

# **LECTURE 10:**

## **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: Ddiffraction, reflection & refraction, total reflection, critical angle, incident angle**

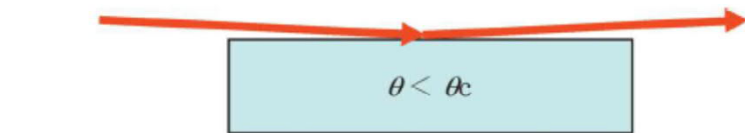
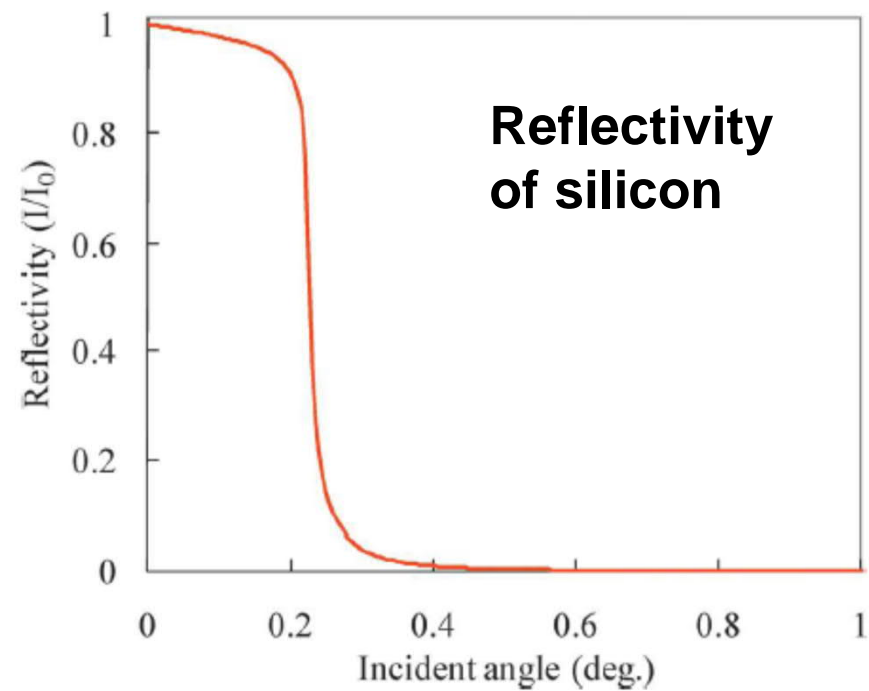
- **DIFFRACTION (Sironta):** Bulk phenomenon, takes place also within the material, but only at certain angles. Light waves bend around obstacles and bend into the shadow region; responsible for interference patterns. **Bragg Equation:** conditions and positions of interference bands.
- **REFLECTION (Heijastuminen):** Surface phenomenon, takes place at all angles. Light rays strike a surface and bounce back (reflect off it). **Law of Reflection:** reflection angle = incidence angle
- **REFRACTION (Taittuminen):** Light rays enter a different medium of different optical density and change direction or bend. **Snell's Law:** degree of refraction.



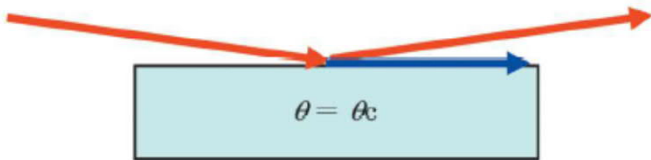
TOTAL INTERNAL REFLECTION  
in a wine glass

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.

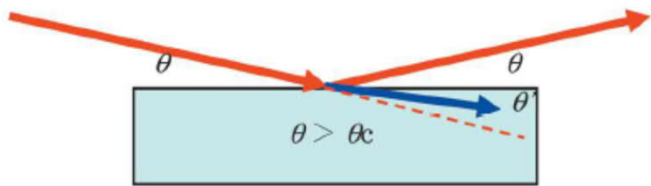
Diffused reflections specularly reflected



- 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.



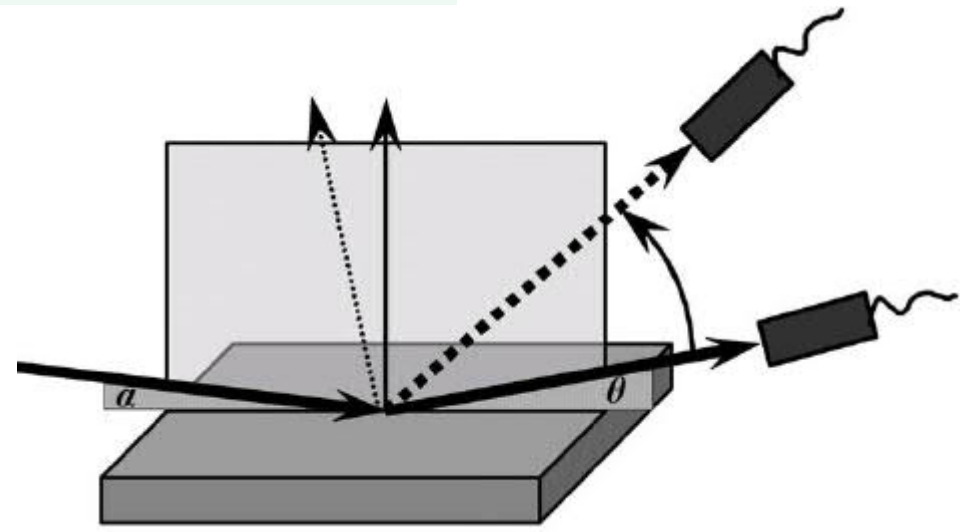
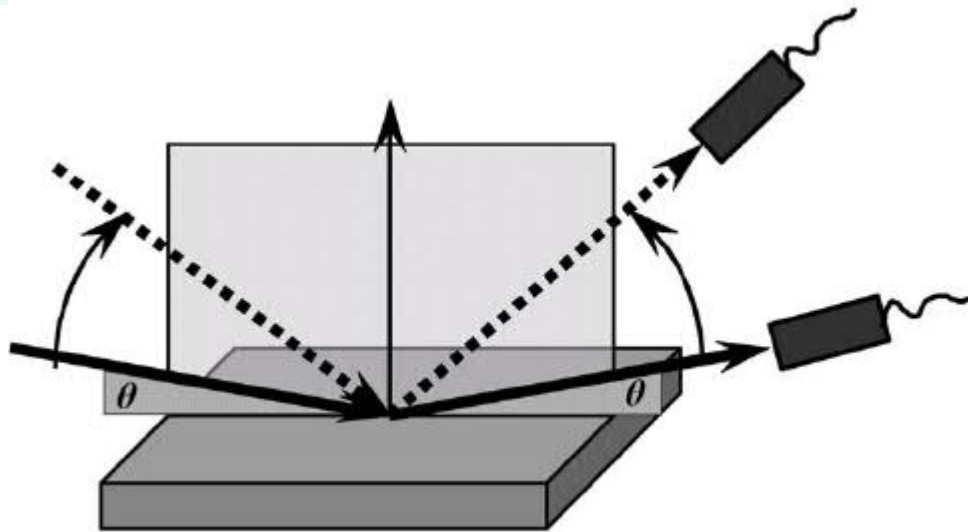
- C) Incident angle  $>$  Total reflection critical angle  
Incident X-rays penetrate into the material by refraction

## CRITICAL ANGLE

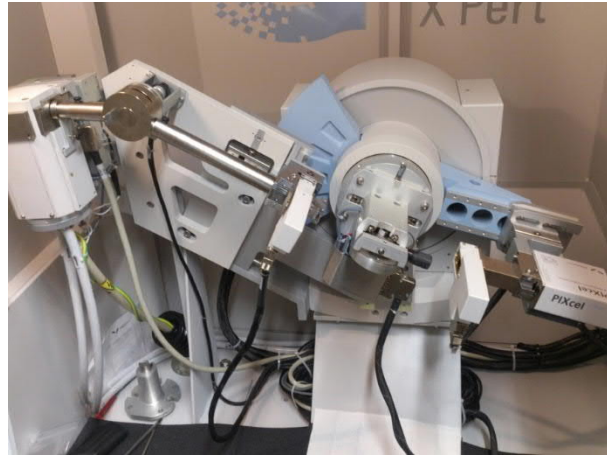
- With very tiny incident angles X-rays only reflect from the sample surface (no refraction)
- At the critical angle ( $\alpha_c$ ), X-rays begin to penetrate (= refract) the material (below  $\alpha_c$  no penetration)
- Above  $\alpha_c$  the reflectivity rapidly drops
- Material property  $\rightarrow$  Proportional to the square root of electronic density

# Grazing Incidence X-ray Diffraction (GI-XRD)

- Small incident angles for the incoming X-ray beam  
→ surface sensitive XRD
- Thin films: 1~1000 nm
- Penetration depth of X-rays:  
10~100  $\mu\text{m}$  (depending on the elemental composition)
- Conventional XRD with symmetric  $\theta/2\theta$  configuration:  
reflected radiation mostly due to the substrate
- Small incident angle ( $\alpha$ ) lowers the penetration depth  
→ information mostly from a thin surface layer
- Depth profiling is also possible: control of  $\alpha$



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

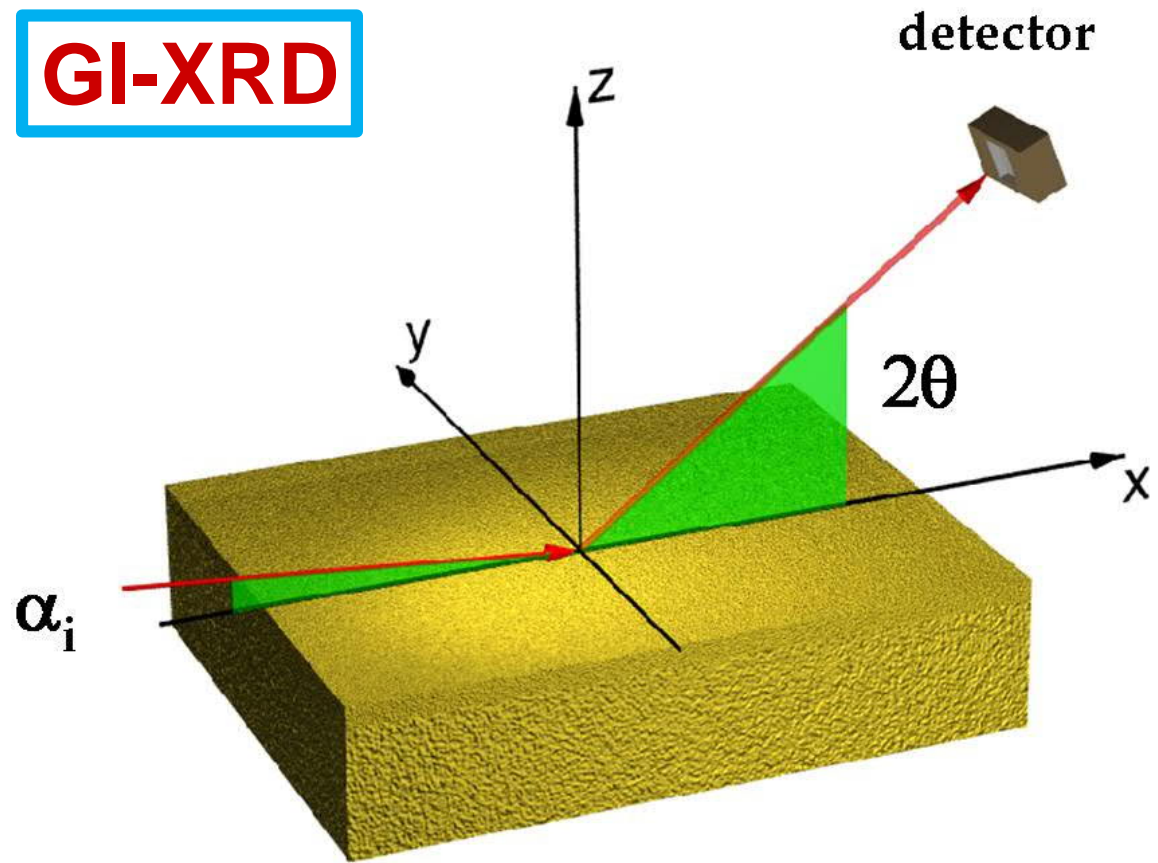


XRD

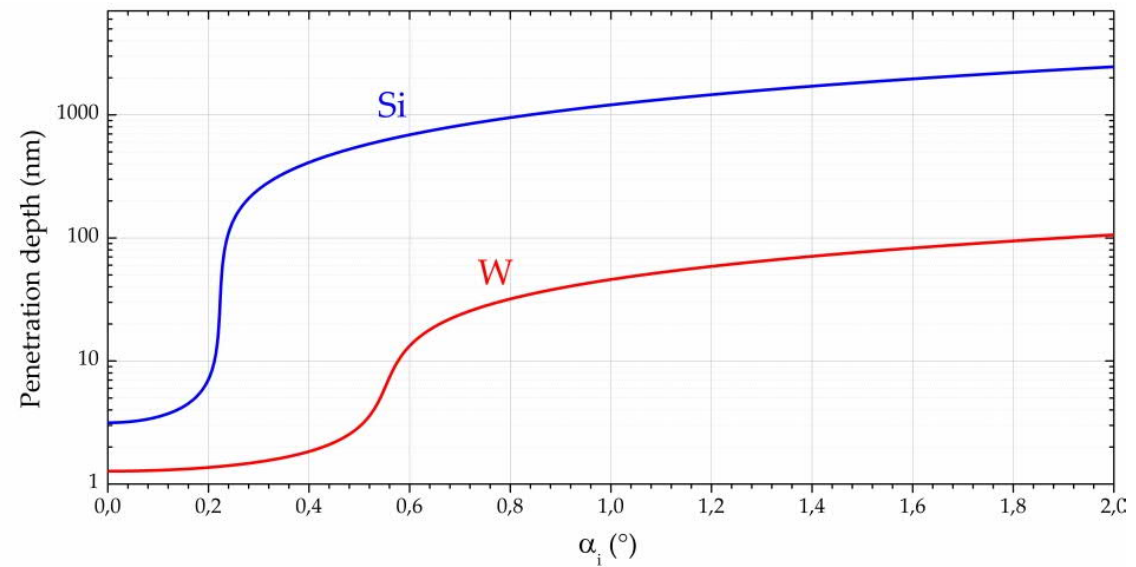


GI-XRD

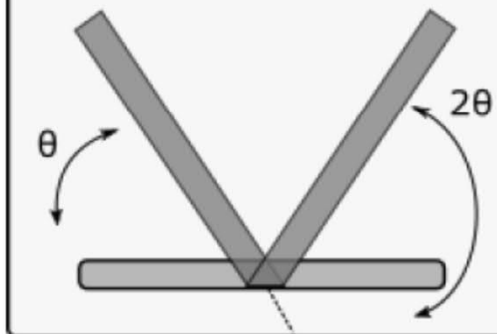
## GI-XRD



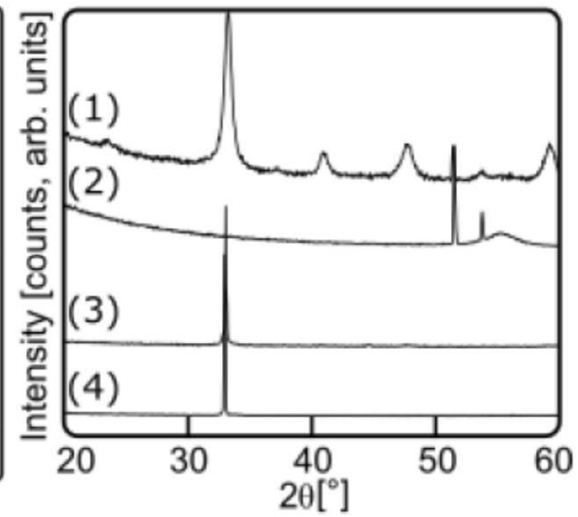
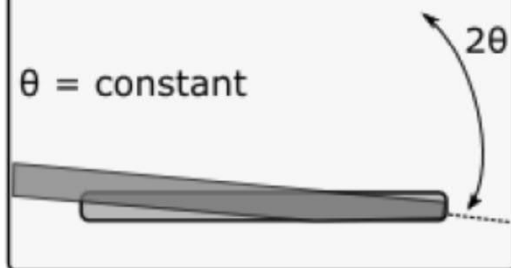
Critical angle: Si (=  $0.223^\circ$ ) and W (=  $0.552^\circ$ )



## XRD



## GIXRD



## GI-XRD

(1) Thin film + subs.

(2) Substrate

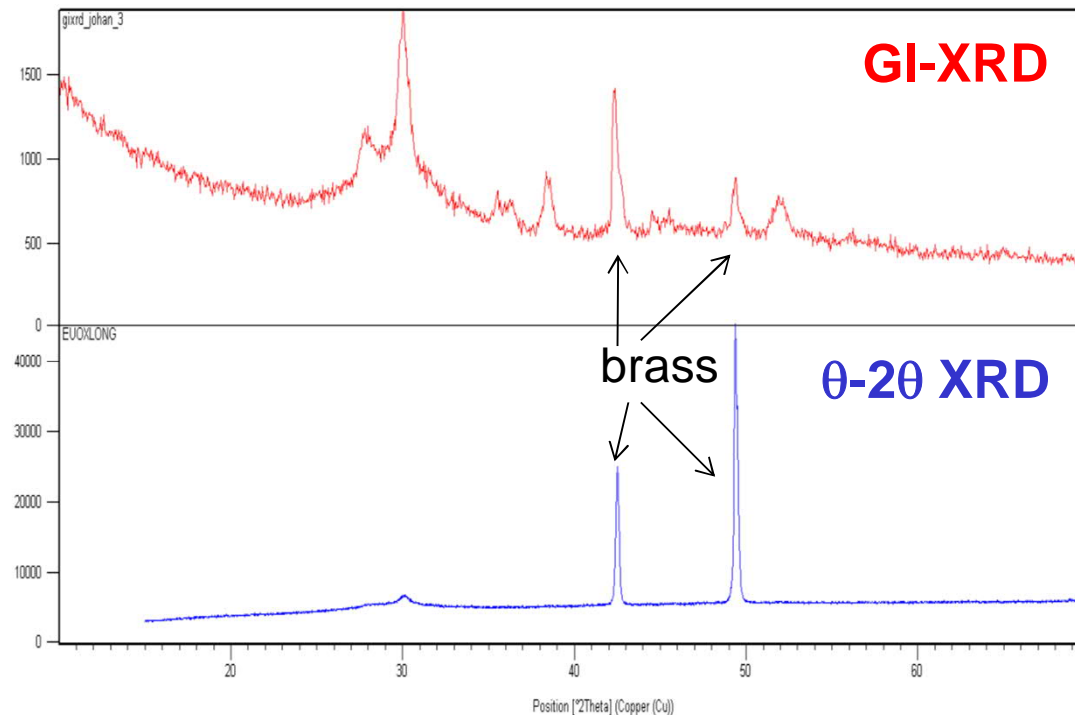
## XRD

(3) Thin film + subs.

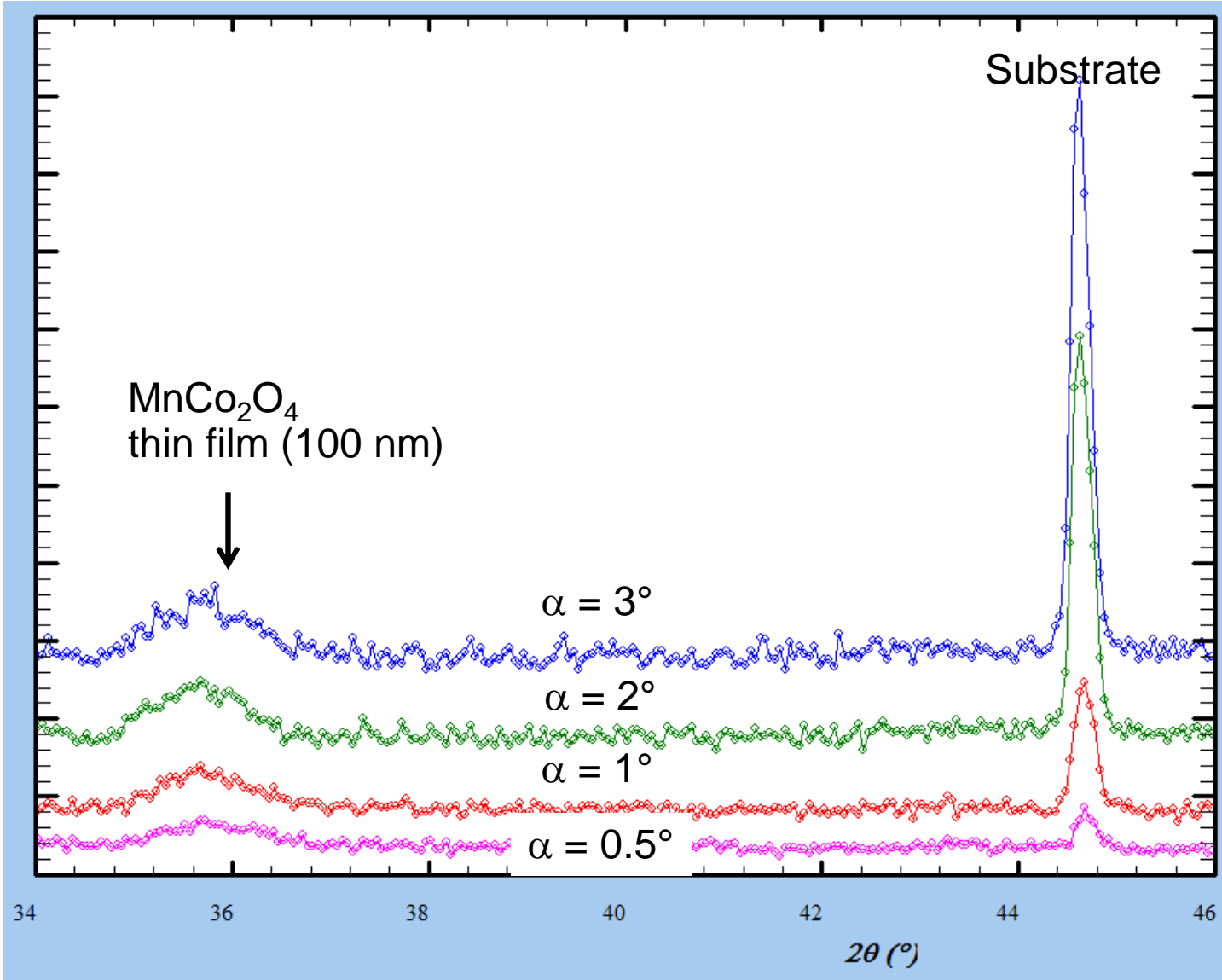
(4) Substrate



**EXAMPLE:  $\text{Eu}_2\text{O}_3$  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  $\text{Eu}_2\text{O}_3$  film**

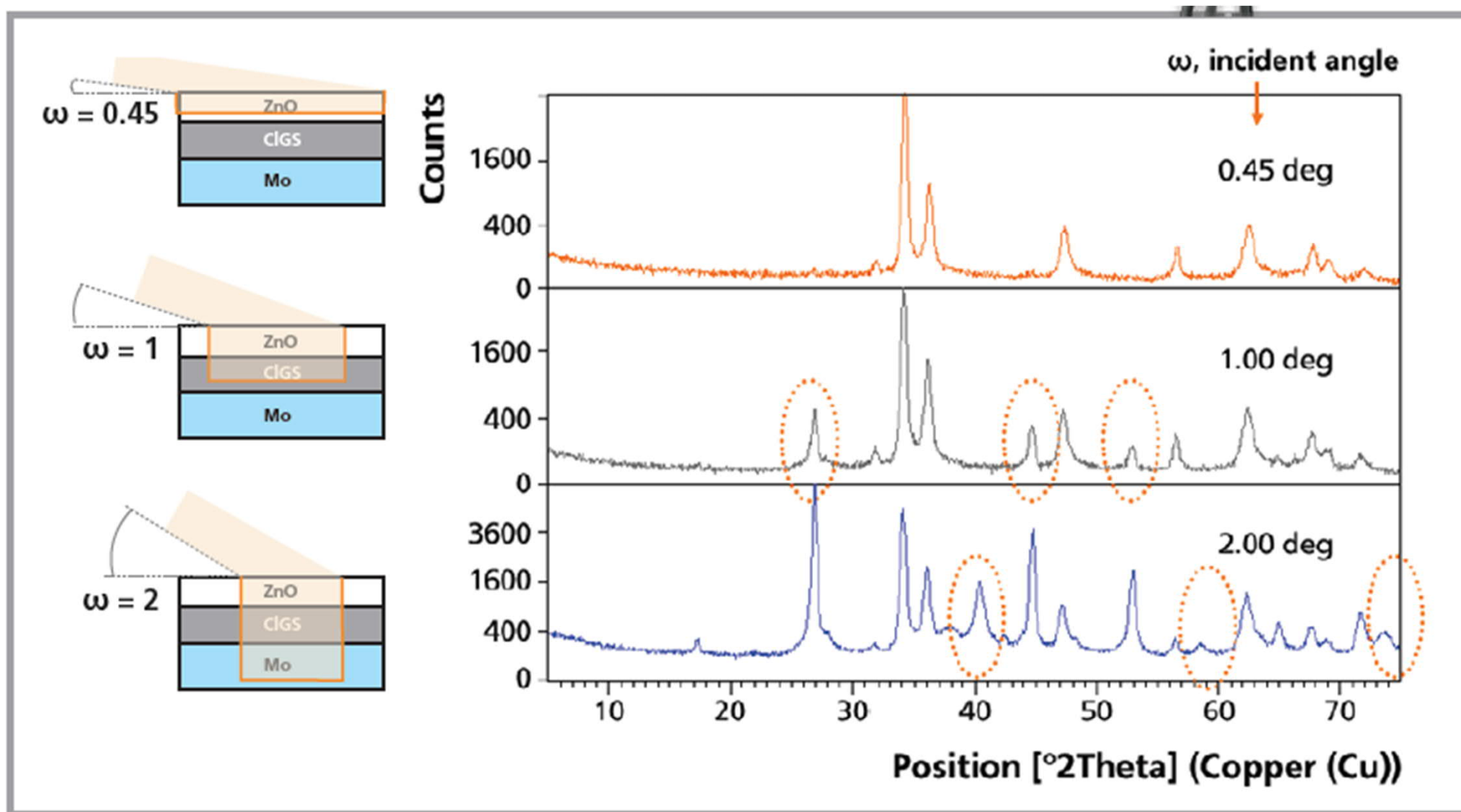






- With increasing incident angle ( $\alpha$ ), X-rays penetrate deeper
- Peaks due to the thin film increase in intensity
- Also the substrate peaks (may) get enhanced
- NOTE the different peak widths for substrate and thin film (different crystallite sizes)

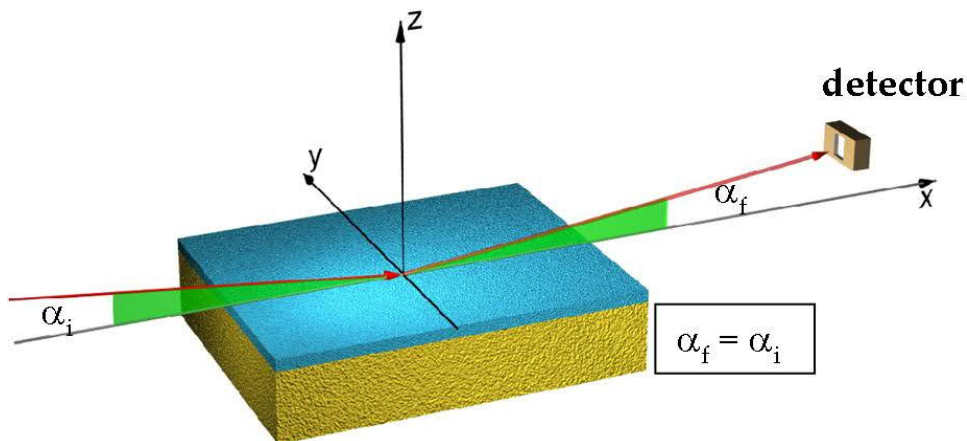
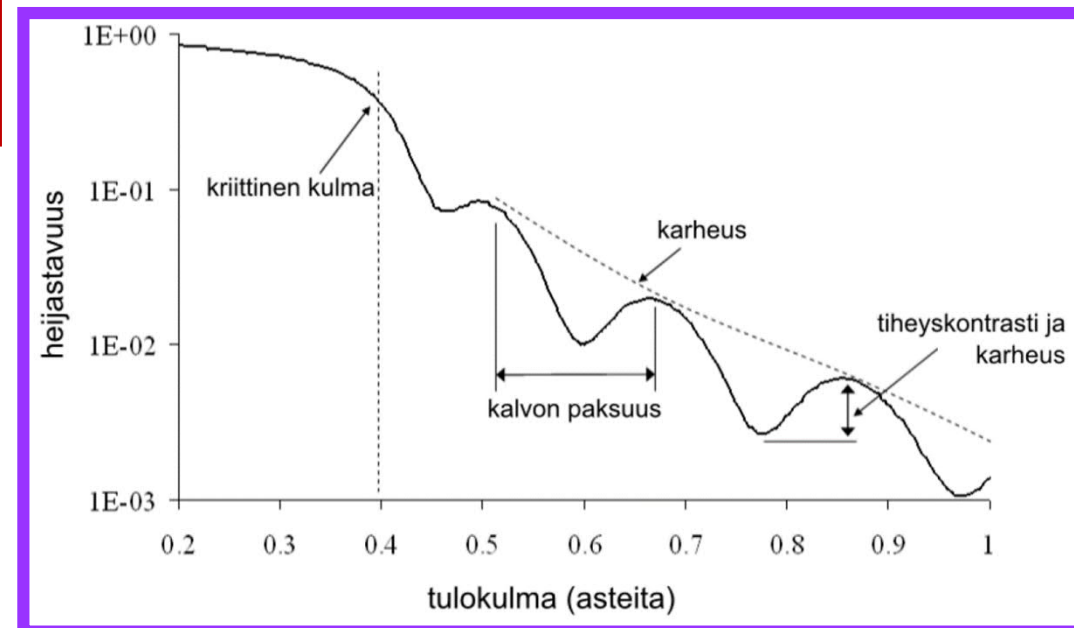
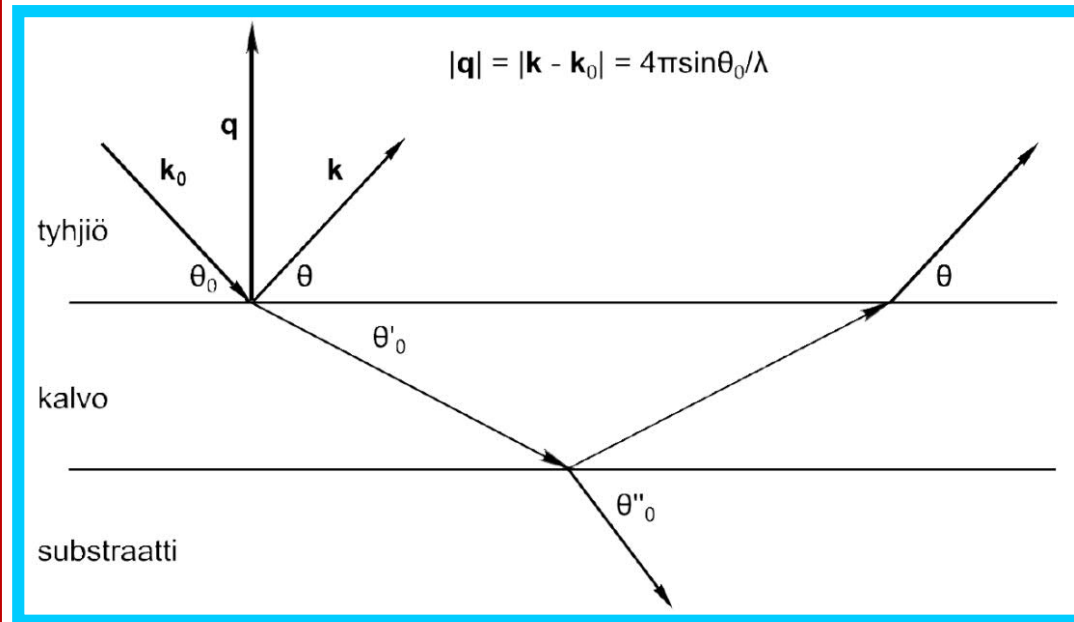
# GI-XRD: Depth profile analysis

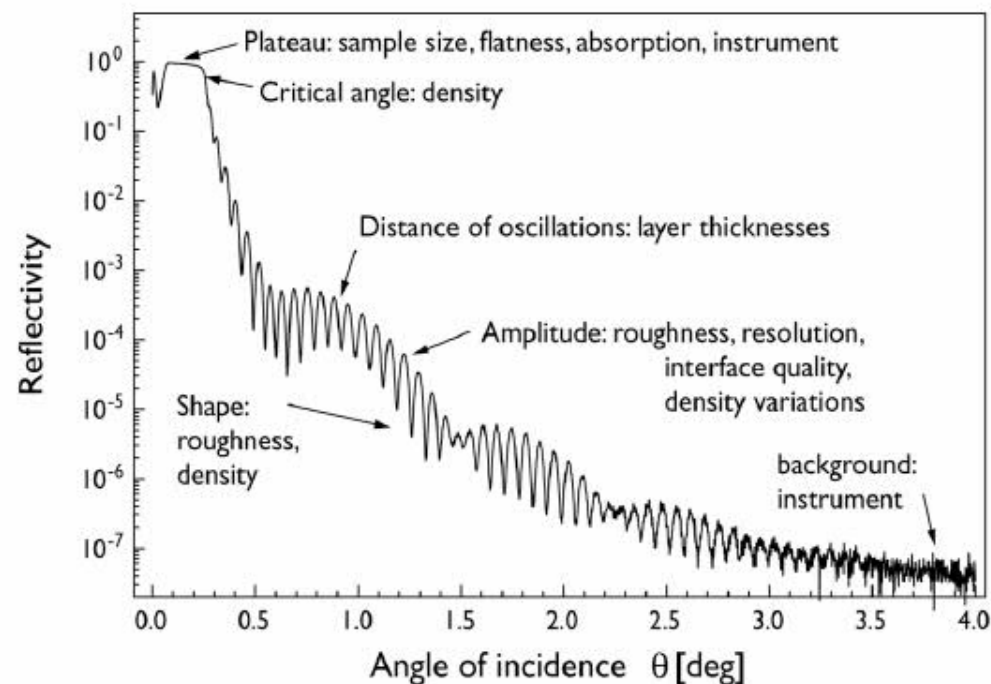
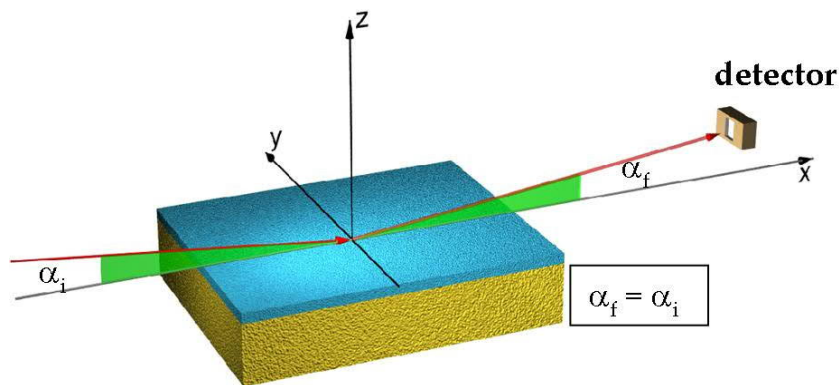


An example of depth probing on a CIGS solar structure, showing the different layers exposed to the parallel X-ray beam in a sequential mode by varying the incident angle. Top pattern is from the conductive oxide layer only, with CIGS coming in (middle, highlighted) and next the Mo metal contact layer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



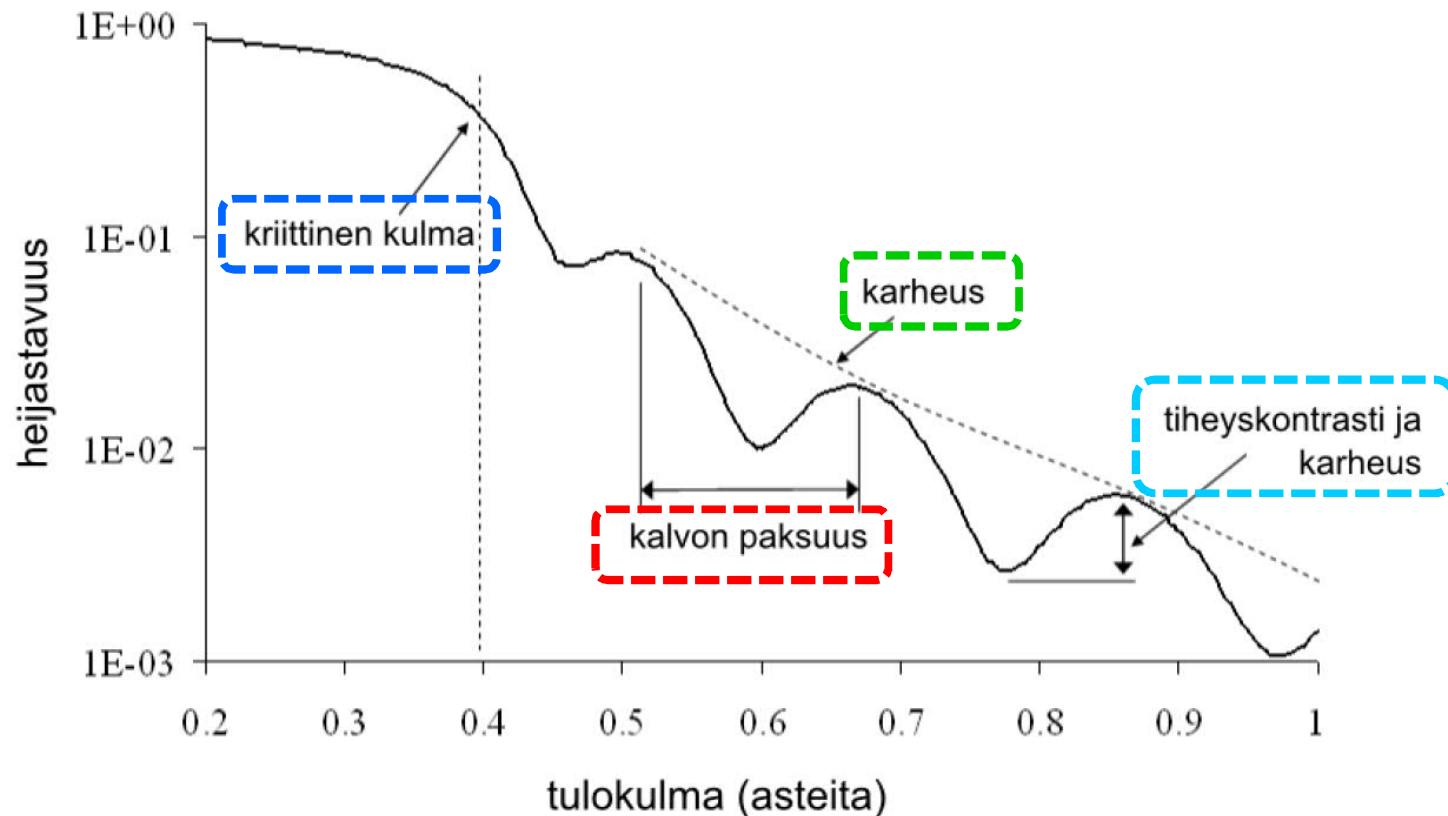


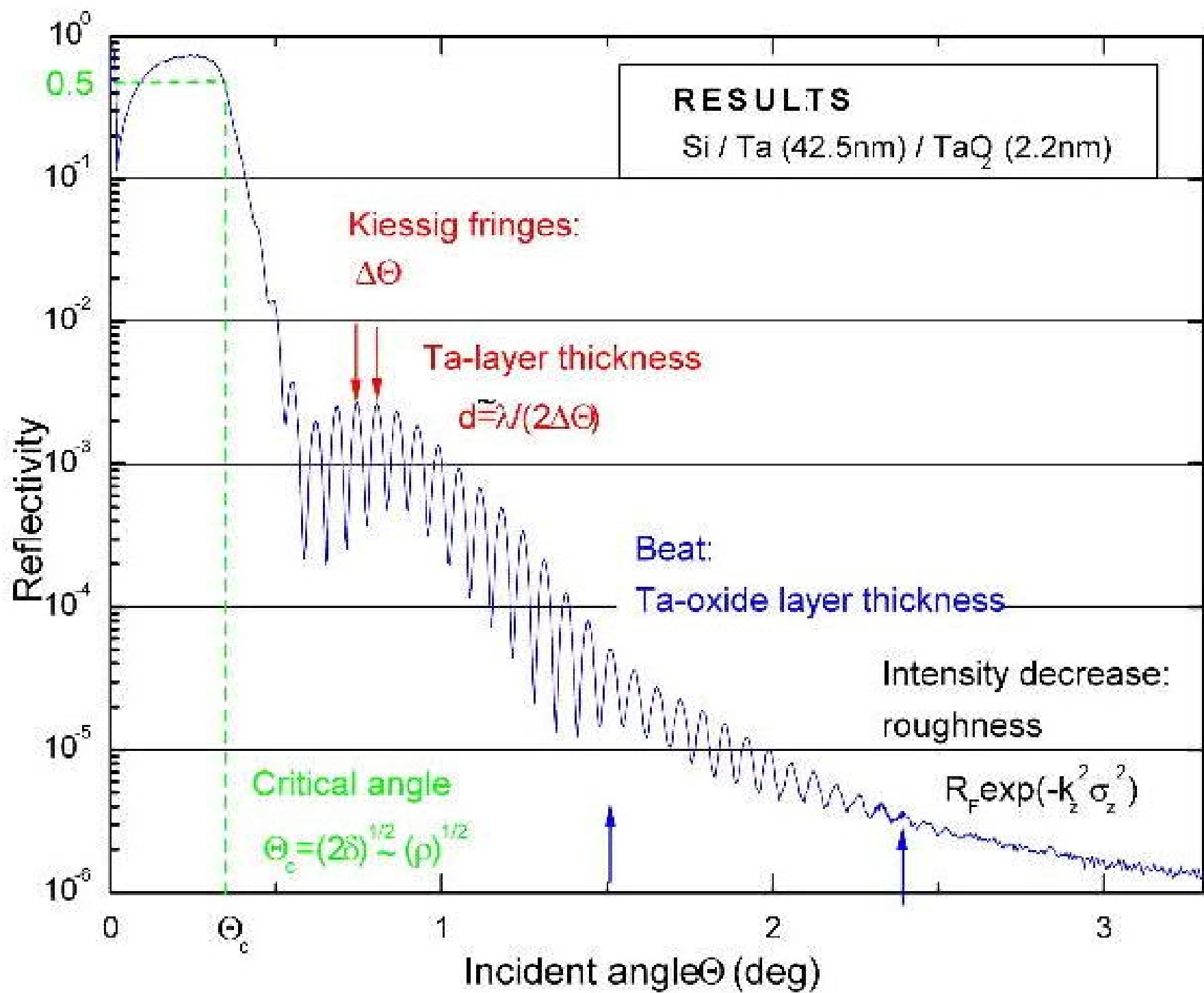
## XRR Measurement

- ❖ XRR device 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 ( $\alpha_c$ ; total reflection limit) → **DENSITY**
- Periodic oscillations or so-called *Kiessig fringes* provide us lot of information
  - Distance between two Kiessig fringes → **THICKNESS**
  - Height of Kiessig fringes → **(INTERFACE) ROUGHNESS**
  - Decay rate of intensity → **(SURFACE) ROUGHNESS**

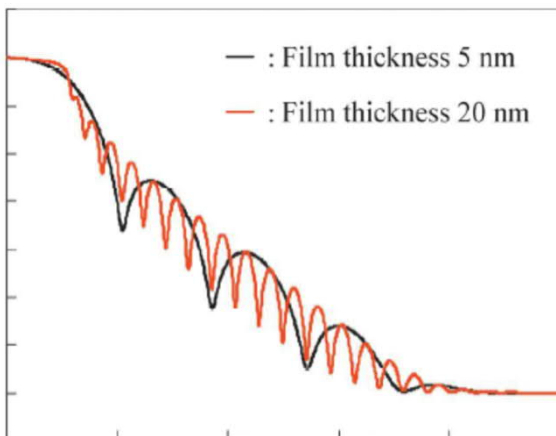
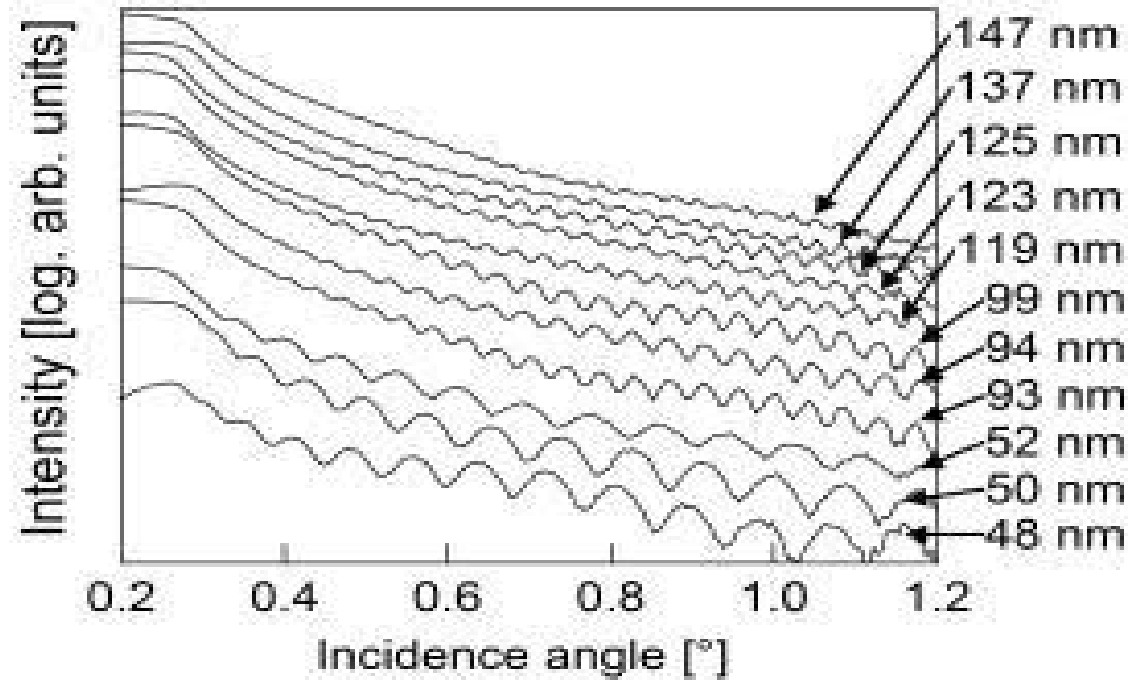
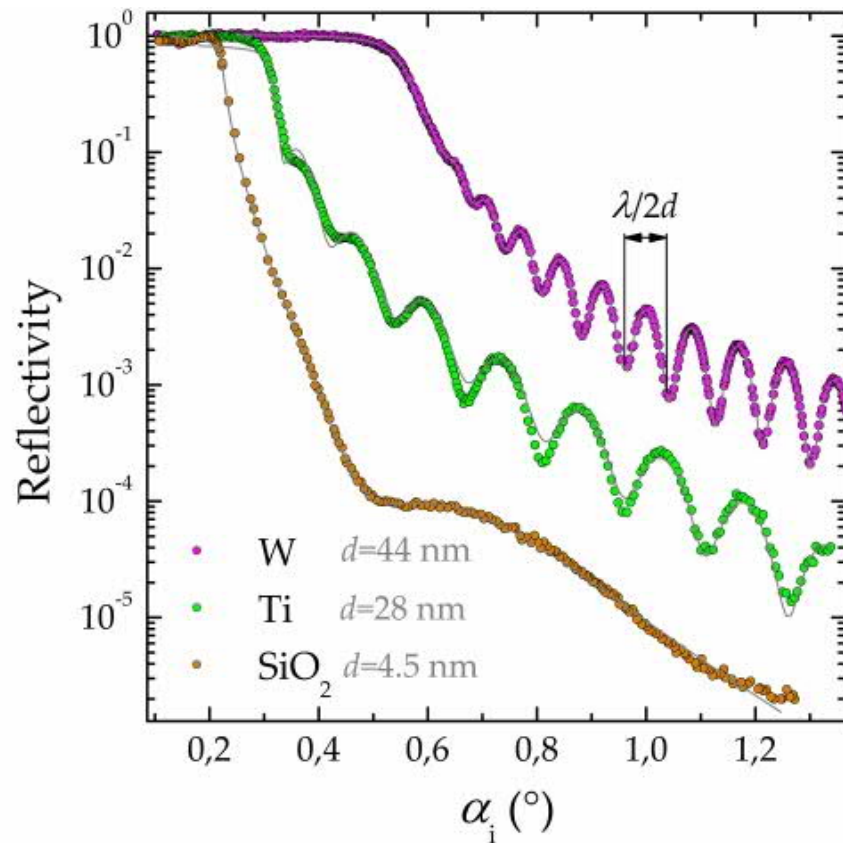




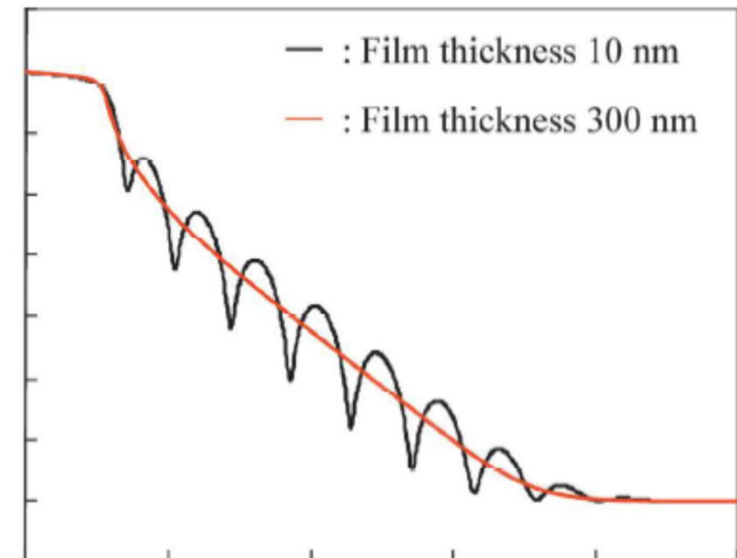


## (La,Sr)CoO<sub>3</sub> ALD thin films

### XRR: Film Thickness $d$



**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)

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

$\rho_{el}$  : electron density

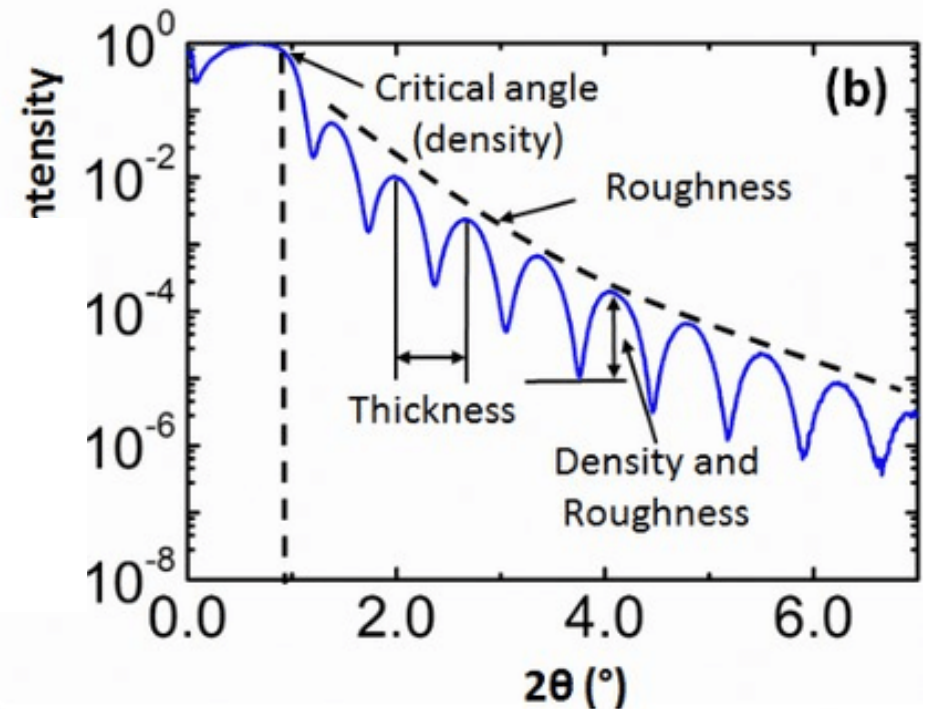
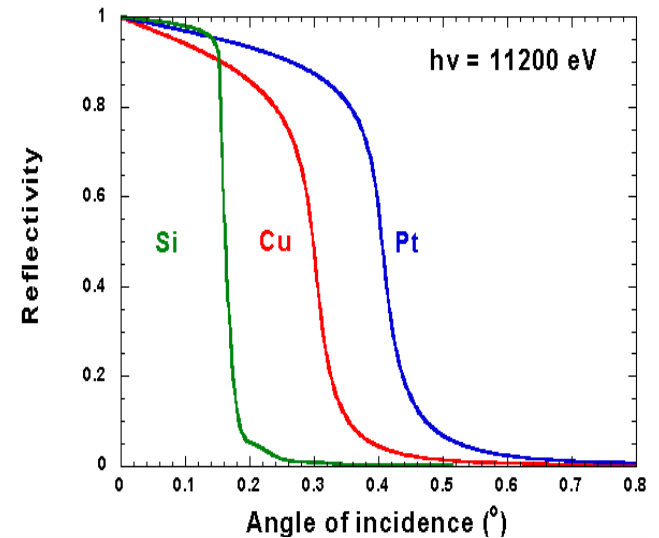
$\rho_m$  : mass density

$\Theta_C$  : critical angle

$r_{el}$  : electron radius

$A$  : Atomic mass

$Z$  : Atomic number



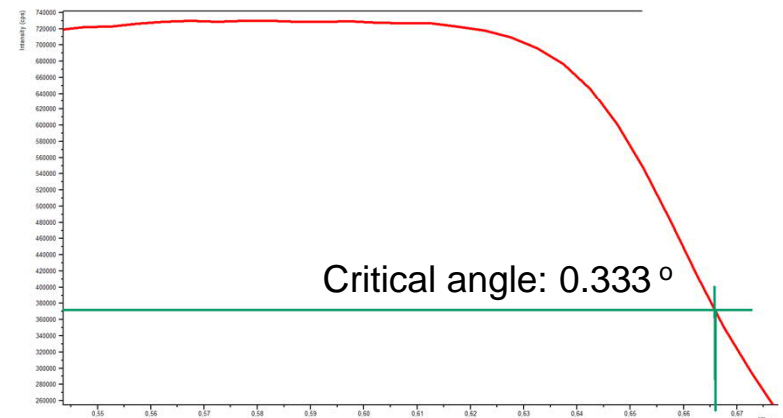
# EXAMPLE: ZnO thin film

$$A_{ZnO} = \frac{16 \frac{g}{mol} + 65.38 \frac{g}{mol}}{2}$$

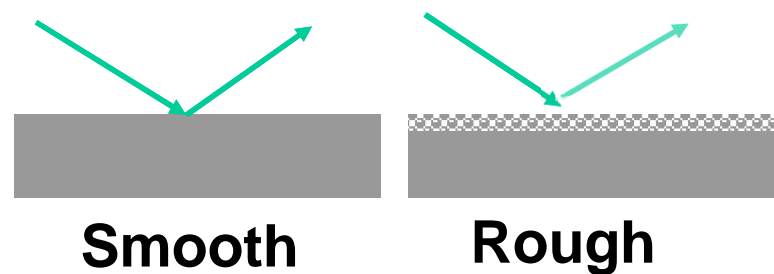
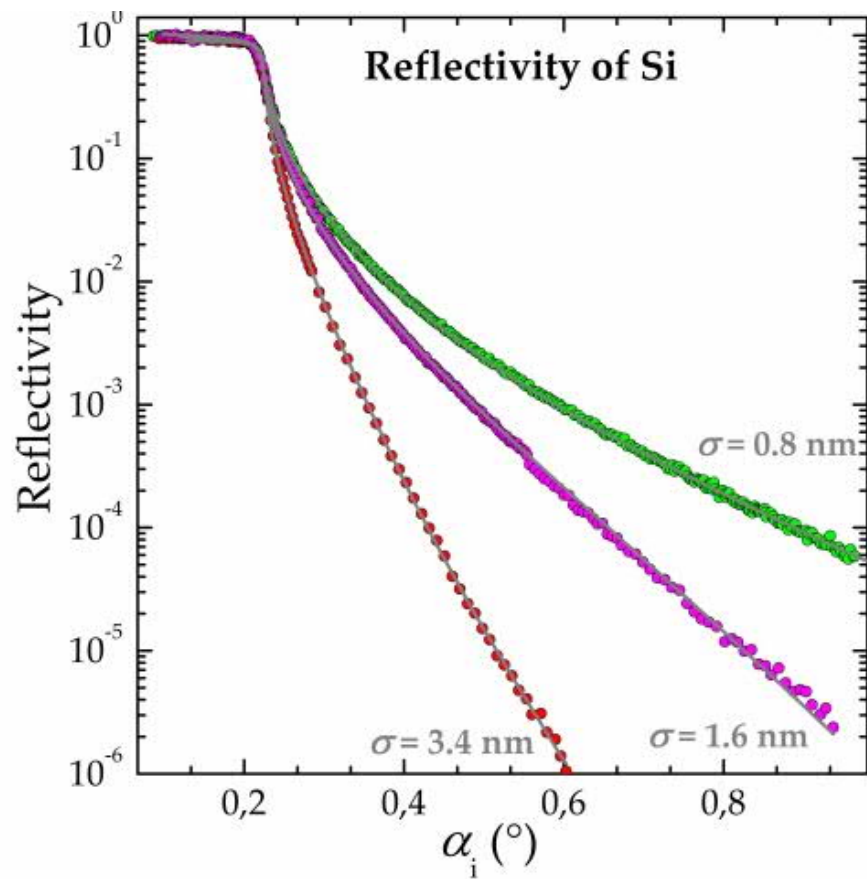
$$Z_{ZnO} = \frac{8 + 30}{2}$$

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

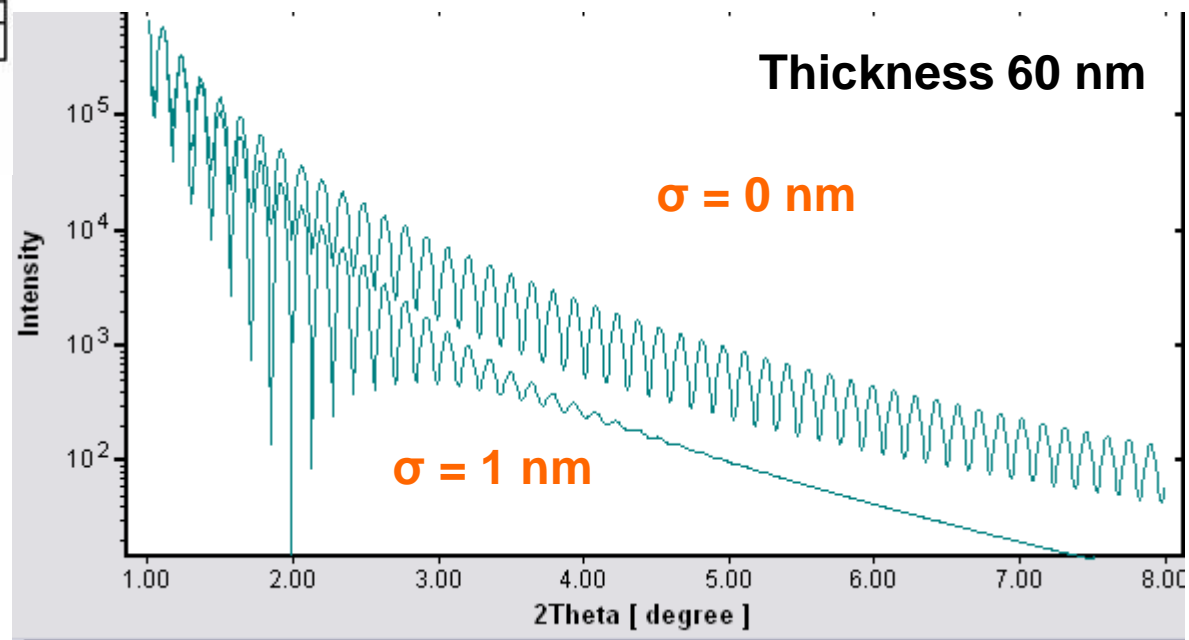
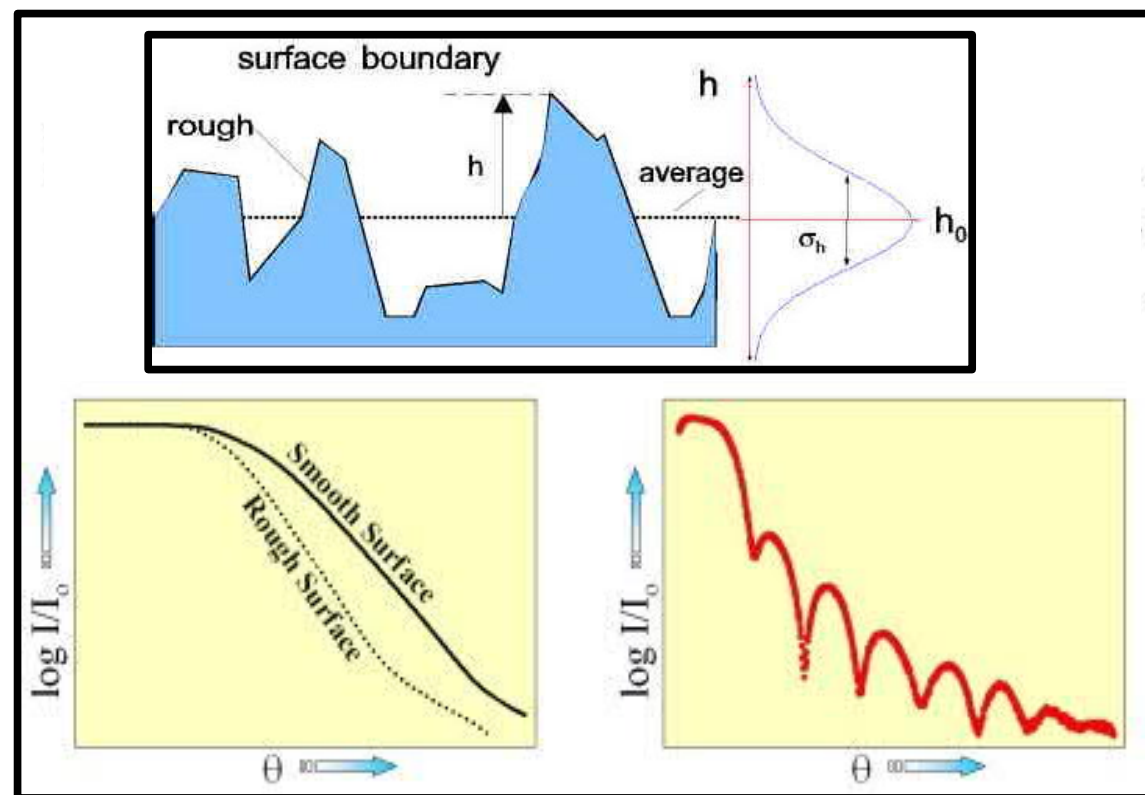
$$\rho_m = \frac{1.642 \cdot 10^{24} cm^{-3} \left( \frac{16 \frac{g}{mol} + 65.38 \frac{g}{mol}}{2} \right)}{6.022 \cdot 10^{23} mol^{-1} \left( \frac{8 + 30}{2} \right)} \approx 5.8 g/cm^3$$

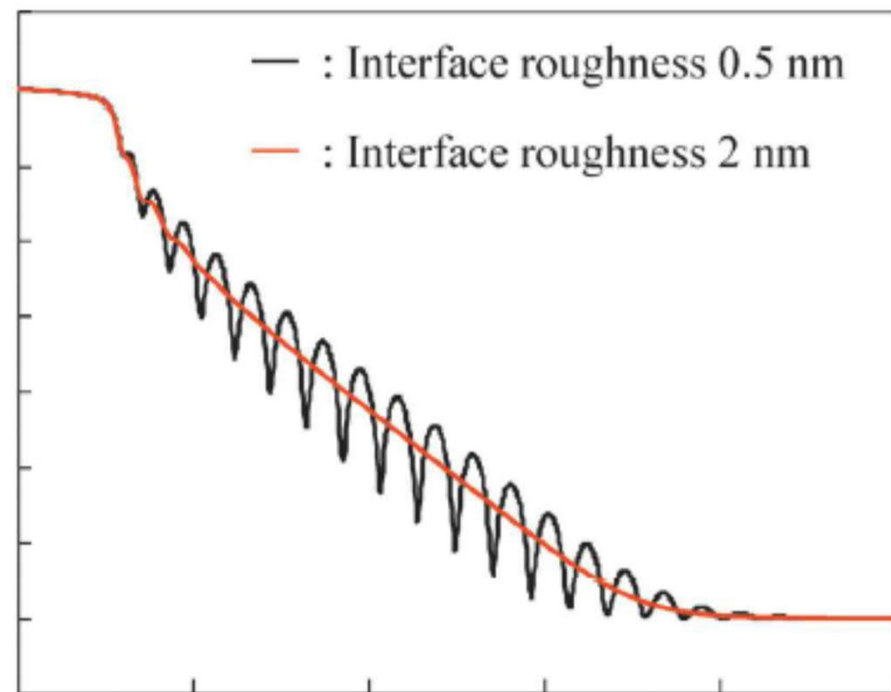
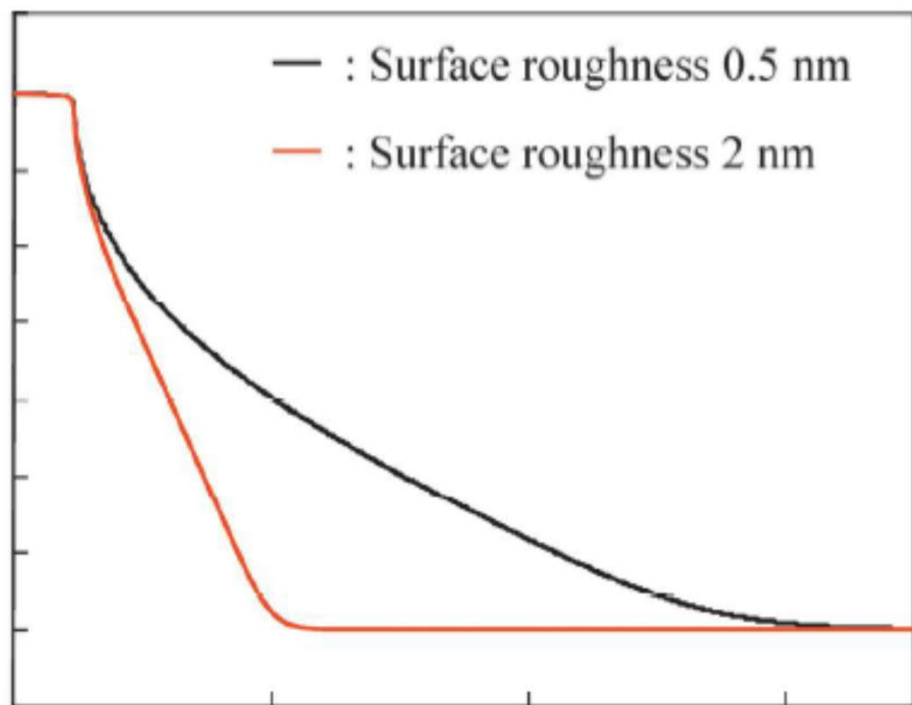


# XRR: Surface roughness $\sigma$



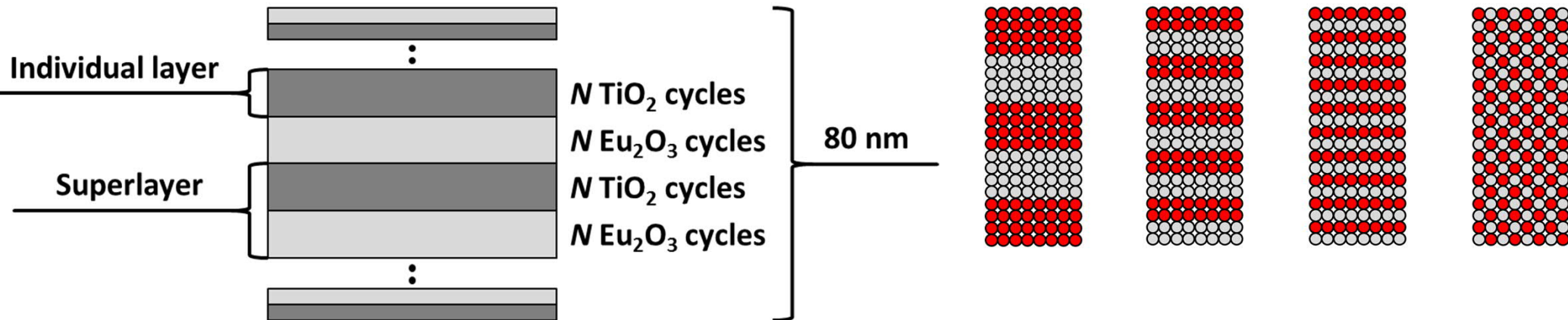
Rough interfaces cause intensity loss





# SUPERLATTICES

ALD-grown superlattice:  $\text{Eu}_2\text{O}_3$  and  $\text{TiO}_2$  layers grown on top of each other with different frequencies: in the XRR pattern you can see clear (more intense) superlattice peaks.

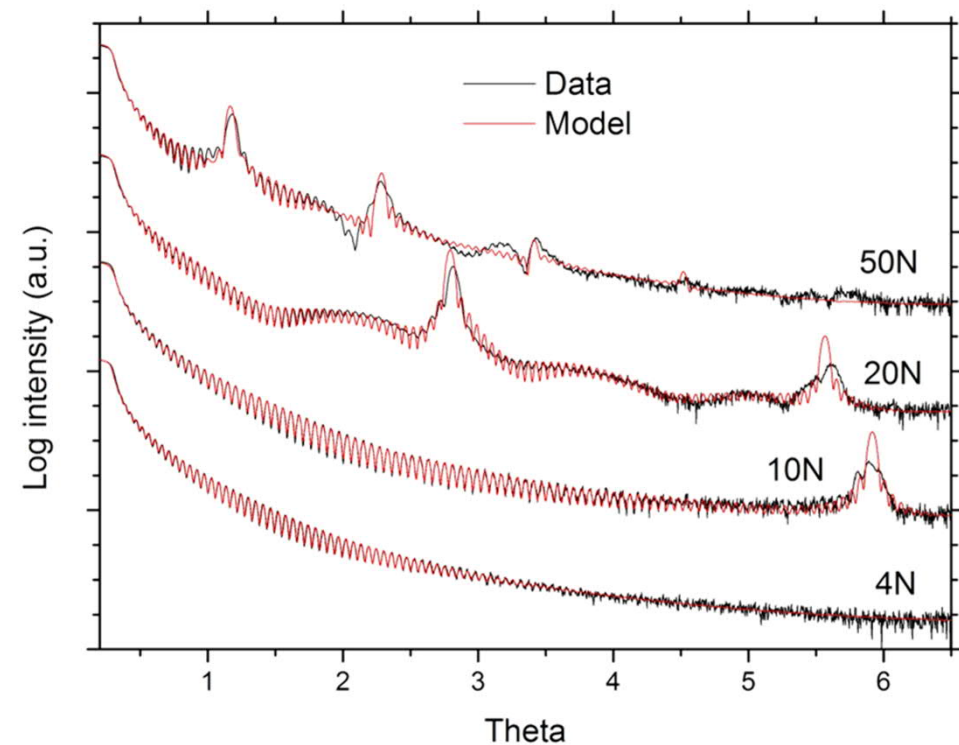


Superlayer thicknesses:

$$10N = 7.5 \text{ \AA}$$

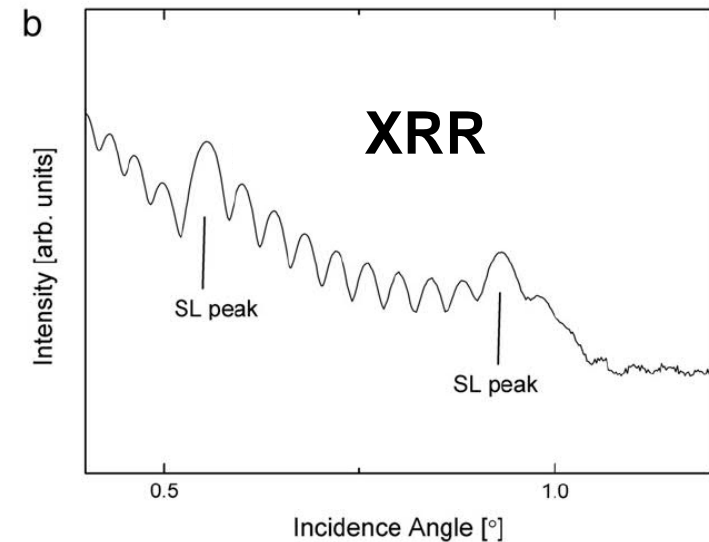
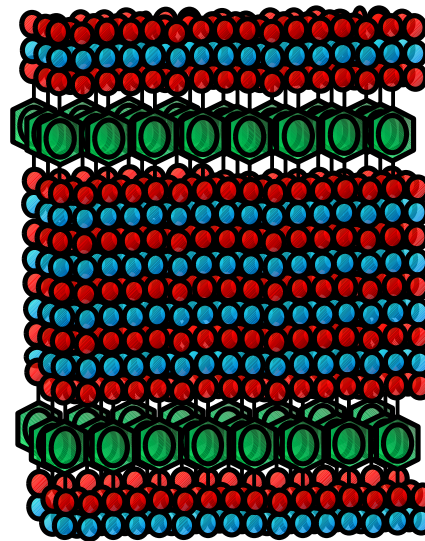
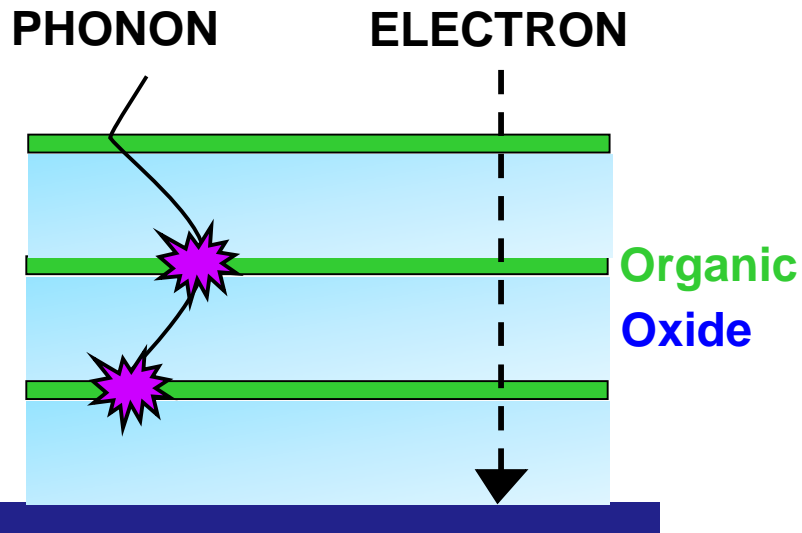
$$20N = 15.9 \text{ \AA}$$

$$50N = 29.1 \text{ \AA}$$



# 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



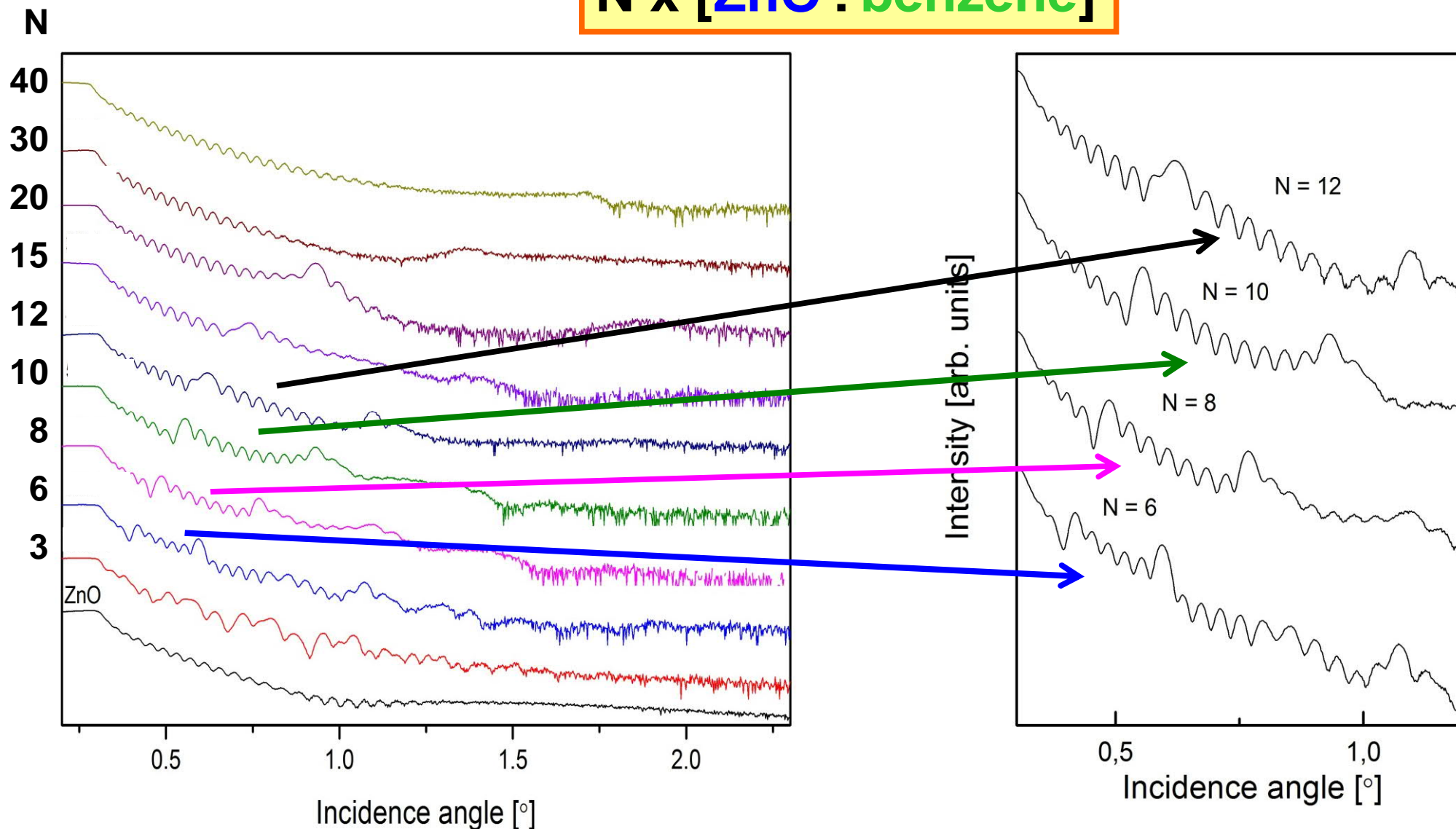
J.-P. Niemelä, A.J. Karttunen & M. Karppinen,  
Inorganic-organic superlattice thin films for thermoelectrics,  
*J. Mater. Chem. C* **3**, 10349 (2015).



## 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]





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

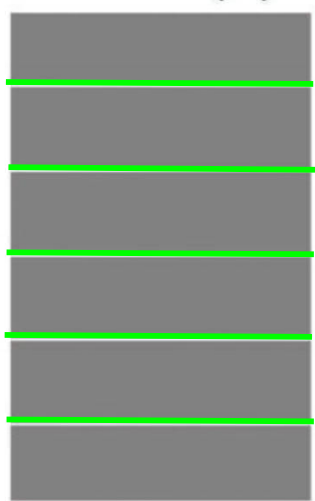
Number of organic layers: 5

Average ZnO layer thickness: ~17 nm

**Superlattice:** all ZnO layers ~17 nm

**Gradient film:** ZnO layers 9 ~ 28 nm

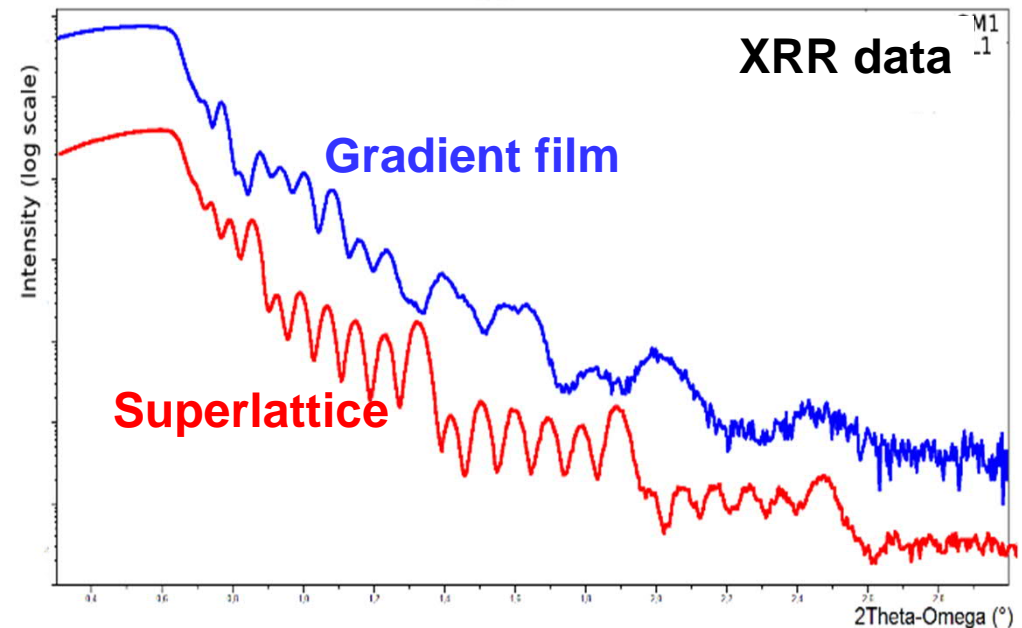
**ONLY** for the former the SL peaks are seen in XRR data



**Superlattice**



**Gradient film**



F. Krah, 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).