incident angle = Total reflection critical angle
Incident X-rays propagate along the sample surface.



C) Incident angle > Total reflection critical angle
Incident X-rays penetrate into the material by refraction

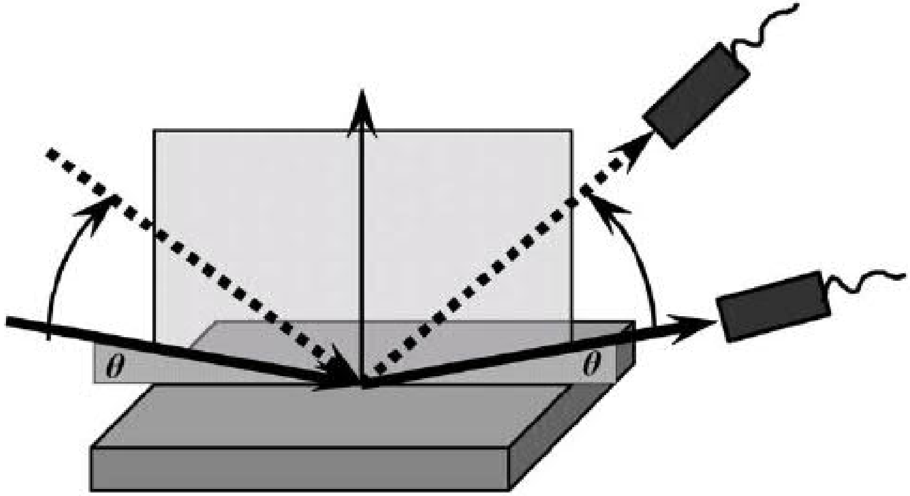


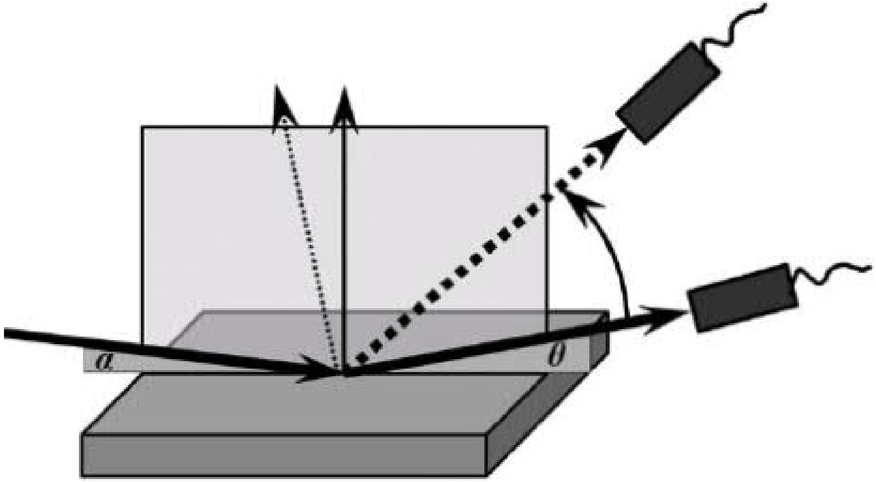
CRITICAL ANGLE

- **With very tiny incident angles X-rays only reflect from the sample surface (no refraction)**
- **At the critical angle (α_c), X-rays begin to penetrate (= refract) the material**
- **Above α_c the reflectivity rapidly drops**
- **α_c is material property → proportional to the square root of electronic density**

Grazing Incidence X-ray Diffraction (GI-XRD)

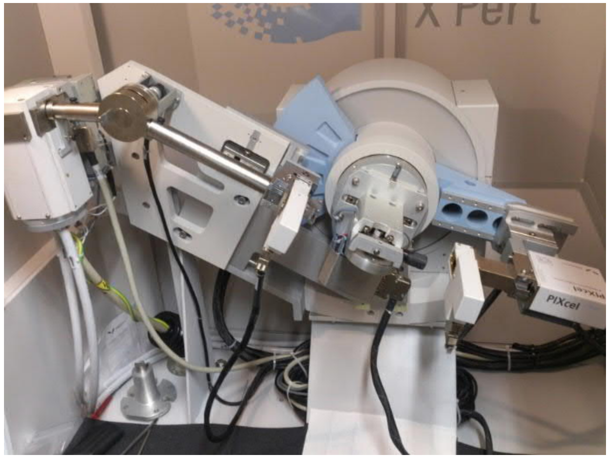
- **Surface sensitive XRD: small incident angle for the incoming X-ray beam**
- **Thin films typically: 1~1000 nm**
- **Penetration depth of X-rays: 10~100 µm (depending on elemental composition)**
- **Conventional XRD with symmetric θ/2θ configuration: diffracted radiation mostly due to the substrate**
- **Small incident angle (α) lowers the penetration depth → information mostly from a thin surface layer**
- **Measure at a fixed α**
- **Depth profiling is also possible: control of α**





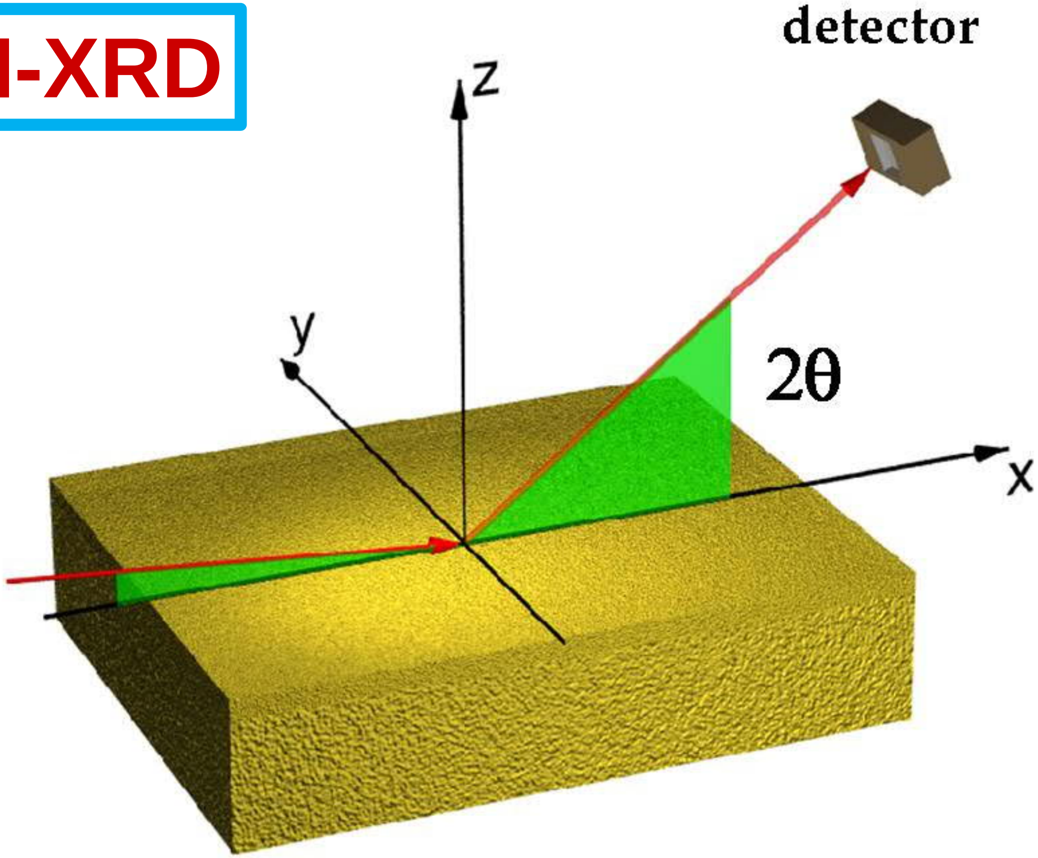
GI-XRD

- Similar (same) device as in ordinary powder XRD, but slightly different configuration
- Fixed incident angle (α)
- Value of α (0.5 – 4°) selected to be little larger than the material-dependent “critical angle” (= total reflection limit)

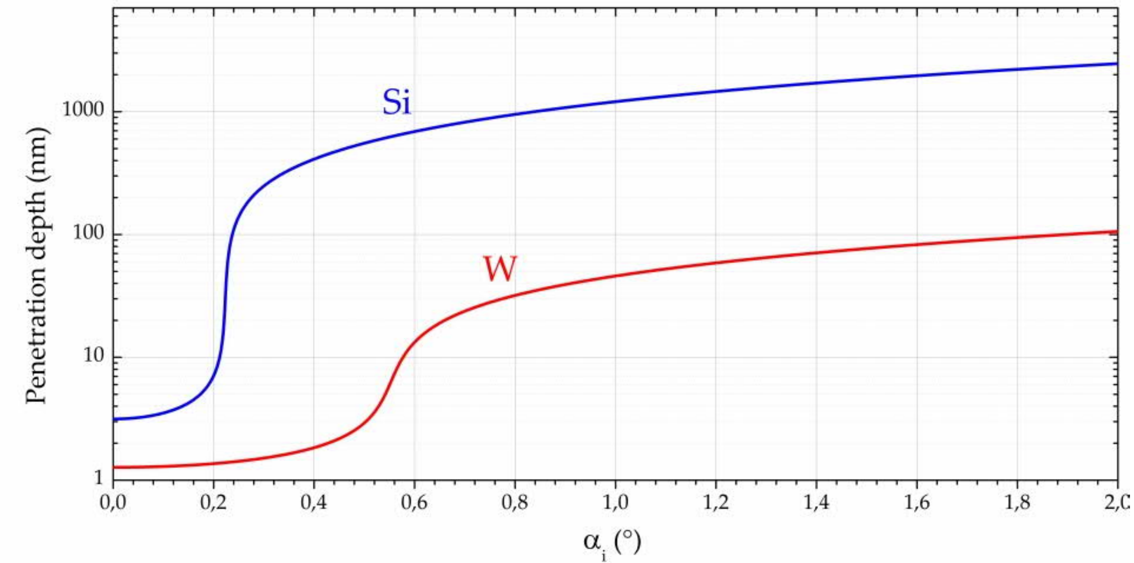


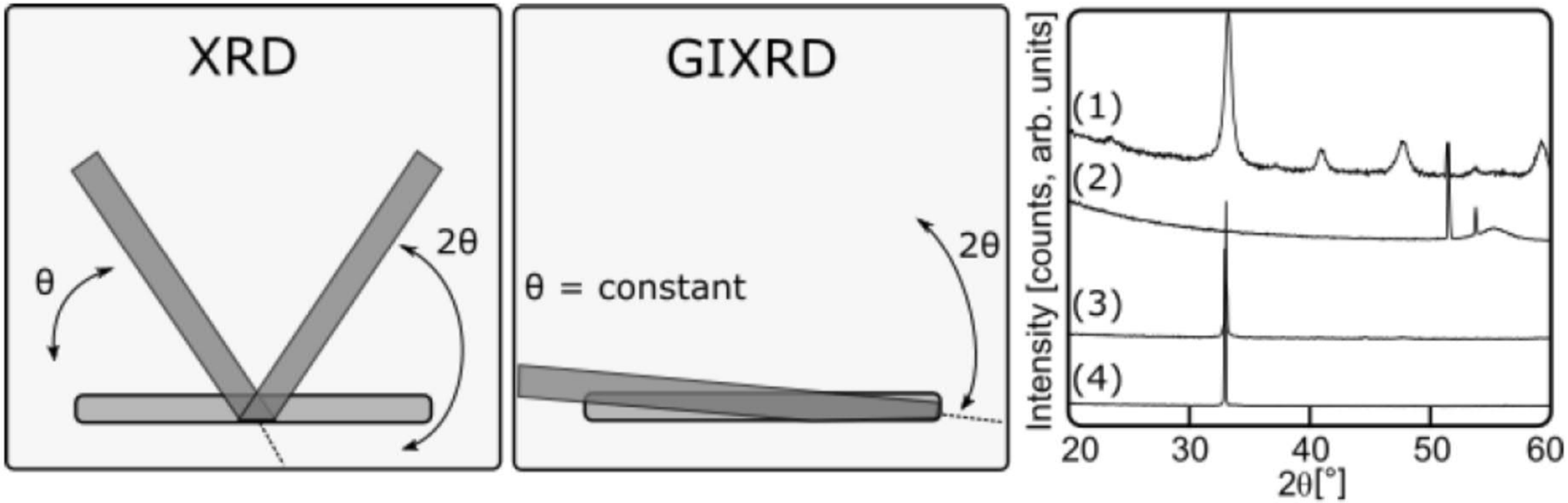
XRD

GI-XRD



Critical angle: Si (= 0.223°) and W (= 0.552°)





GI-XRD

(1) Thin film + subs.

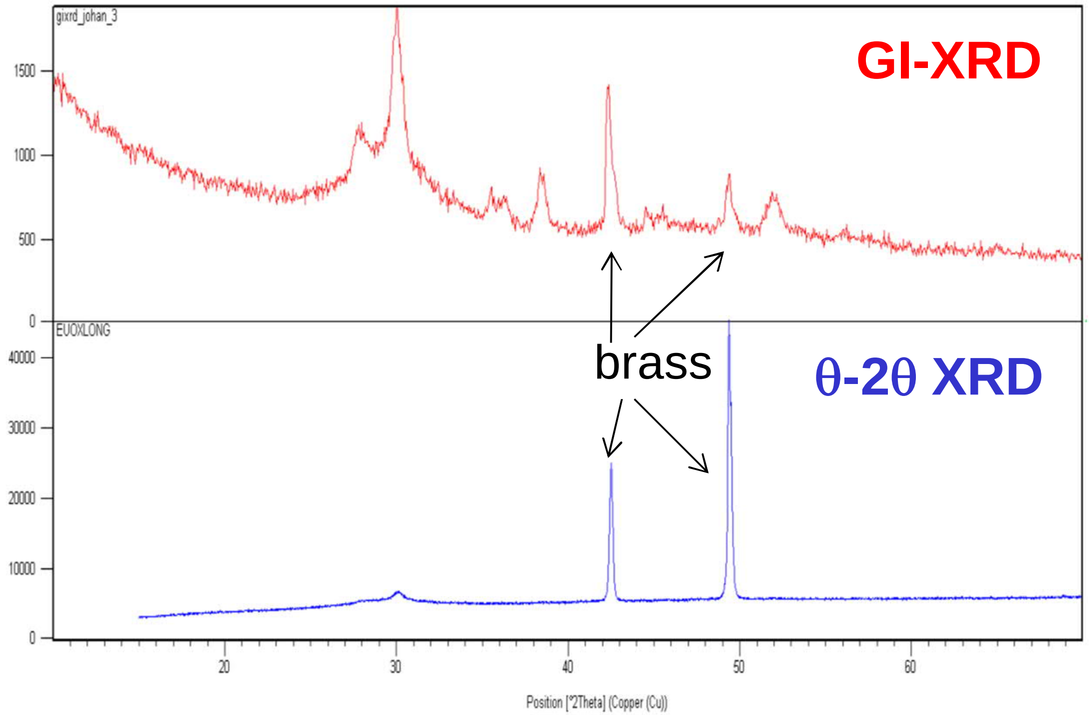
(2) Substrate

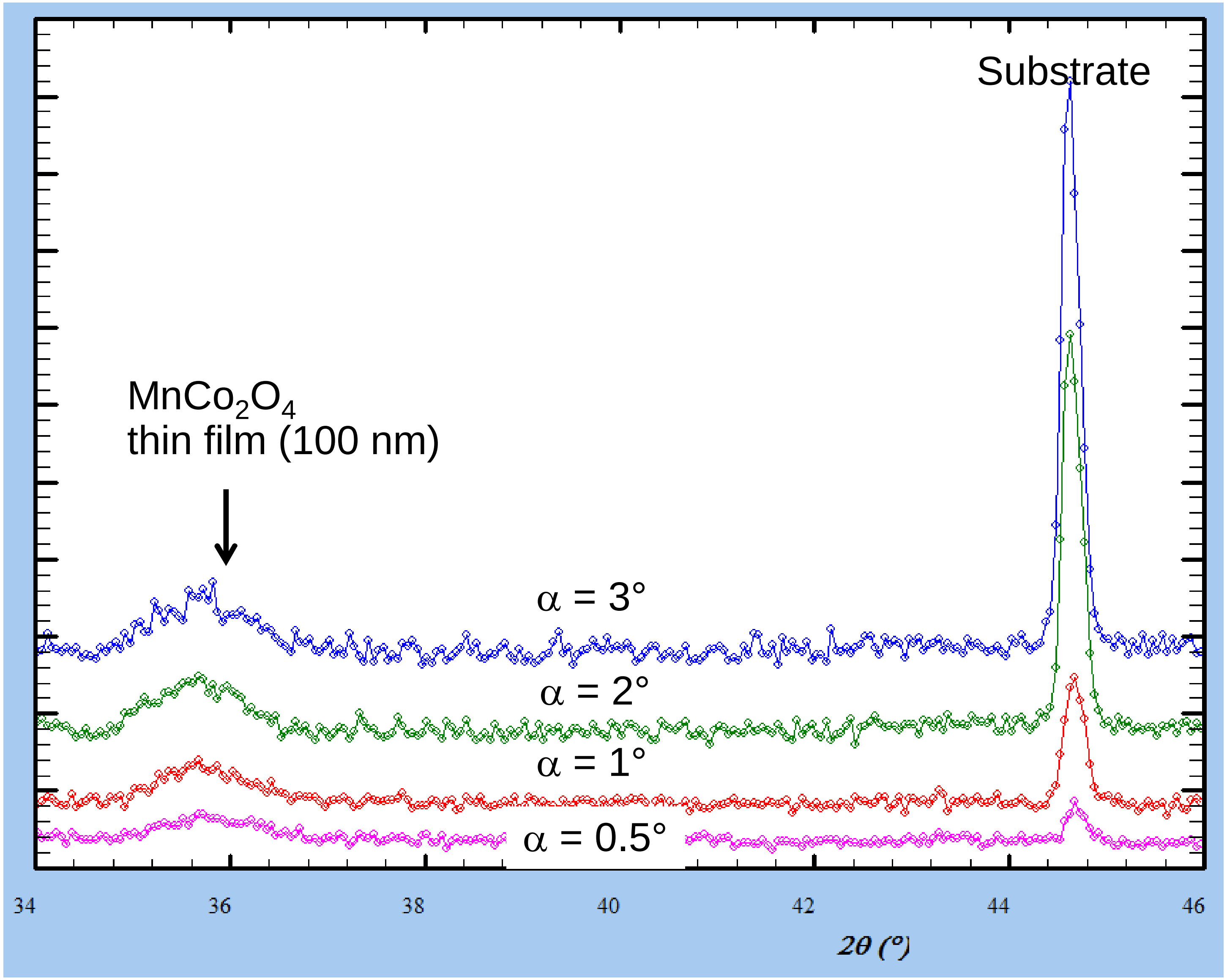
XRD

(3) Thin film + subs.

(4) Substrate

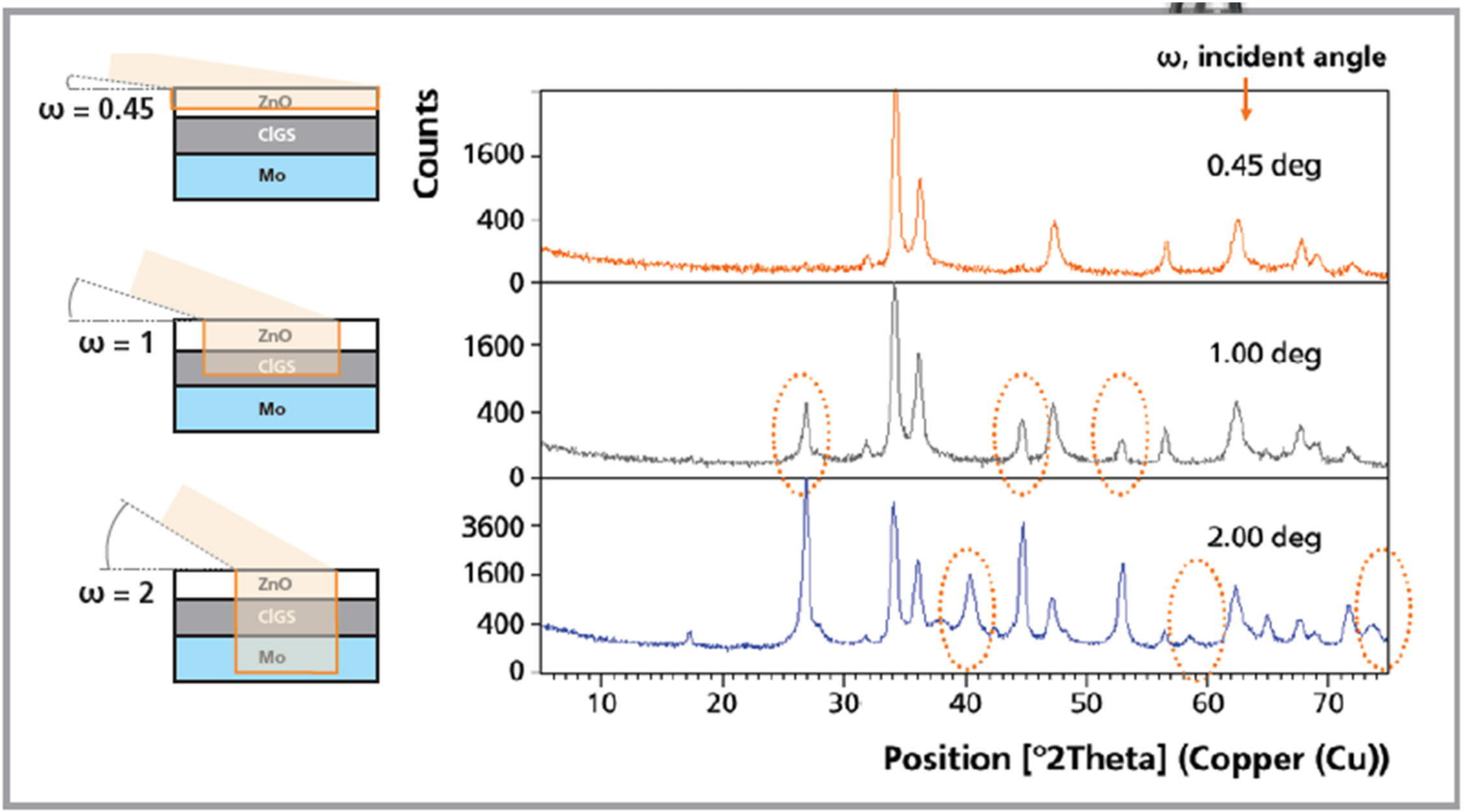
**EXAMPLE: Eu_2O_3 thin film on top of a brass substrate;
conventional XRD shows only the substrate diffraction peaks,
while in GI-XRD also a number of new peaks appear due to the Eu_2O_3 film**





- With increasing incident angle (α), X-rays penetrate deeper
- Peaks due to the thin film increase in intensity
- Also the substrate peaks (may) get enhanced
- NOTE the different peak widths for substrate and thin film (different crystallite sizes)

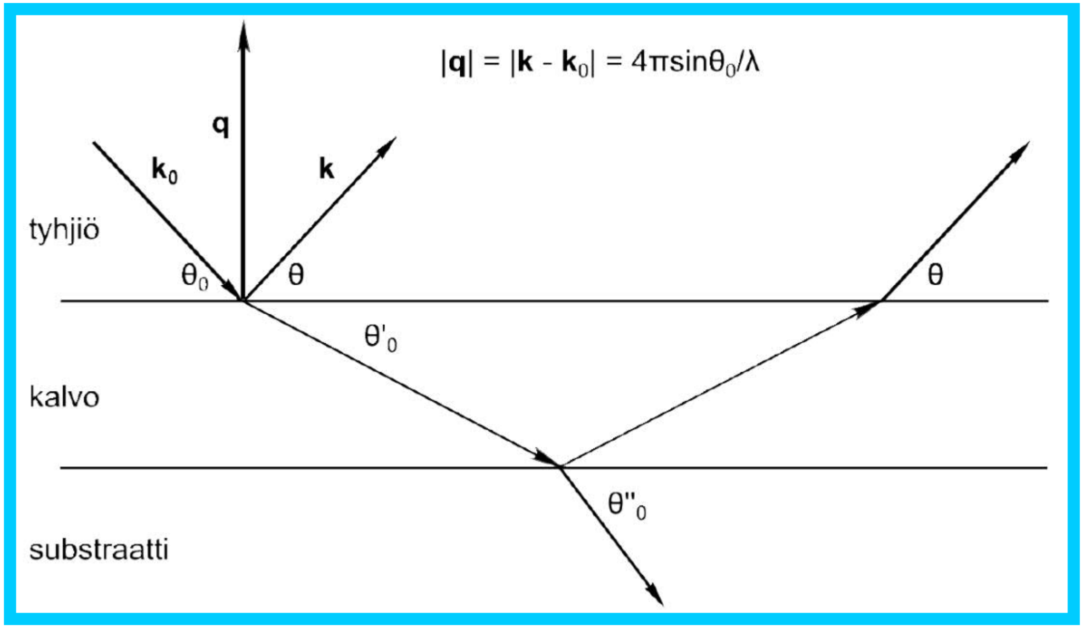
GI-XRD: Depth profile analysis

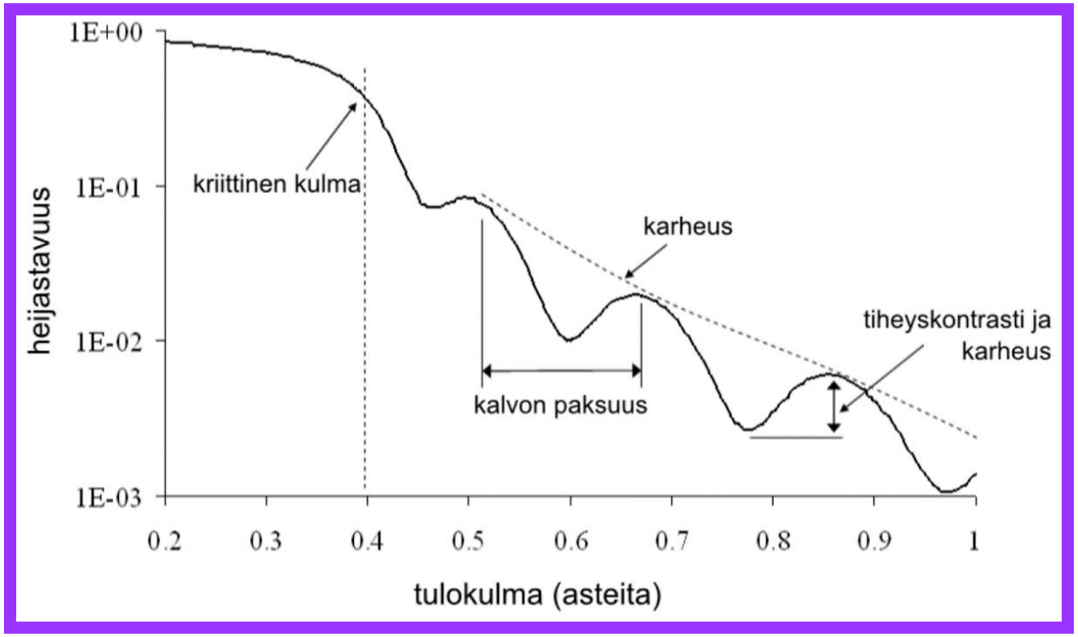


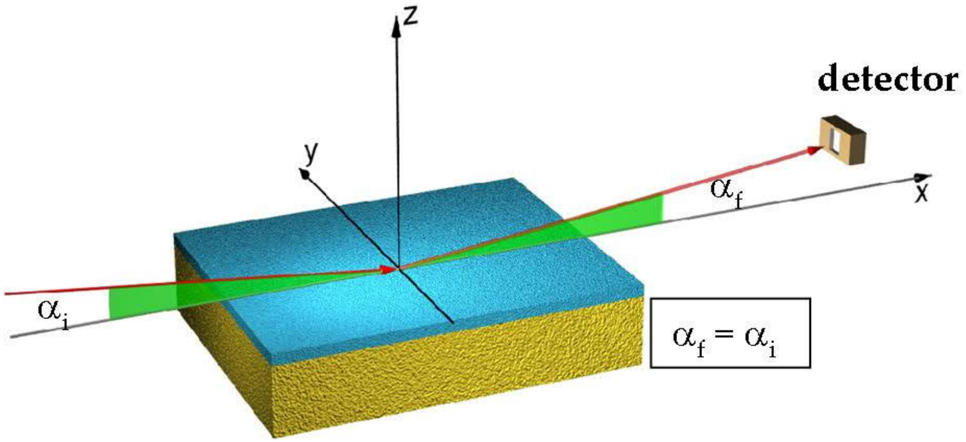
An example of depth probing on a CIGS solar structure, showing the different layers exposed to the parallel X-ray beam in a sequential mode by varying the incident angle . Top pattern is from the conductive oxide layer only, with CIGS coming in (middle, highlighted) and next the Mo metal contact layer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

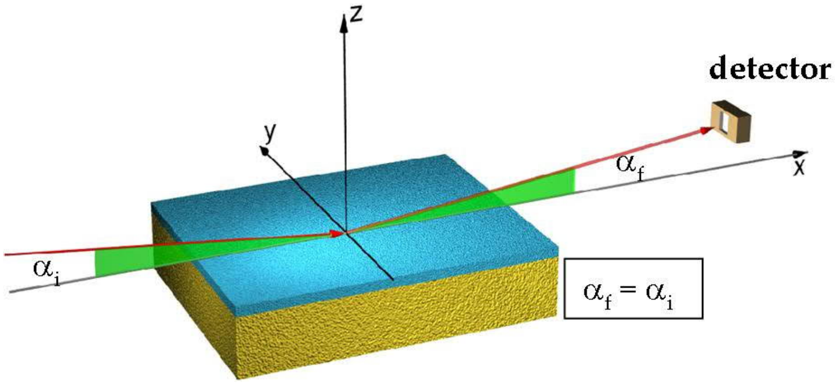
XRR (X-Ray Reflectivity)

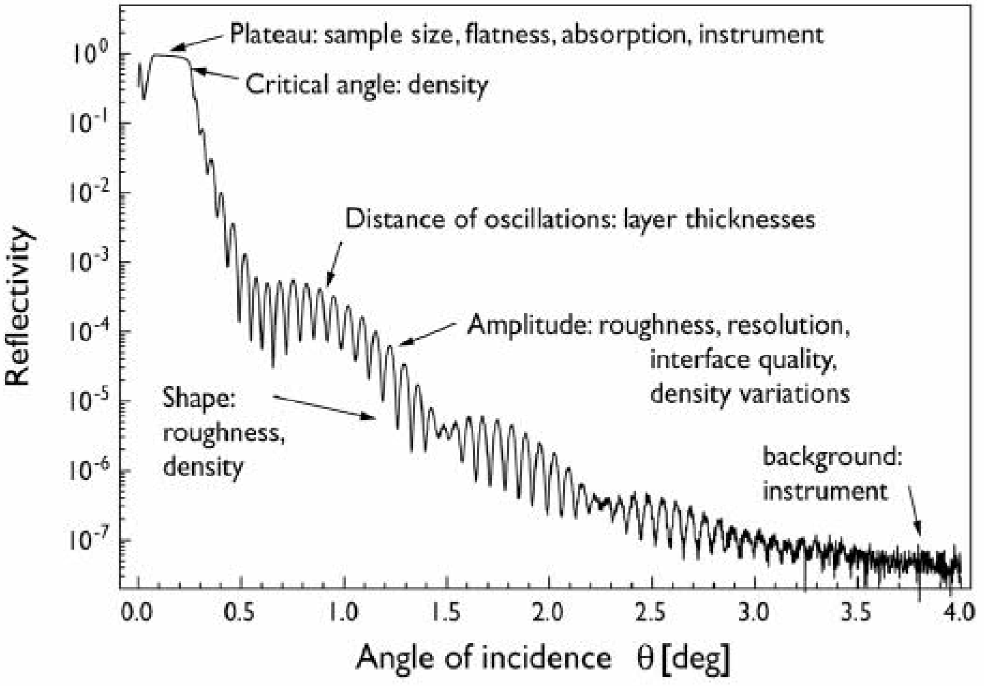
- **Incident angle = Reflection angle: specular (mirror-like) reflection**
- **No scattering from diffraction planes, only from surface/interfaces (where there is a change in refractive index)**
- **Scattering depends on the properties of the two interface material layers**
- **IDEALLY: scattering intensity depends on the layer thicknesses and electron densities of the two materials**
- **IN PRACTISE: intensity depends also on surface (or interface) roughness**











XRR Measurement

- **XRR devise similar (same) to XRD device but the optical parts somewhat different**
- **SCATTERING ANGLE fixed to the INCIDENT ANGLE**
- **With the lowest incident angles, sample surface reflects all X-ray radiation intensity**
- **When the incident angle increases above the critical angle X-rays start to penetrate to the sample (top layer)**
- **When the incident angle is further increased the intensity starts to oscillate**
- **Oscillation (so-called Kiessig fringes) is related to the mass densities and layer thicknesses**
- **Oscillation provides us with important information of the sample**
- **Typical measurement range: few degrees**

  (with higher angles the background noise level considerably increases)

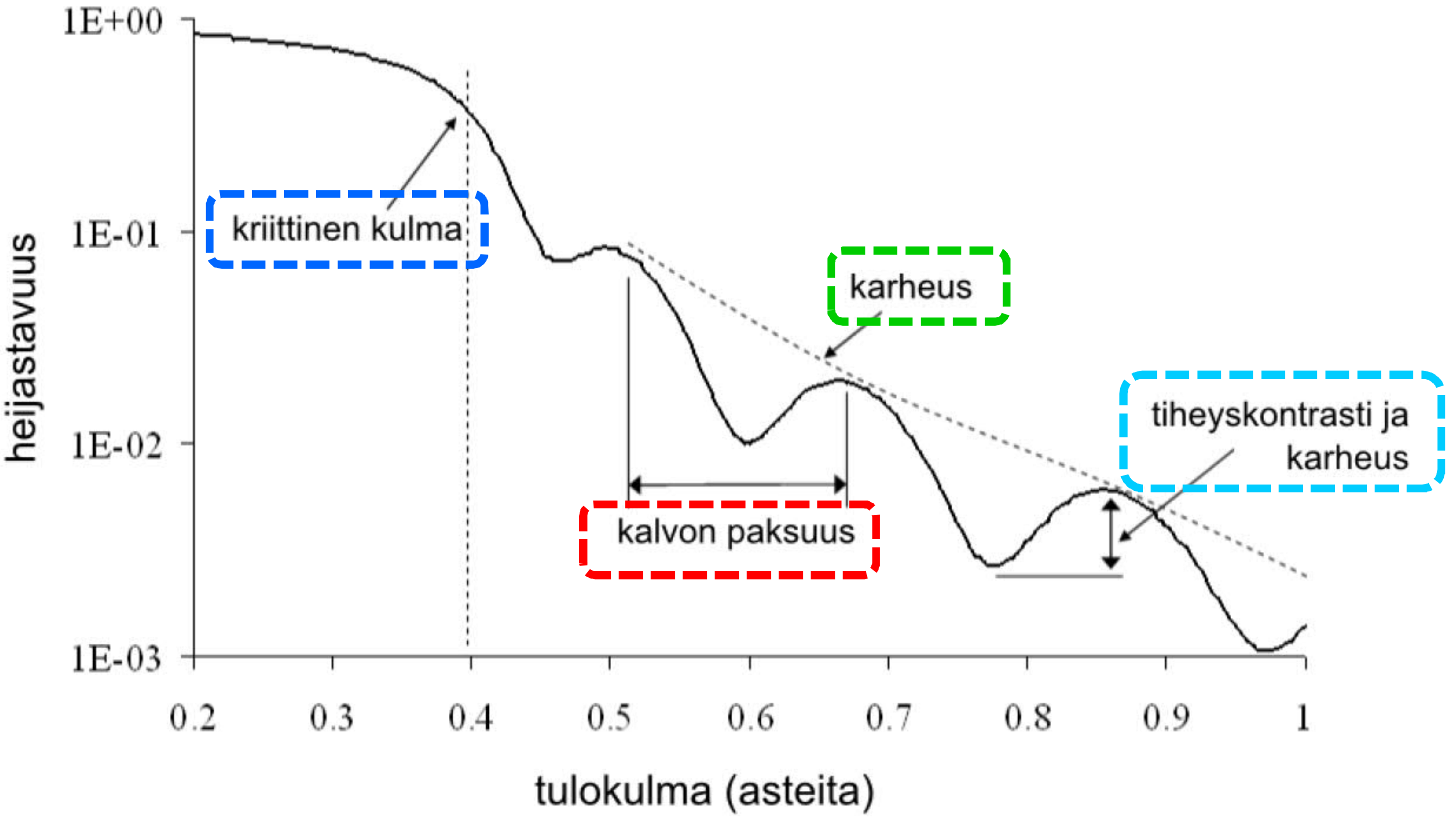
Information from XRR data

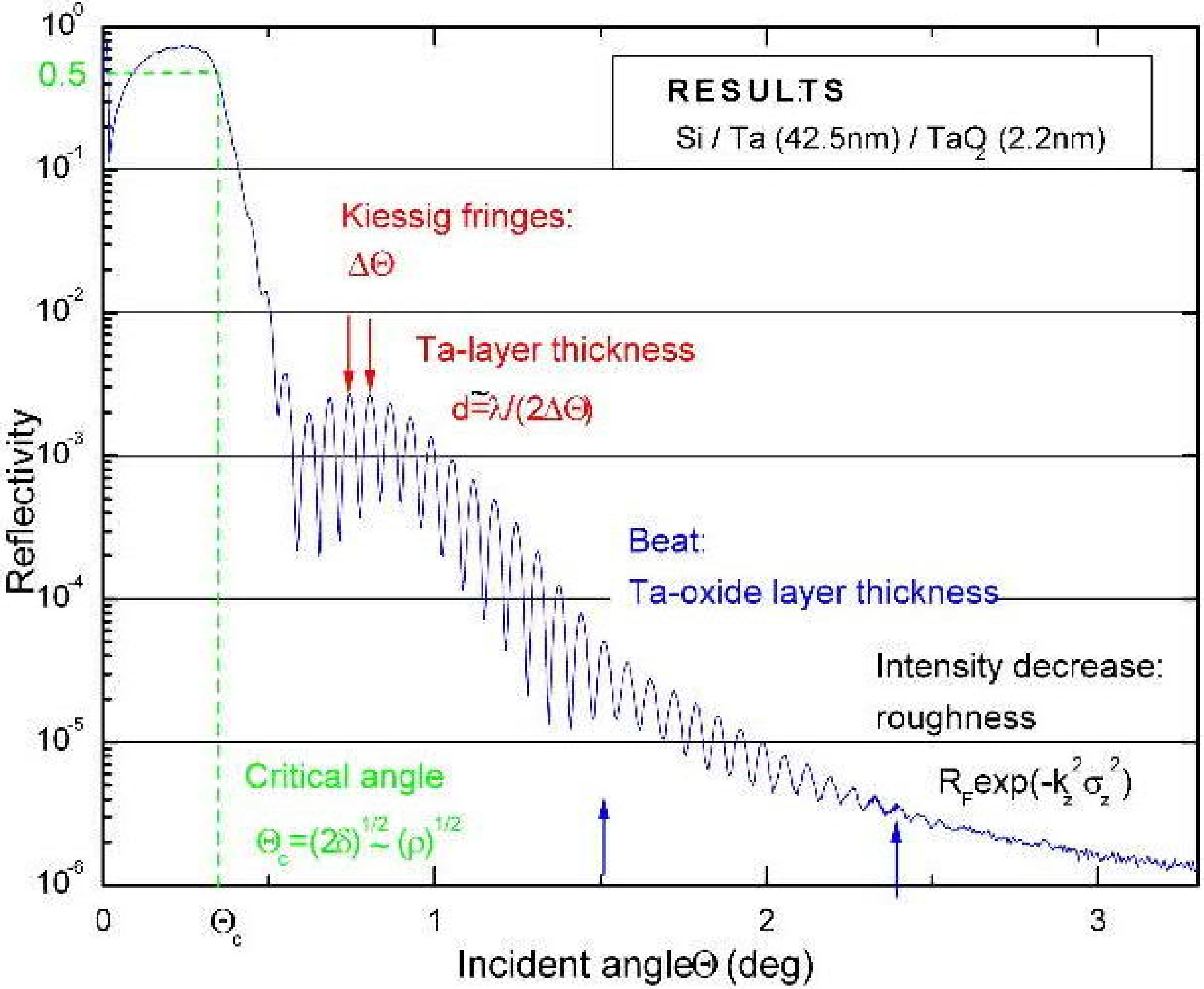
- **You will see in the Exercise Session that the pattern can be simulated to get quantitative values, but even by eye observation, quite much information is obtained**
- **Critical angle (α_c; total reflection limit) → DENSITY**
- **Periodic oscillations or so-called *Kiessig fringes* provide us lot of information**

  - Distance between two Kiessig fringes → THICKNESS

  - Hight of Kiessig fringes → (INTERFACE) ROUGHNESS

  - Decay rate of intensity → (SURFACE) ROUGHNESS





RESULTS

Si / Ta (42.5nm) / TaO_2 (2.2nm)

Kiessig fringes:

$\Delta\Theta$

Ta-layer thickness

$d \cong \lambda/(2\Delta\Theta)$

Beat:

Ta-oxide layer thickness

Intensity decrease:

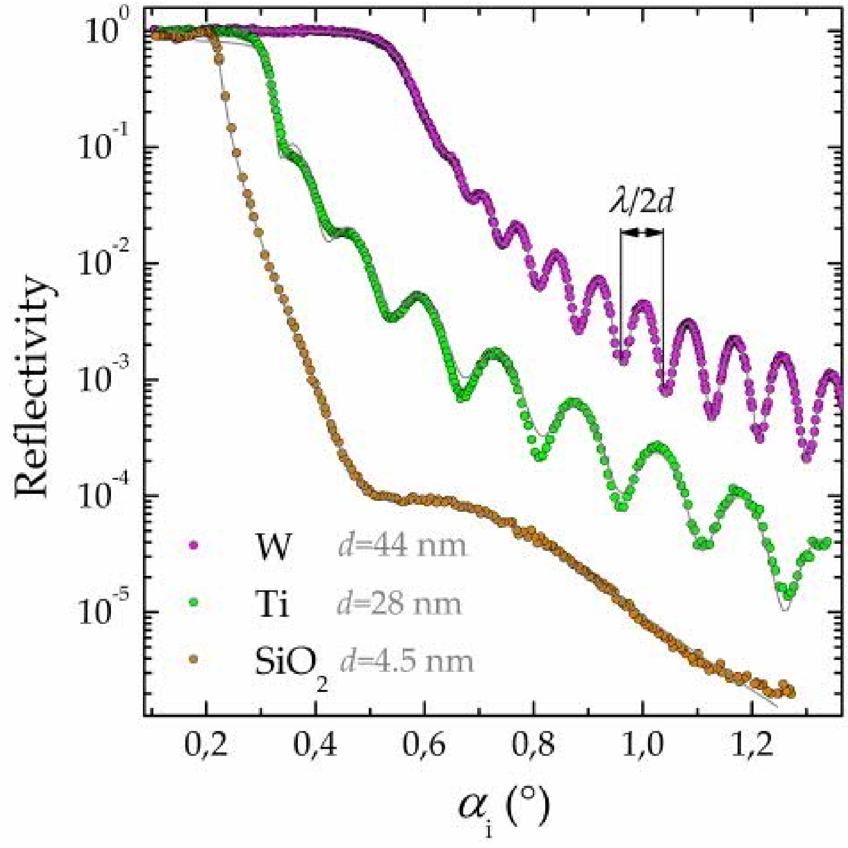
roughness

$R_F \exp(-k_z^2 \sigma_z^2)$

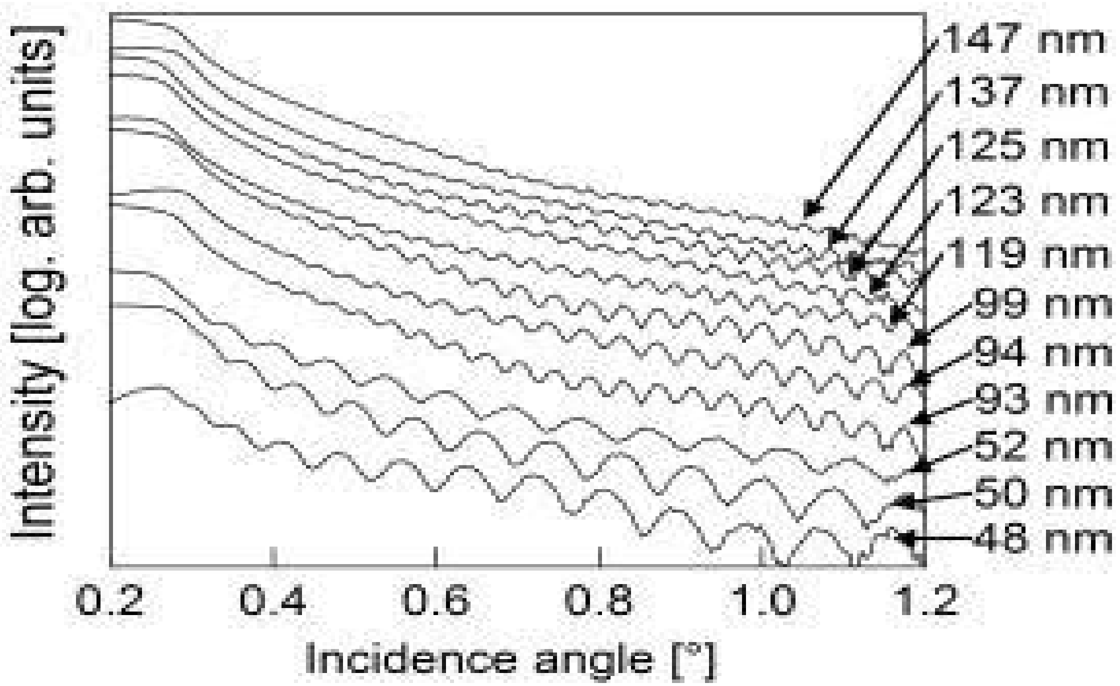
Critical angle

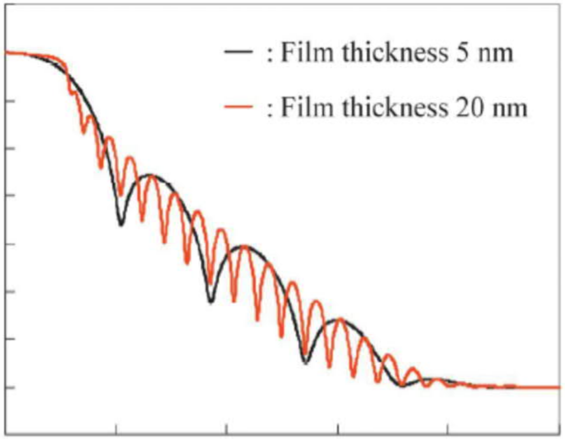
$\Theta_c = (2\delta)^{1/2} \sim (\rho)^{1/2}$

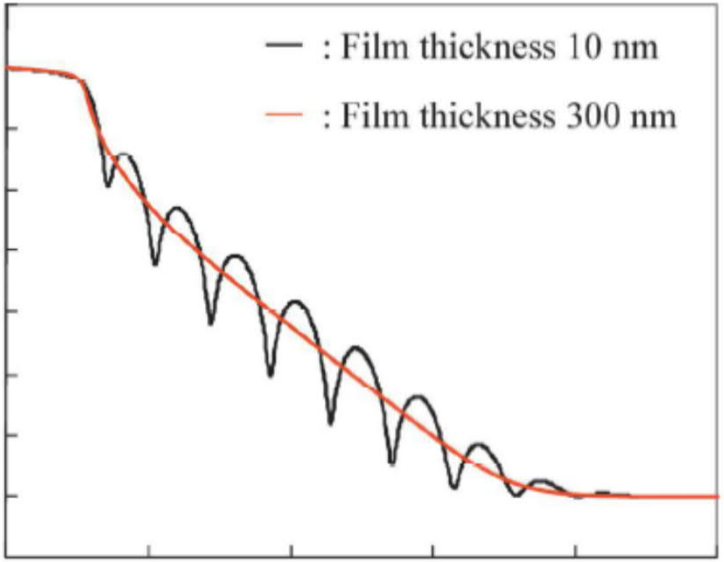
XRR: Film Thickness d



$(La,Sr)CoO_3$ ALD thin films







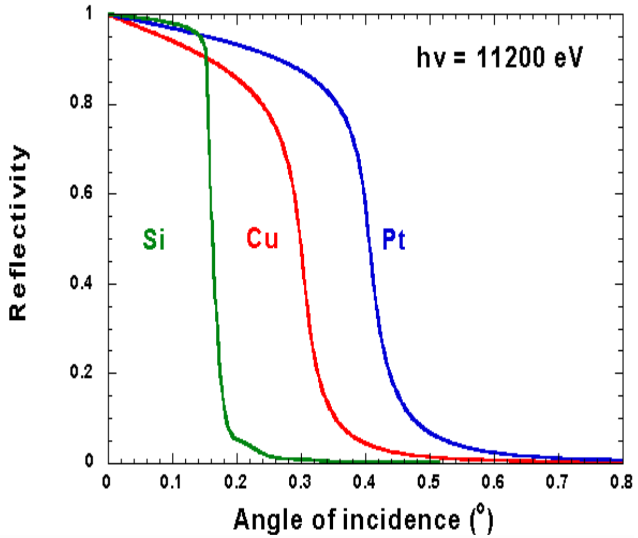
300 nm thick film is already too thick for XRR

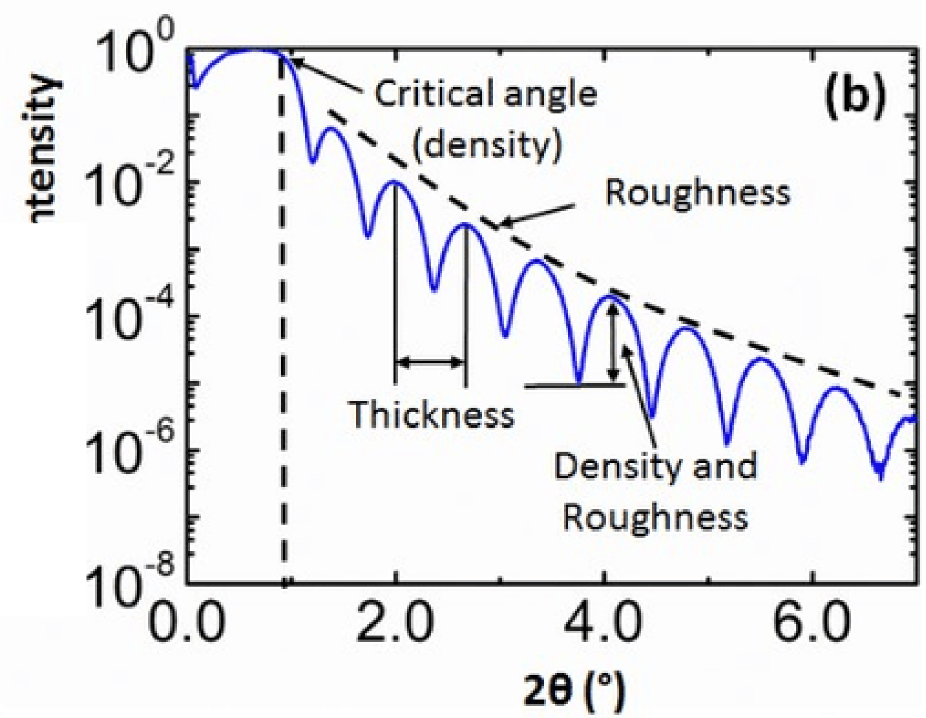
XRR: Film Density

- With increasing density critical angle increases
- Amplitude of Kiessing fringes increases with increasing density difference (film vs. substrate)

$$\rho_{el} = \frac{\Theta_C^2 \pi}{\lambda^2 r_{el}} \qquad \rho_m = \frac{\rho_{el} A}{N_A Z}$$

ρ_{el} : electron density
ρ_m: mass density
Θ_C: critical angle
r_{el}: electron radius
A : Atomic mass
Z: Atomic number



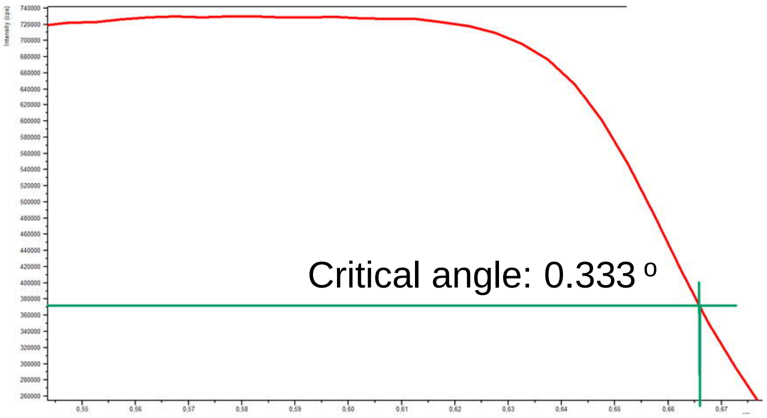


EXAMPLE: ZnO thin film

$$A_{ZnO} = \frac{16\,\frac{g}{mol} + 65.38\,\frac{g}{mol}}{2} \qquad\qquad Z_{ZnO} = \frac{8+30}{2}$$

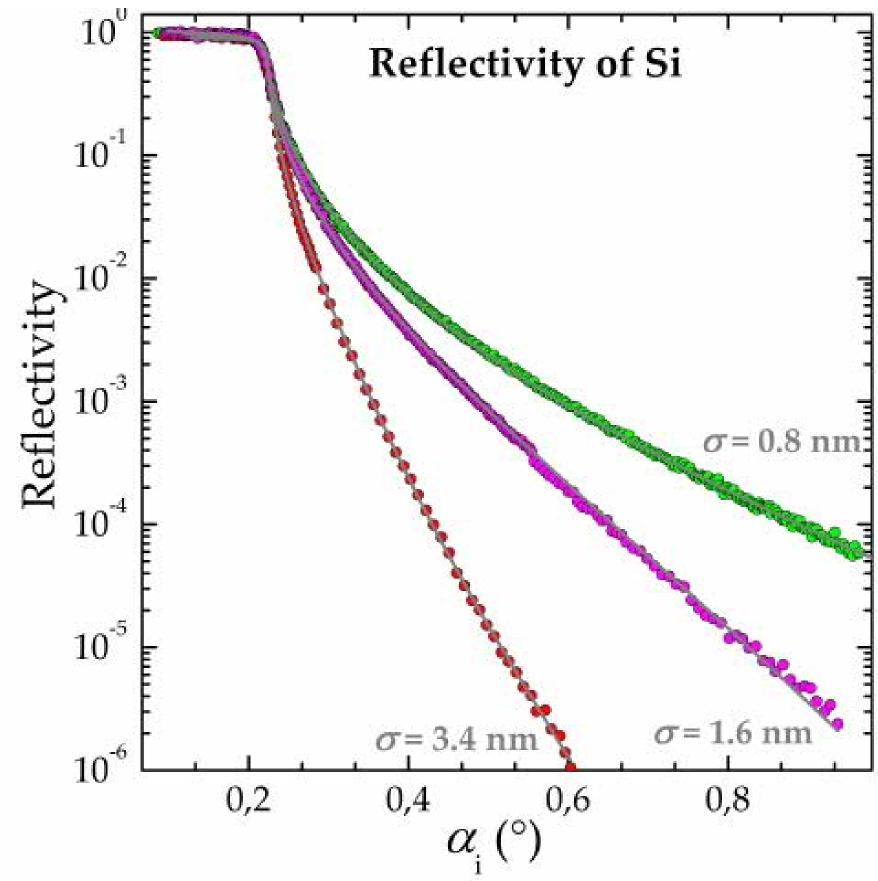
$$\rho_{el} = \frac{0.005912^2\pi}{(1.54\cdot 10^{-10}\,m)^2 \cdot 2.82\cdot 10^{-15}\,m} = 1.642\cdot 10^{30}\,m^{-3} = 1.642\cdot 10^{24}\,cm^{-3}$$

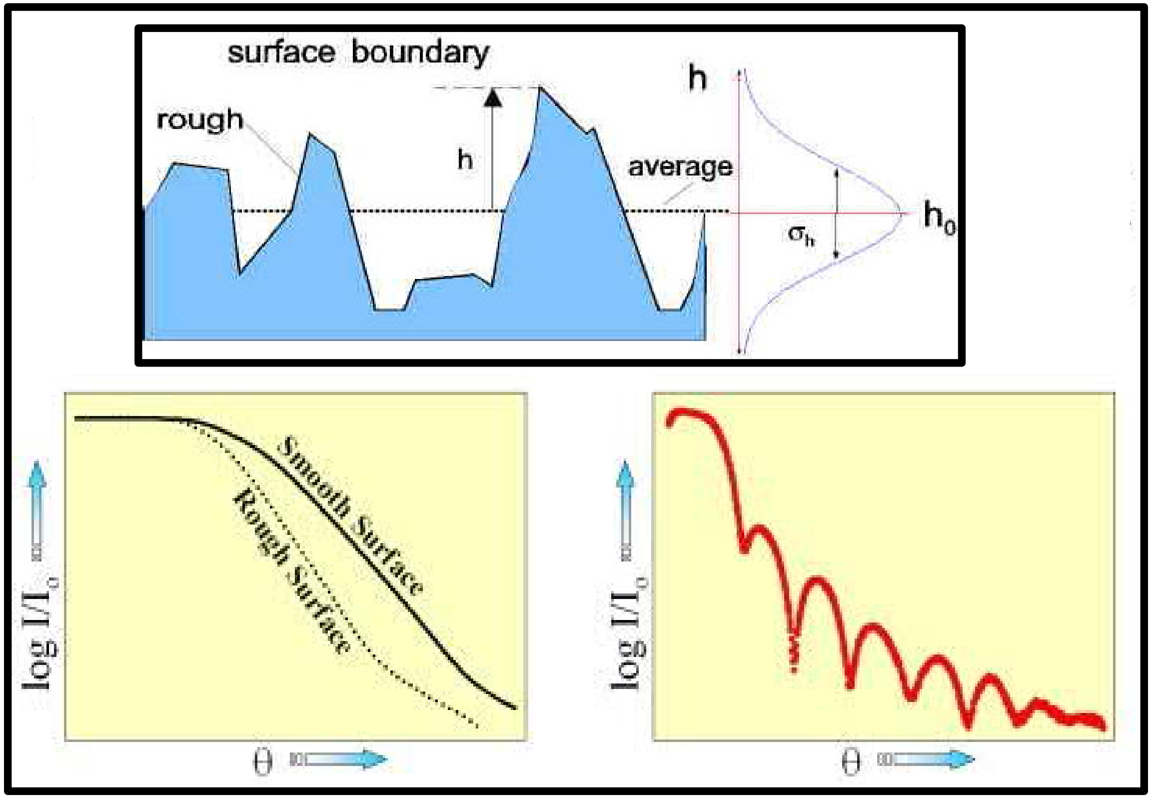
$$\rho_m = \frac{1.642\cdot 10^{24} cm^{-3}\,\left(\frac{16\,\frac{g}{mol} + 65.38\,\frac{g}{mol}}{2}\right)}{6.022\cdot 10^{23}\,mol^{-1}\,\left(\frac{8+30}{2}\right)} \approx 5.8\,g/cm^3$$

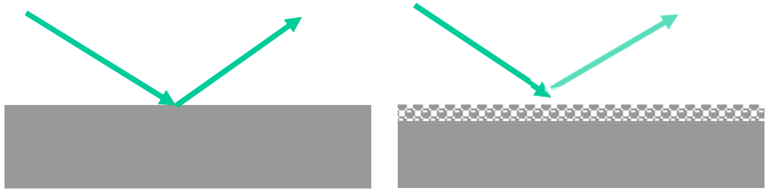


Critical angle: 0.333 º

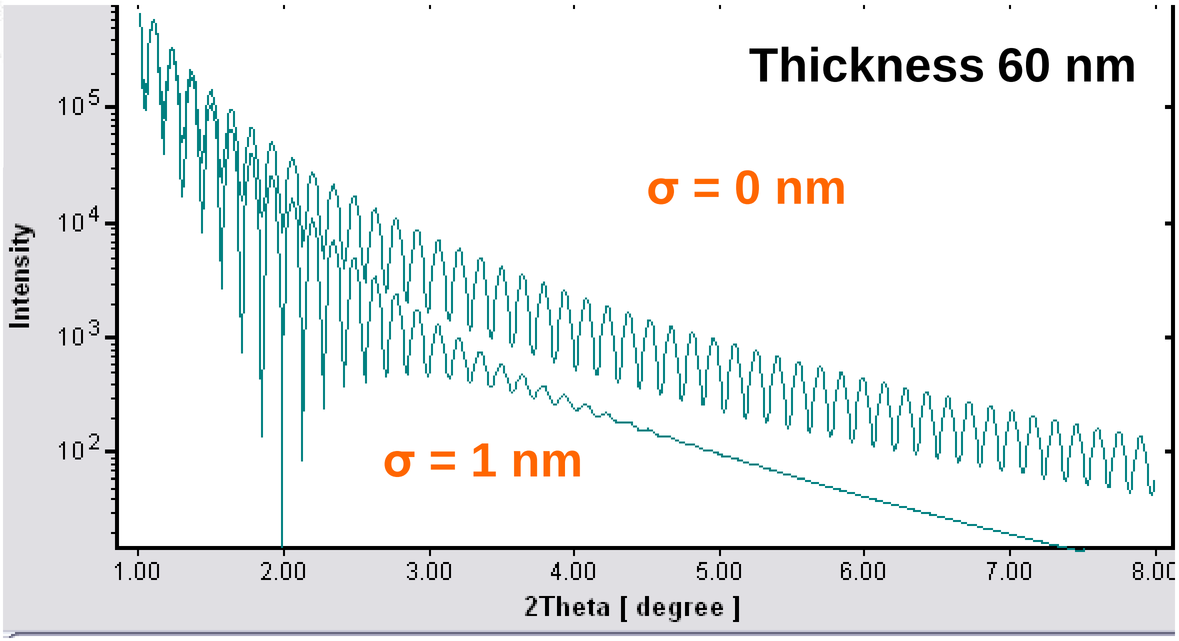
XRR: Surface roughness σ







Smooth **Rough**

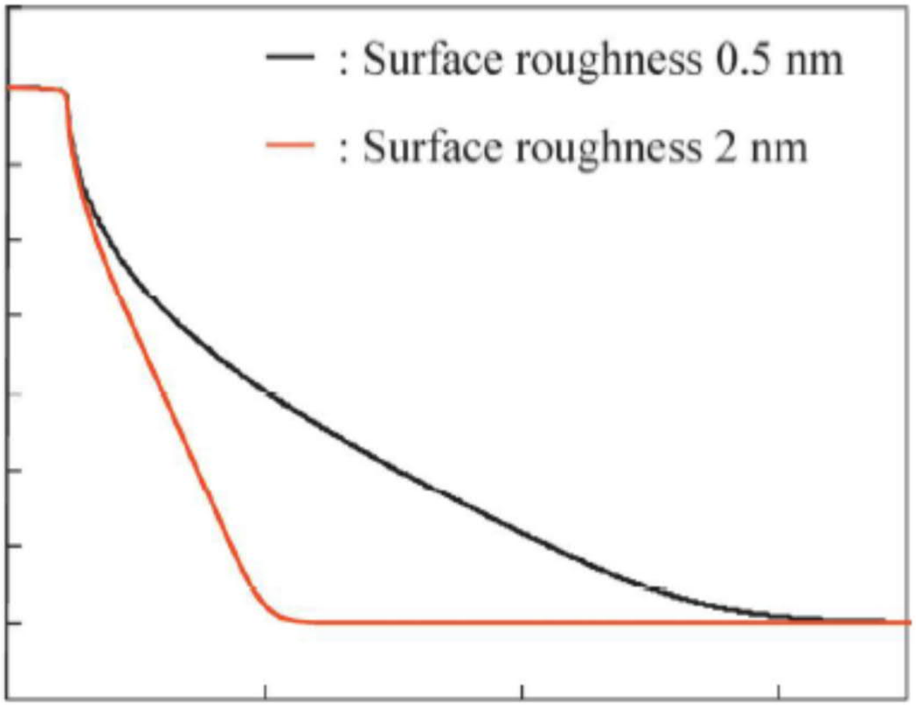


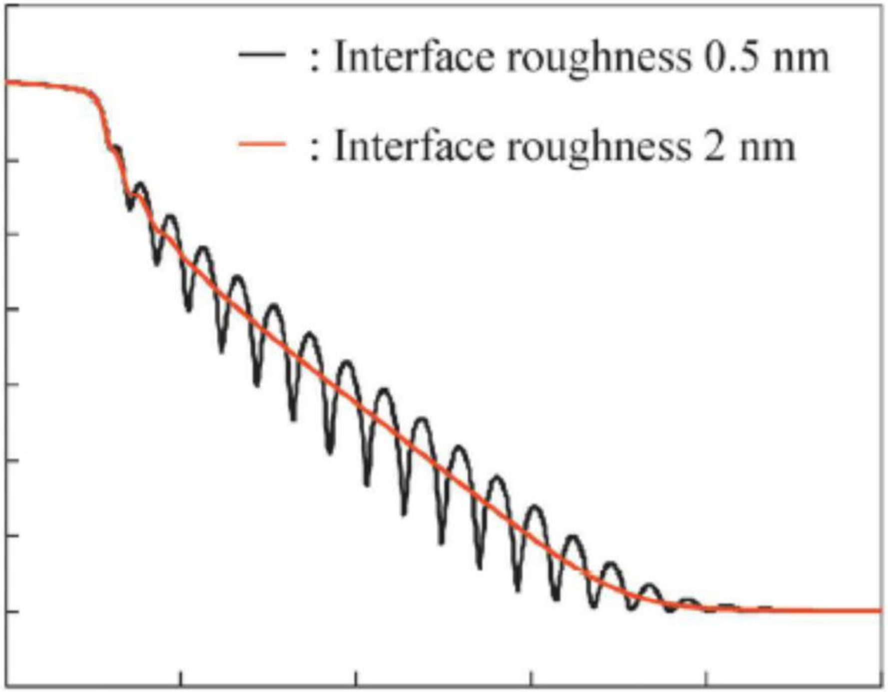
Thickness 60 nm

σ = 0 nm

σ = 1 nm

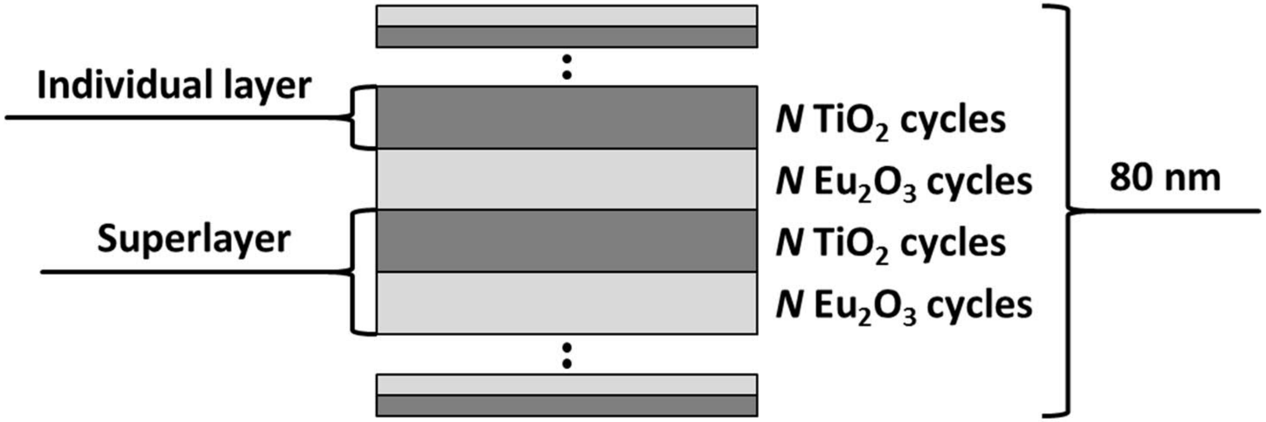
Rough interfaces cause intensity loss

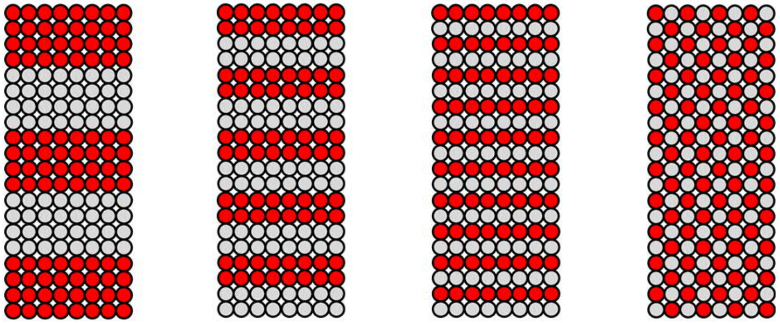

: Surface roughness 0.5 nm
: Surface roughness 2 nm


: Interface roughness 0.5 nm
: Interface roughness 2 nm

SUPERLATTICES

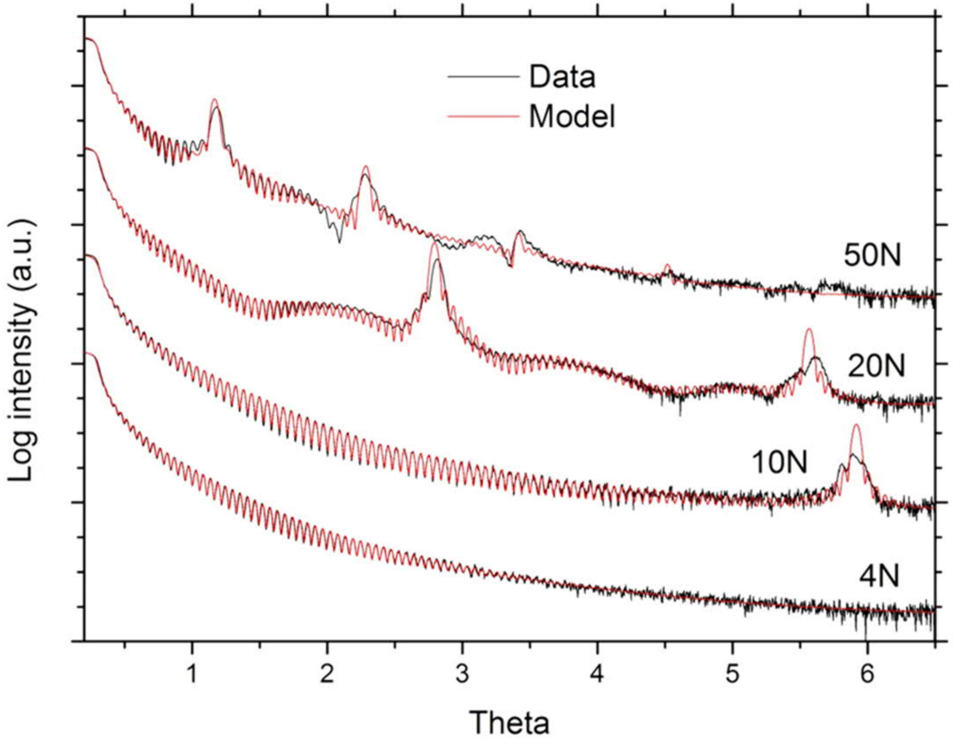
ALD-grown superlattice: Eu_2O_3 and TiO_2 layers grown on top of each other with different frequencies: in the XRR pattern you can see clear (more intense) superlattice peaks.





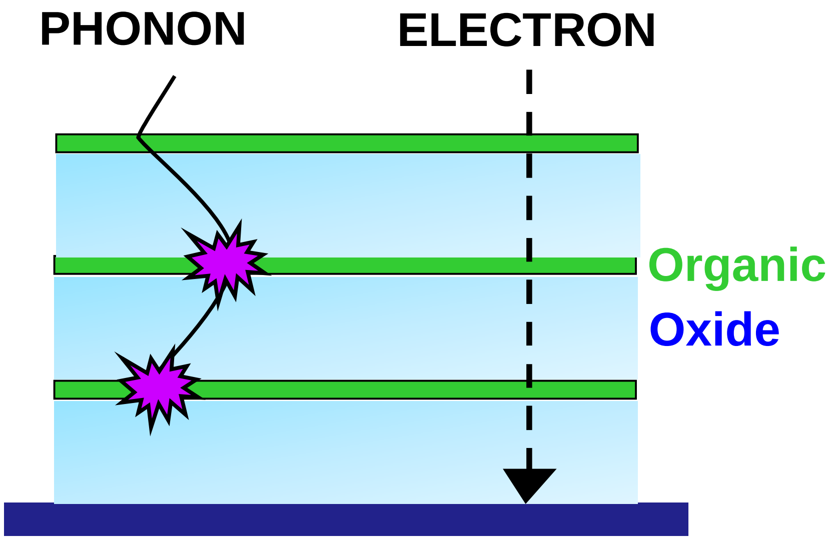
Superlayer thicknesses:

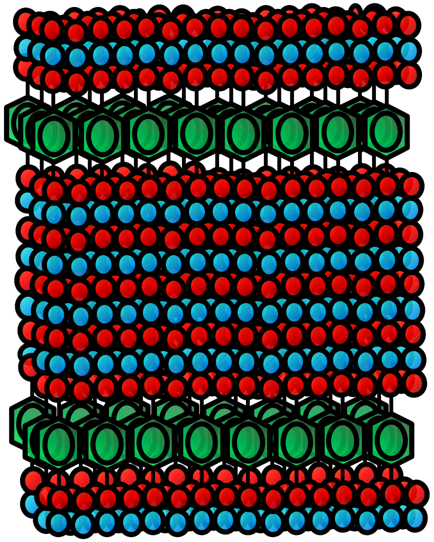
10N = 7.5 Å
20N = 15.9 Å
50N = 29.1 Å

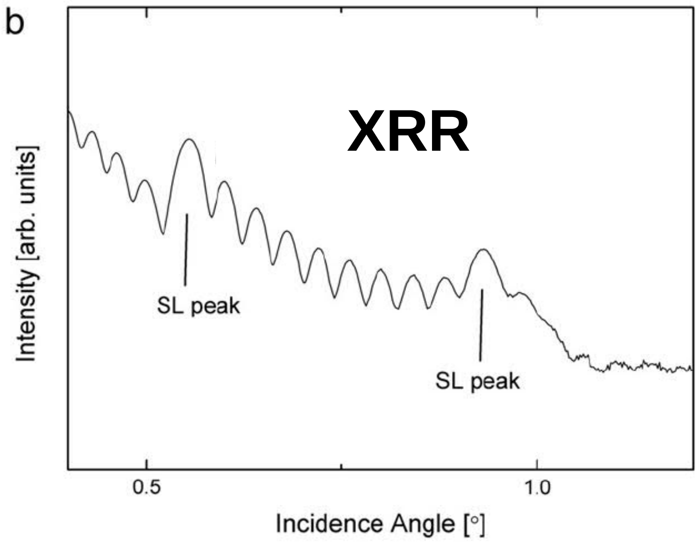


EXAMPLE: THERMOELECTRIC MATERIALS

- **High electrical conductivity & Low thermal conductivity**
  → Difficult combination to be achieved with conventional materials
- **ALD/MLD thin-film technology → nanoscale SUPERLATTICE (SL):**
  - thermoelectric oxide layers (ZnO) by ALD & organic (benzene) layers by MLD
  - thermal conductivity decreases but electrical conductivity remains the same
- **XRR: we can see SL peaks as an indication of the regular ordered SL structure**





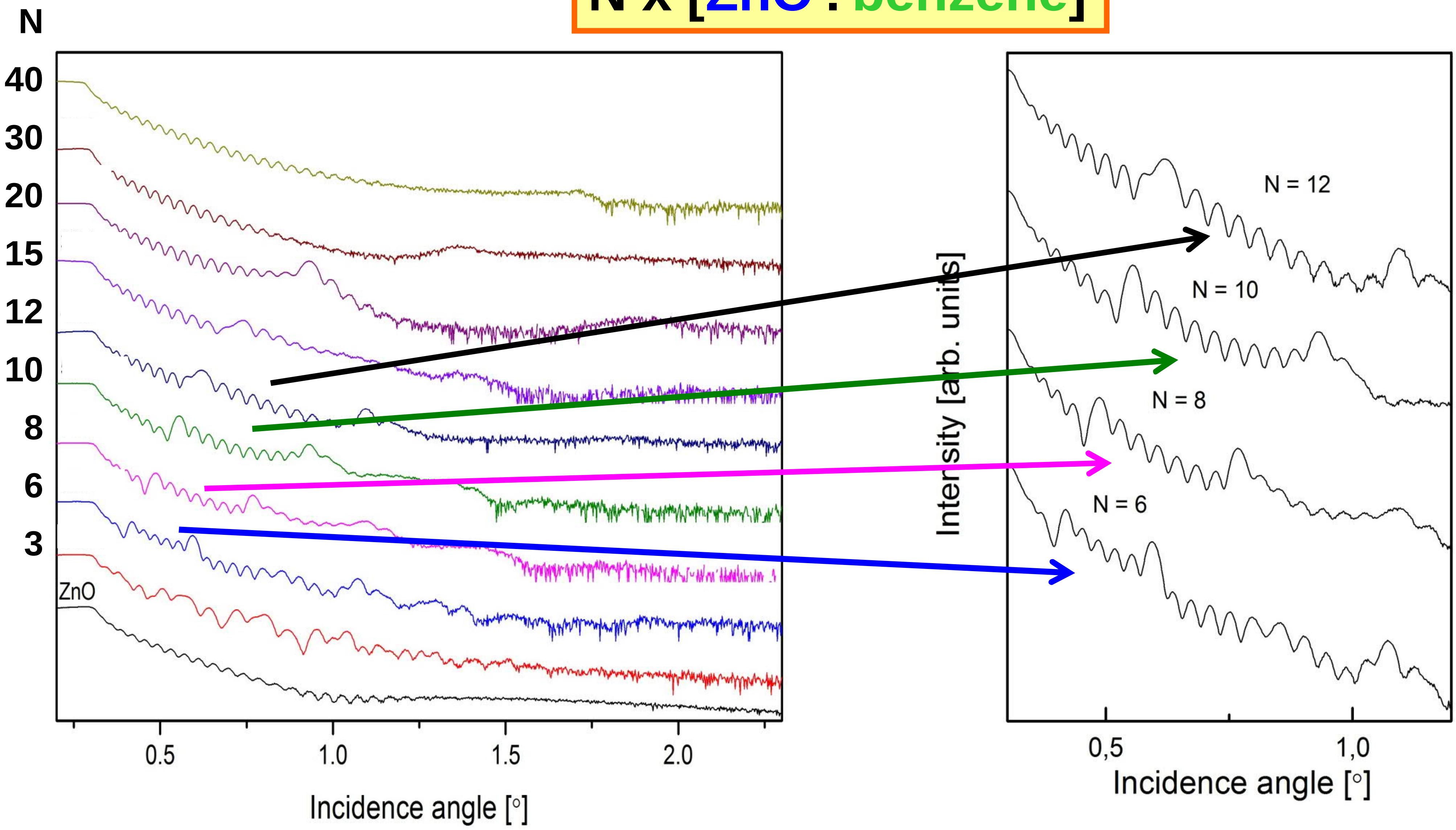


J.-P. Niemelä, A.J. Karttunen & M. Karppinen,
Inorganic-organic superlattice thin films for thermoelectrics,
J. Mater. Chem. C **3**, 10349 (2015).

XRR:

- **We can see/count the number (N) of ”superlayer” units in the SL thin film; most clearly for N = 6 to 12; for N > 12 the oscillations start to overlap**
- **NOTE: for ZnO no SL peaks are seen**

N x [ZnO : benzene]



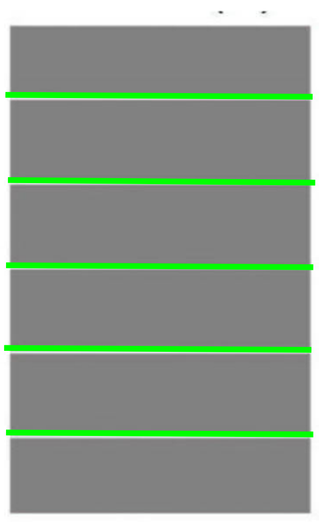
T. Tynell, I. Terasaki, H. Yamauchi & M. Karppinen, *J. Mater. Chem. A* **1**, 13619 (2013).

Using the ALD/MLD technique it is possible to perfectly control where within the ZnO film the organic (benzene) layers are placed → We can grow both regular superlattice films and irregular "gradient" ZnO-organic films. In this EXAMPLE we compare two films:

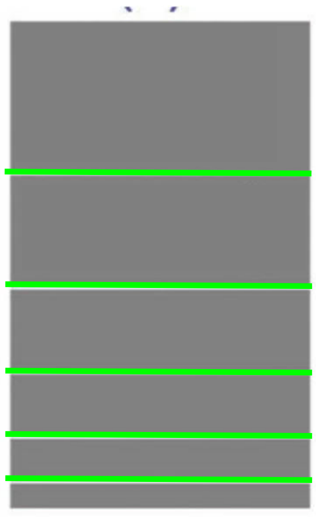
In both: total film thickness: ~105 nm
Number of organic layers: 5
Average ZnO layer thickness: ~17 nm

Superlattice: all ZnO layers ~17 nm
Gradient film: ZnO layers 9 ~ 28 nm

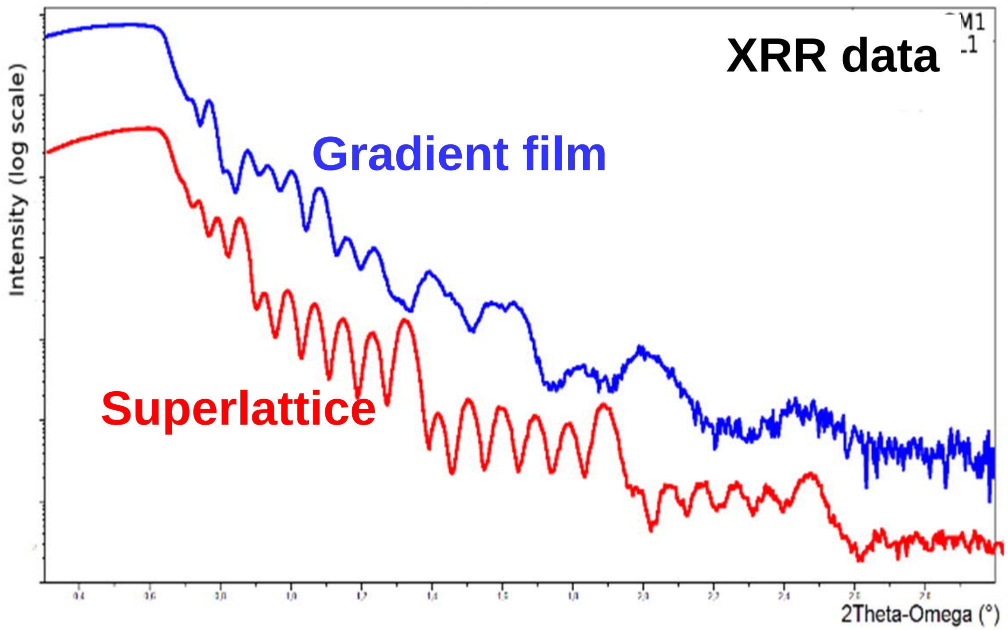
ONLY for the former the SL peaks are seen in XRR data



Superlattice



Gradient film



F. Krahl, A. Giri, J.A. Tomko, T. Tynell, P.E. Hopkins & M. Karppinen, Thermal conductivity reduction at inorganic-organic interfaces: from regular superlattices to irregular gradient layer sequences, *Adv. Mater. Interfaces* **5**, 1701692 (2018).