SCHEDULE

	Date		Topic
1.	Wed	28.02.	Lec-1: Introduction
2.	Mon	04.03.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Mon	04.03.	EXERCISE 1
4.	Wed	06.03.	Lec-3: Crystal Chemistry & BVS
5.	Fri	08.03.	Lec-4: Symmetry & Point Groups
6.	Mon	11.03.	EXERCISE 2
7.	Wed	20.03.	Lec-5: Crystallography & Space Groups (Linda)
8.	Fri	22.03.	Lec-6: XRD & Reciprocal lattice (Linda)
9.	Mon	25.03.	EXERCISE 3 (Linda) Ke4
10.	Thu	04.04.	Lec-7: Rietveld (Linda)
11.	Fri	05.04.	EXERCISE 4: Rietveld (Linda)
	Mon	08.04.	EXERCISE 4: Rietveld (Linda)
12.	Thu	11.04.	Lec-8: GI-XRD & ND
13.	Fri	12.04.	Lec-9: XRR & Ellipsometry (Topias) 12:15-14, Ke4
14.	Mon	15.04.	EXERCISE 5: XRR (Topias) 14:15-16 Ke3
	Wed	17.04.	EXERCISE 5: XRR (Topias) 14:15-16 Ke3
15.	Mon	22.04.	Lec-10: Synchrotron radiation & XAS & EXAFS
16.	Thu	25.04.	Lec-11: Mössbauer 12:15-14, Ke3
17.	Fri	26.04.	EXERCISE 6
18.	Mon	29.04.	Seminars
19.	Mon	06.05.	ADDITIONAL DISCUSSION/QUESTION POSSIBILITY
20.	Mon	13.05.	EXAM

LECTURE 9:

XRR (X-ray reflection)

Main topic today

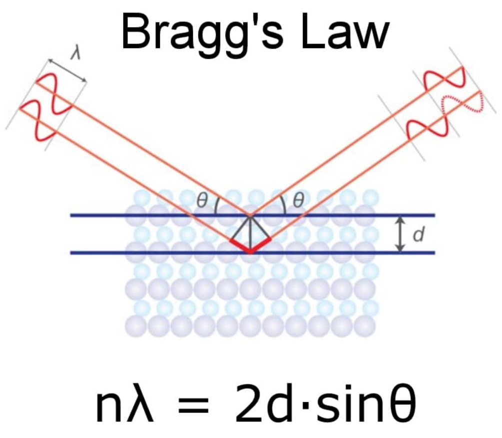
Ellipsometry

XRR (X-ray reflectivity)

- **XRR complements GI-XRD in thin-film characterization**

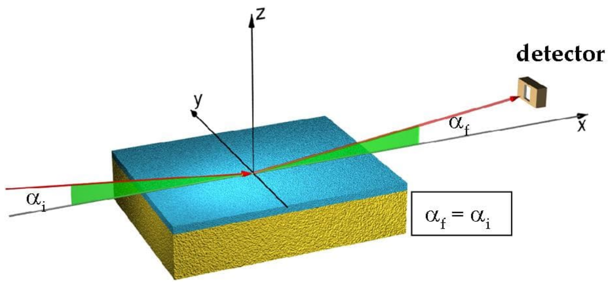
- **<u>XRR: thickness, density, roughness & multilayers</u>**
- **KEYWORDS: diffraction, reflection & refraction, total reflection, critical angle, incident angle**

- **DIFFRACTION (XRD & GI-XRD):** Bulk phenomenon, takes place at the surface and within the material, but only at certain angles → **Bragg's law**: conditions and positions of interference peaks.

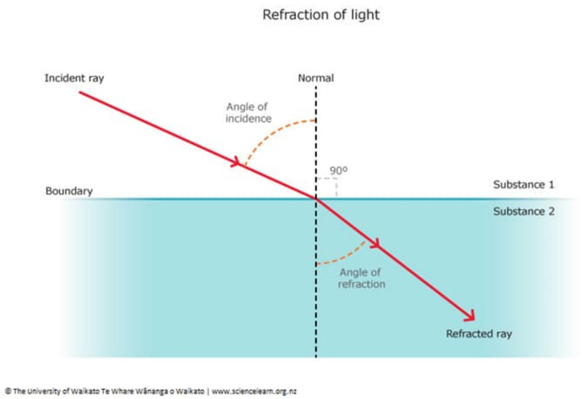


https://rigaku.com/techniques/x-ray-diffraction-xrd

- **REFLECTION (XRR):** Surface (and interface) phenomenon. X-rays reflect on a surface → **Law of Reflection:** reflection angle = incidence angle



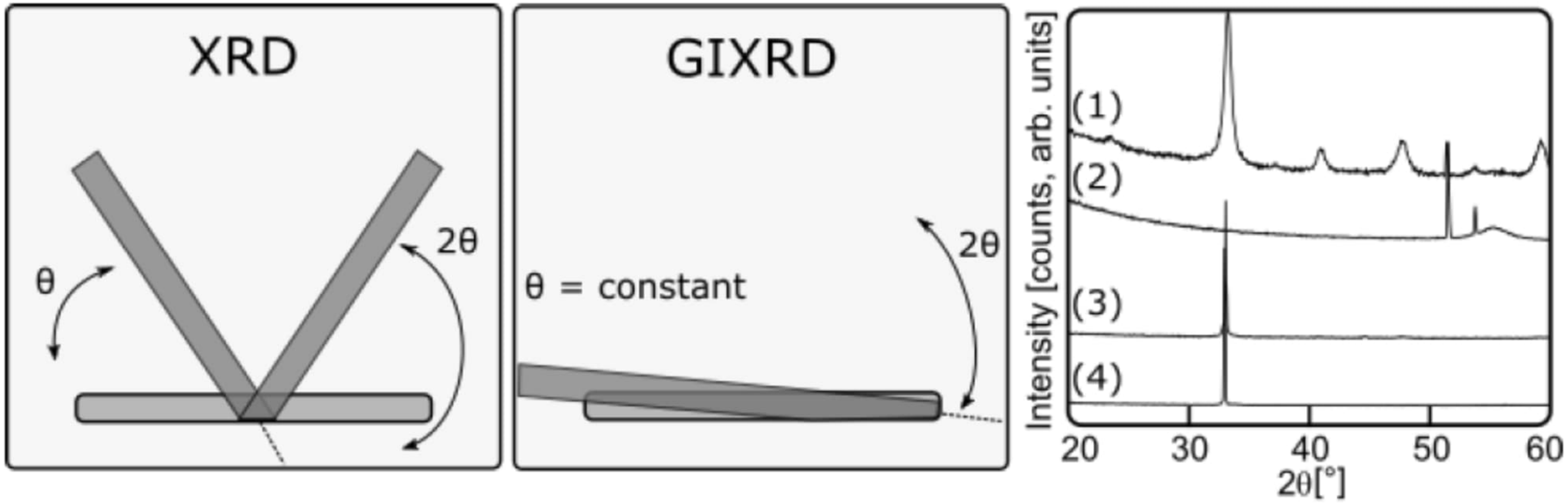
- **REFRACTION:** X-rays enter a different medium of different optical density and change direction or bend. **Snell's Law:** degree of refraction.



https://www.sciencelearn.org.nz/images/49-refraction-of-light-in-water

GI-XRD – last lecture

Small incident angle (θ) → low penetration depth → information mostly from a thin surface layer



GI-XRD

(1) Thin film + subs.

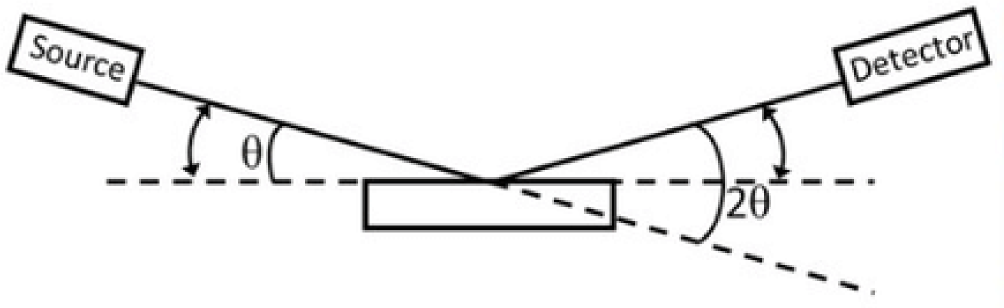
(2) Substrate

XRD

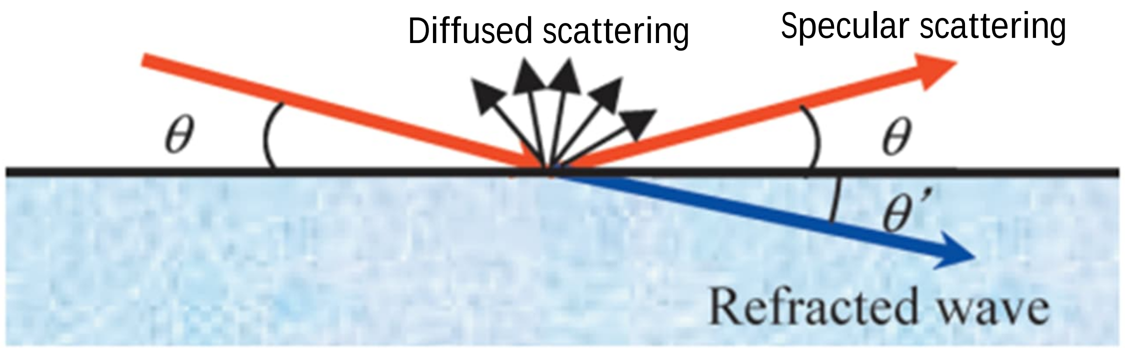
(3) Thin film + subs.

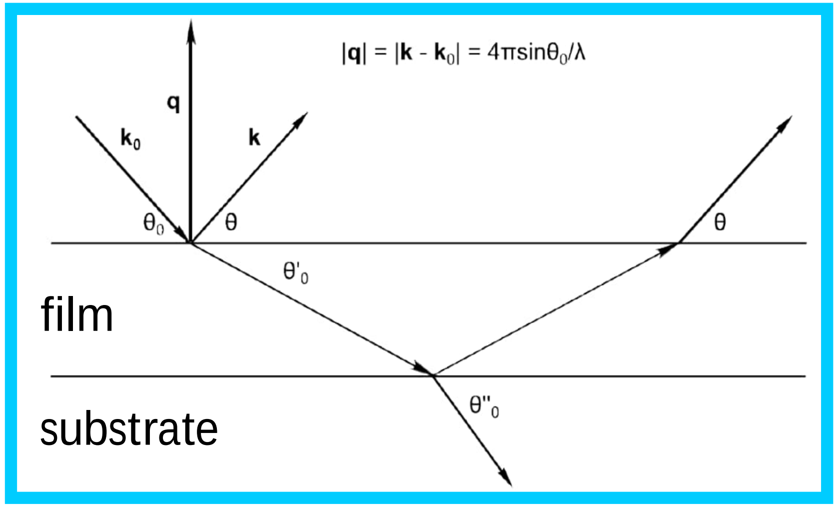
(4) Substrate

How θ & 2θ change in XRR measurement?



- **Incident angle = Reflected angle**
  - **specular (mirror-like) reflection**
- **No reflection 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 electron densities of the two materials**
  - **IN PRACTISE: intensity depends also on surface (or interface) roughness**
    - **We can use this!**





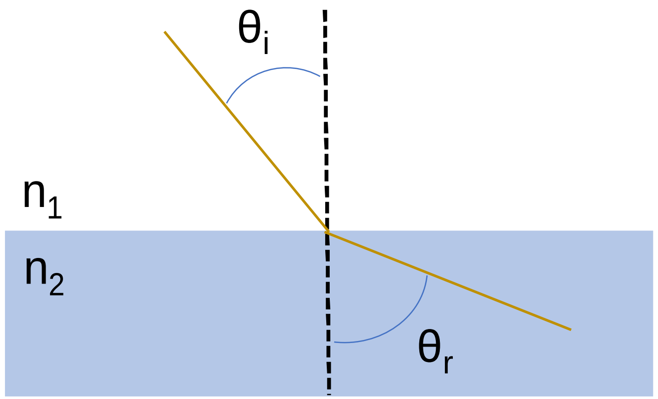
Refraction and total internal reflection

Refractive index n is slightly less than one for all materials

- n=1 for air

→ $n_1 > n_2$ → refracted x-ray bends away from surface normal

Snell-Descartes law: $n_1 \sin(\theta_i) = n_2 \sin(\theta_r)$ → $\sin(\theta_r) = \sin(\theta_i) * n_1/n_2$

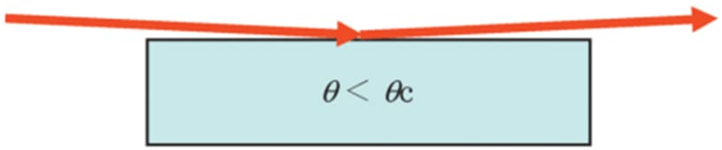


$$\theta_r = \sin^{-1}\left(\frac{n_1}{n_2} \times \sin(\theta_i)\right)$$

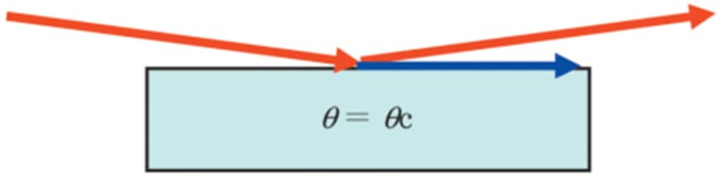
θ_c critical angle

if $\theta_i \le \theta_c$, total internal reflection occurs

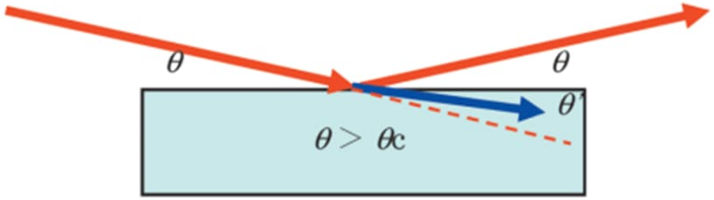
if $\theta_i \ge \theta_c$, refraction (transmittance) occurs



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

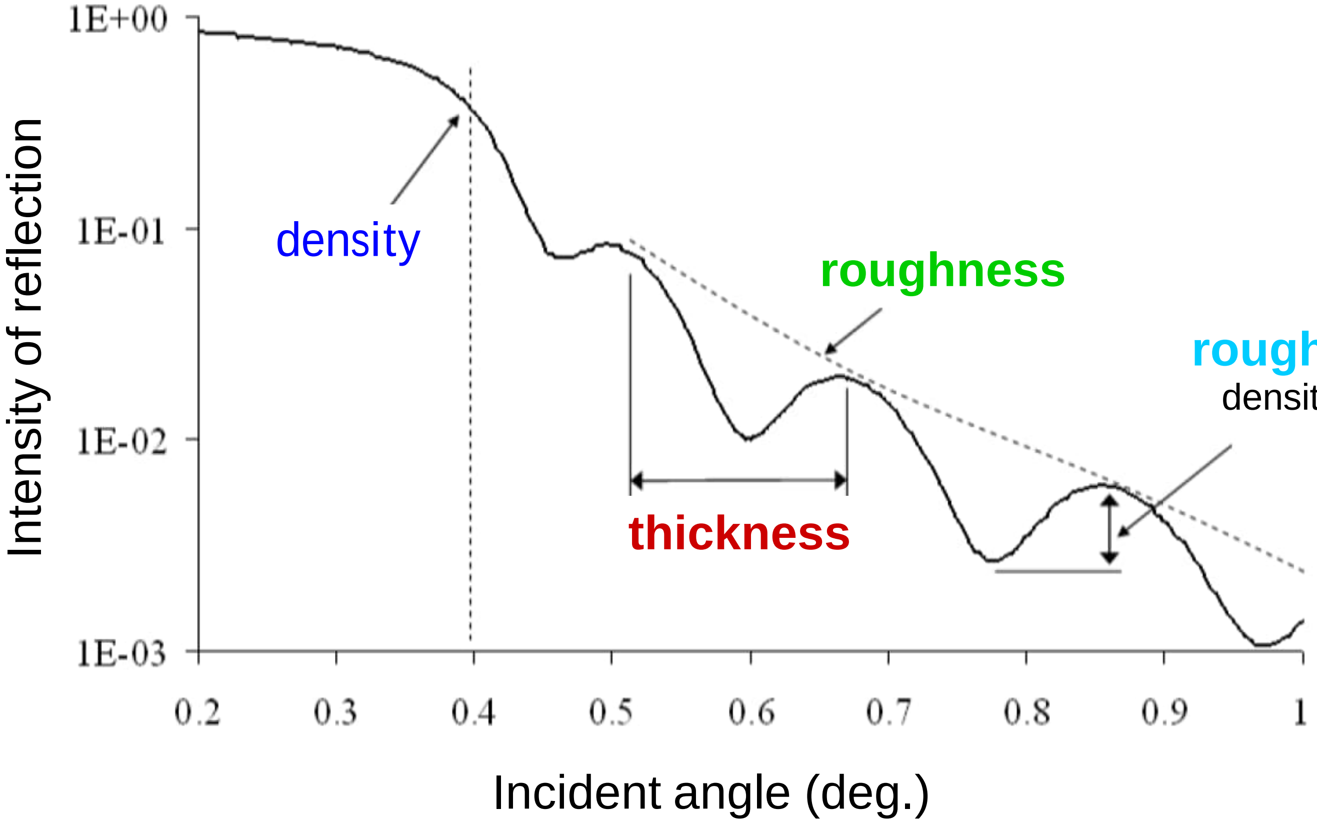


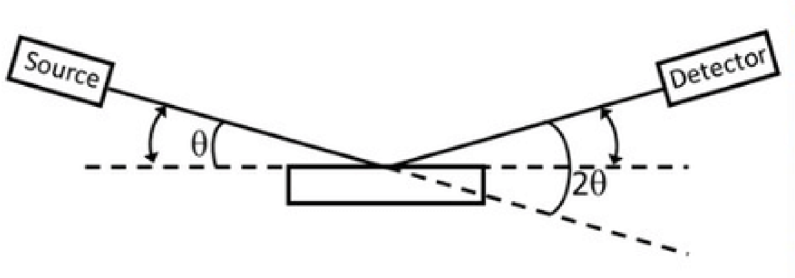
B) Incident angle = Total reflection critical angle
Incident X-rays propagate along the sample surface.

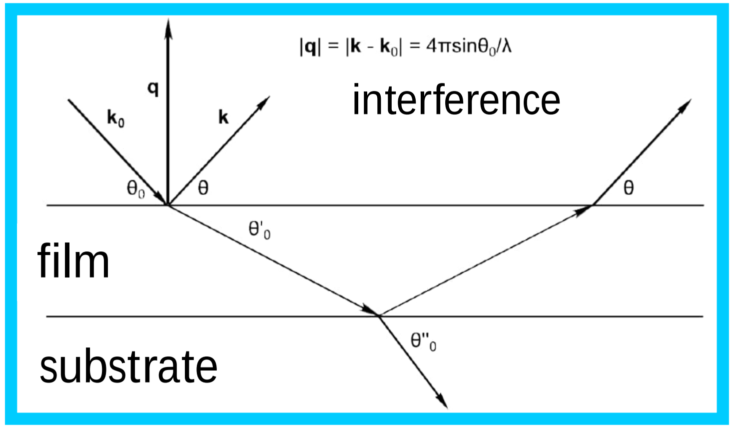


C) Incident angle > Total reflection critical angle
Incident X-rays penetrate into the material by refraction

Information from XRR data







- 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
  - Decay rate of intensity → (SURFACE) ROUGHNESS
  - Hight of Kiessig fringes → (INTERFACE) ROUGHNESS

Film Density

$$\theta_r = \sin^{-1}\left(\frac{n_1}{n_2} \times \sin(\theta_i)\right)$$

dispersion absorption

$$n = 1 - \delta - i\beta$$

$$\delta = \frac{r_e \lambda^2}{2\pi} \rho_{el}\,, \quad \beta = \lambda\mu/4\pi$$

$$\theta_c = \sqrt{2\delta}$$

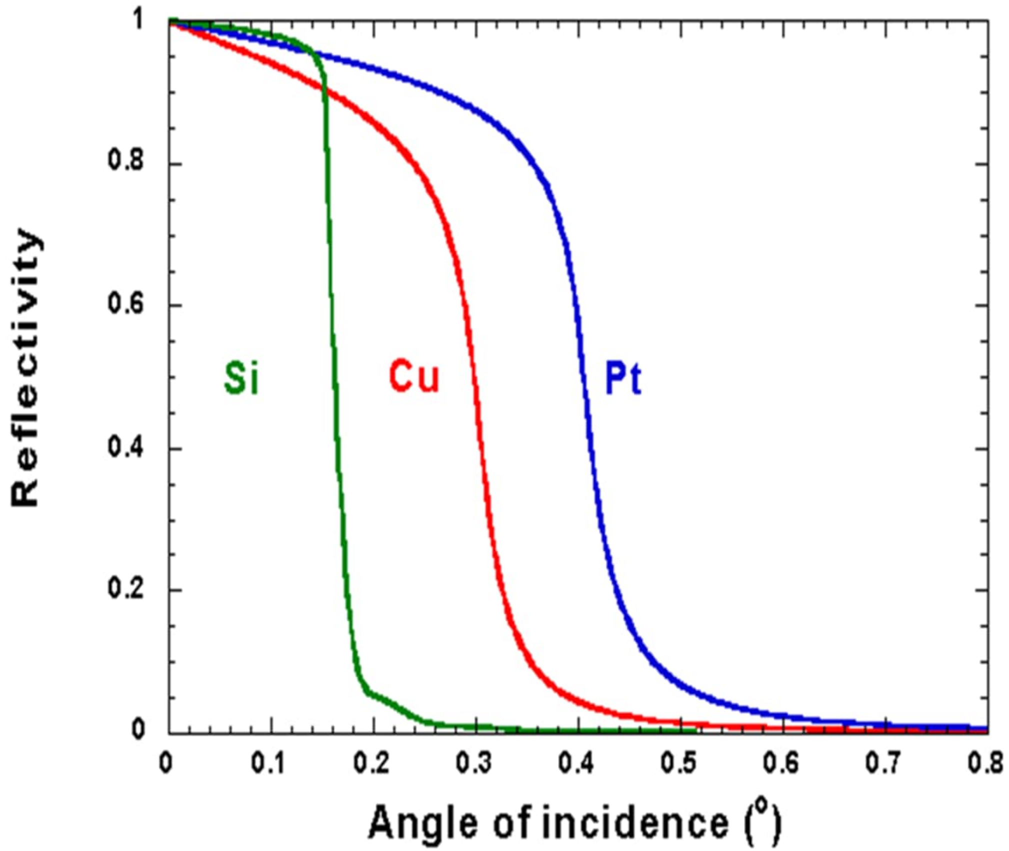
$$\rho_{el} = \frac{\Theta_C^2 \pi}{\lambda^2 r_{el}}$$

$$\rho_m = \frac{\rho_{el} A}{N_A Z}$$

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

$r_{el} = 2.82 \times 10^{-15}$ m

Higher the critical angle, higher the density!



Refractive index (n) depends on electron density

→ Θ_c depends on electron density

→ Θ_c is a material property!

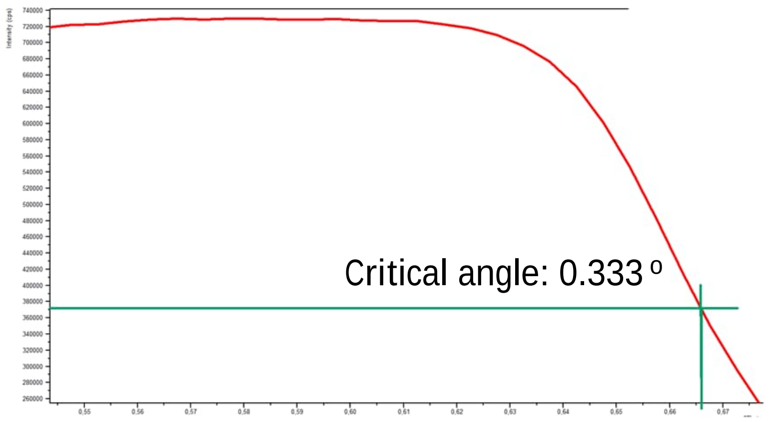
Additionally.....

Higher density contrast = stronger reflection

→ Amplitude of Kiessig fringes increases with increasing density (i.e. refractive index) difference

EXAMPLE: ZnO thin film

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



θ_c

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

ρ_{el}

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

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

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

ρ_m (bulk ZnO) = 5.61 g/cm^3

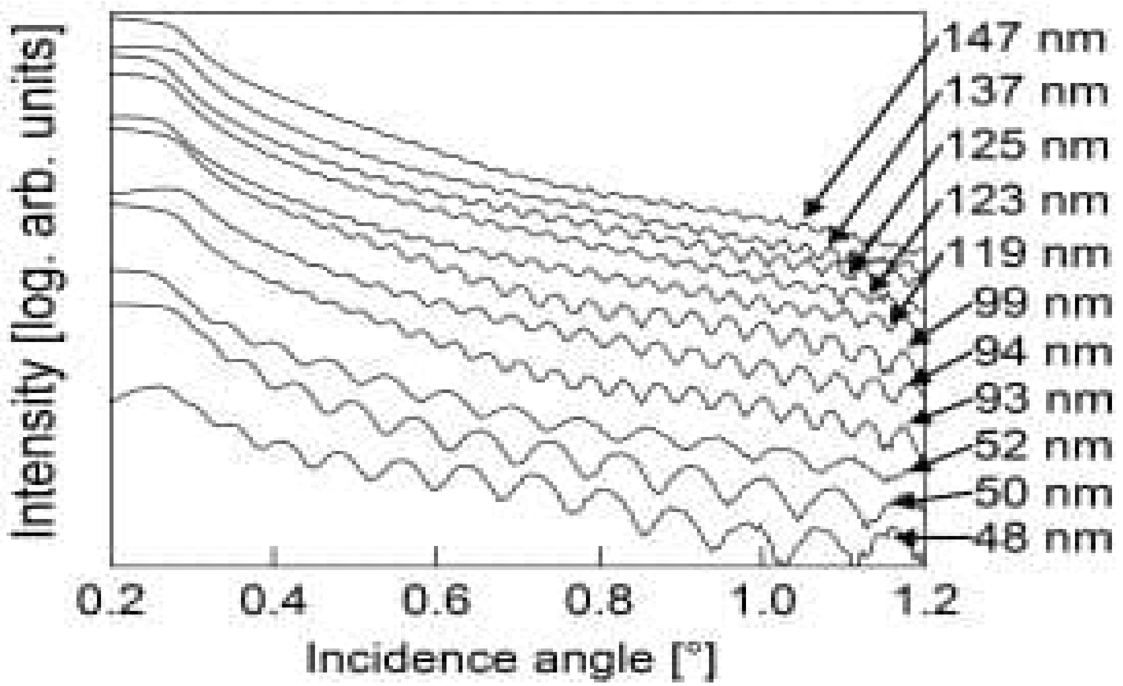
Film Thickness

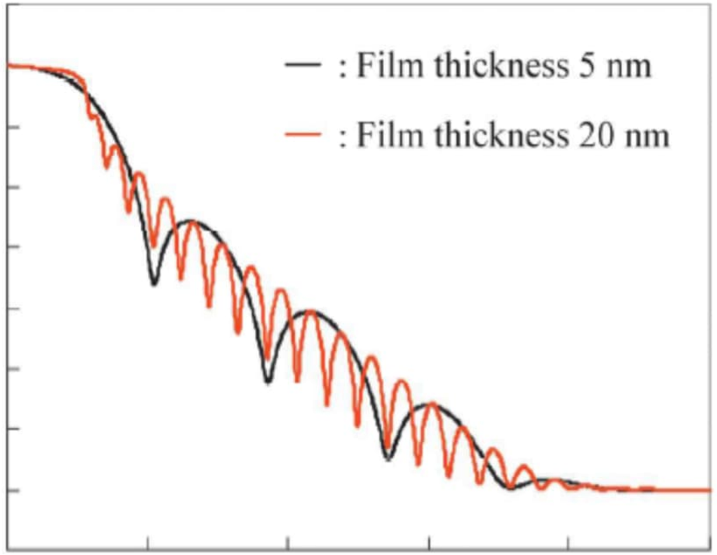
Larger the distance between fringes,
smaller the film thickness

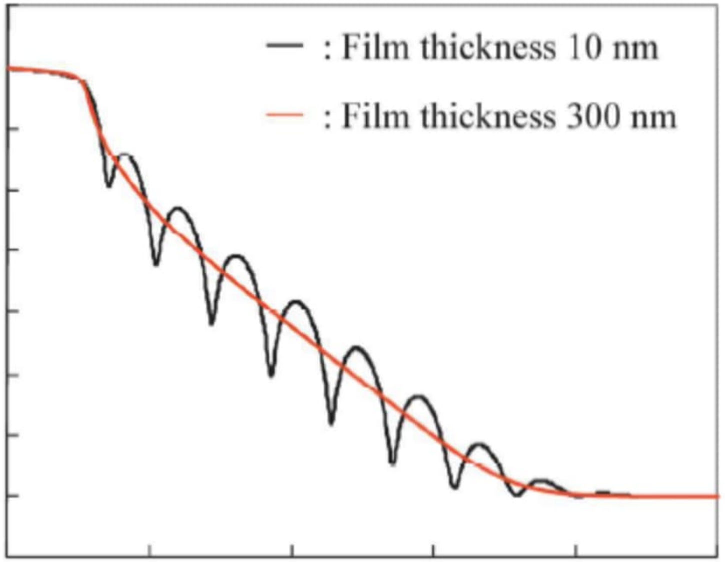
Measurable thickness range 1 – 200 nm

For rough, crystalline samples maximum thickness ~100 nm or slightly above
....The max limit can be increasing with proper optics

$(La,Sr)CoO_3$ ALD thin films

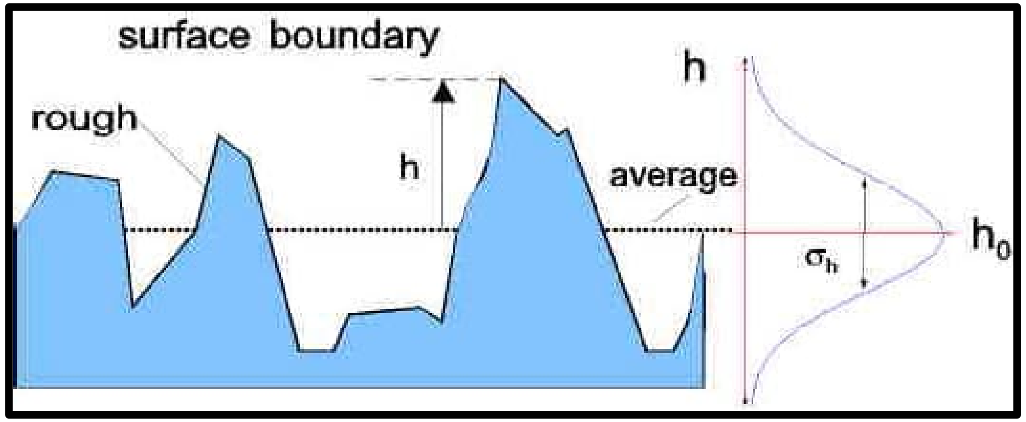


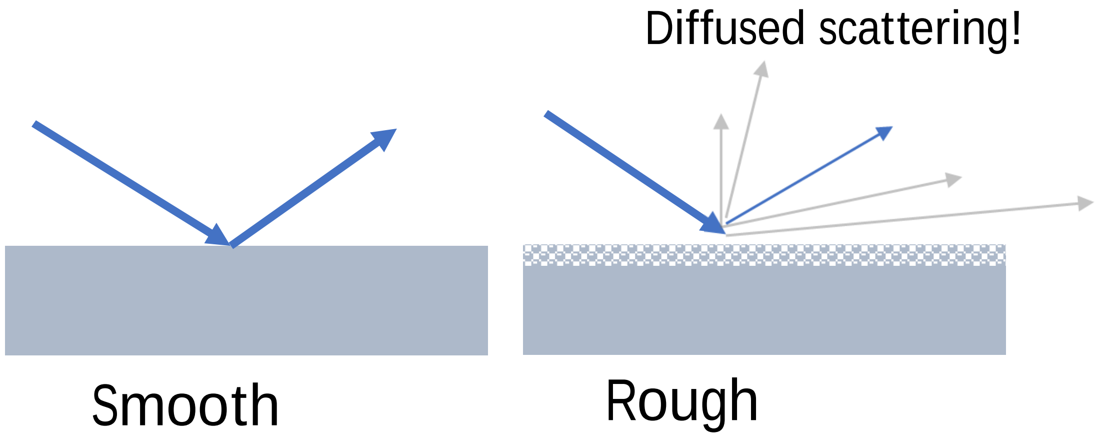




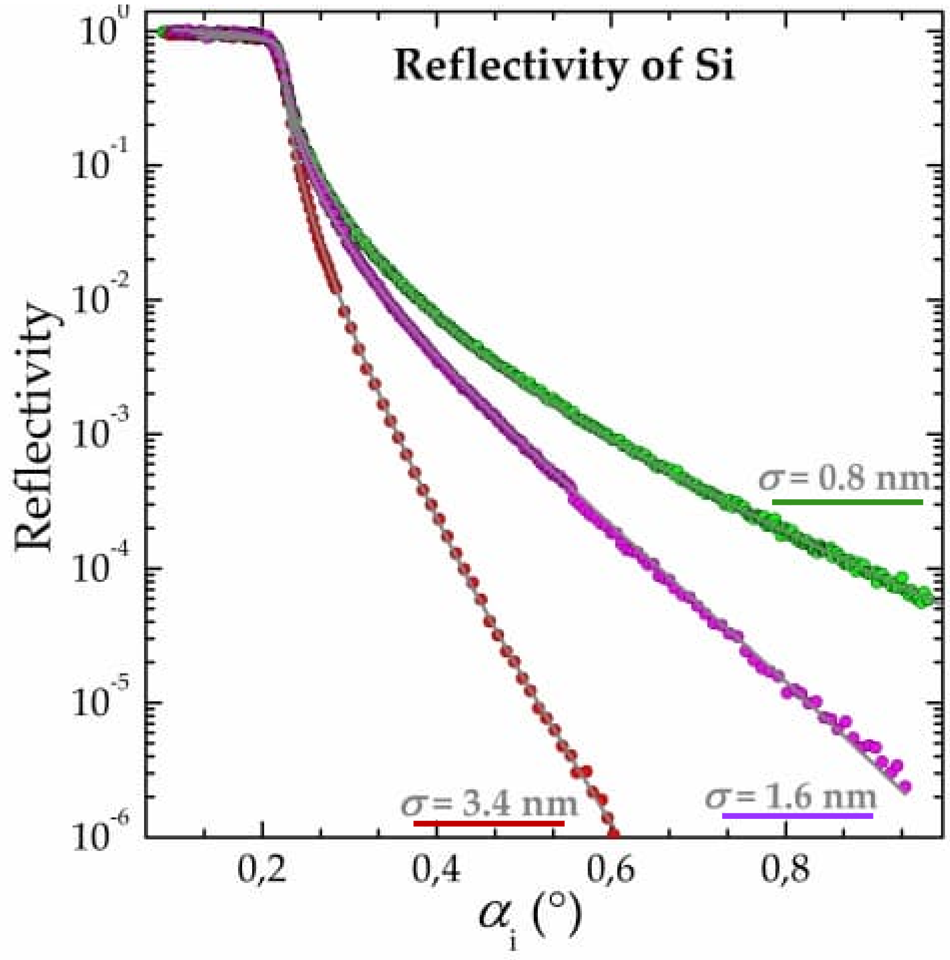
300 nm thick film is
too thick
for XRR

Surface roughness σ

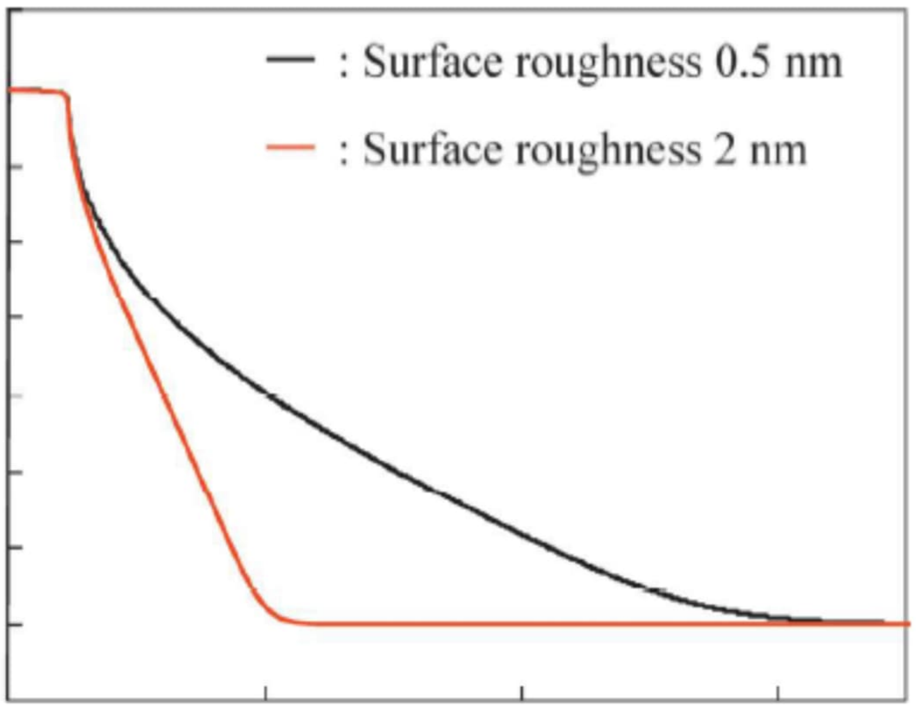




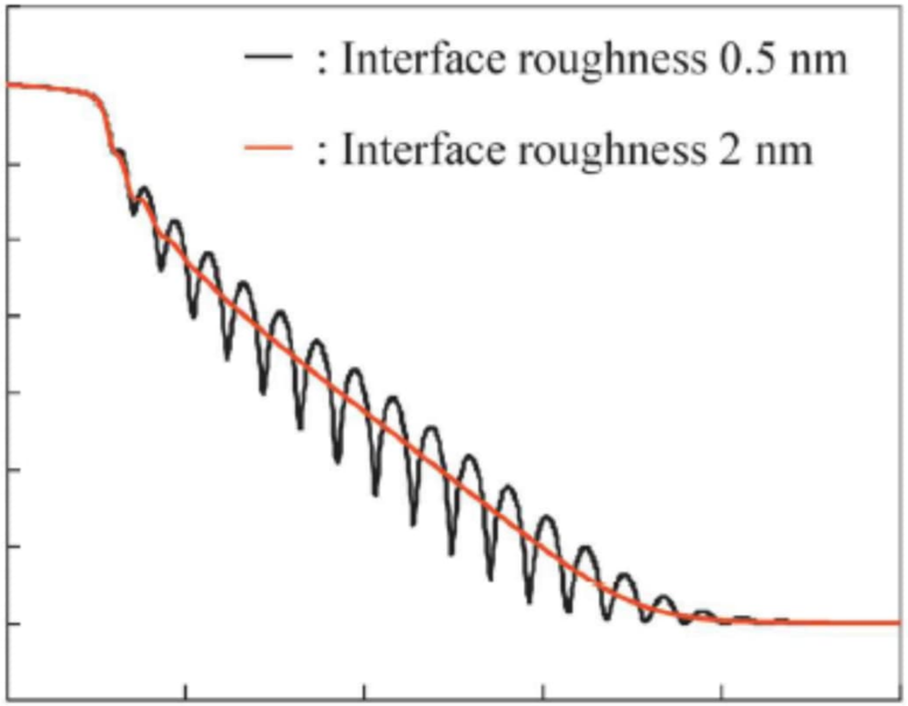
Rough surface causes intensity loss



Interface roughness

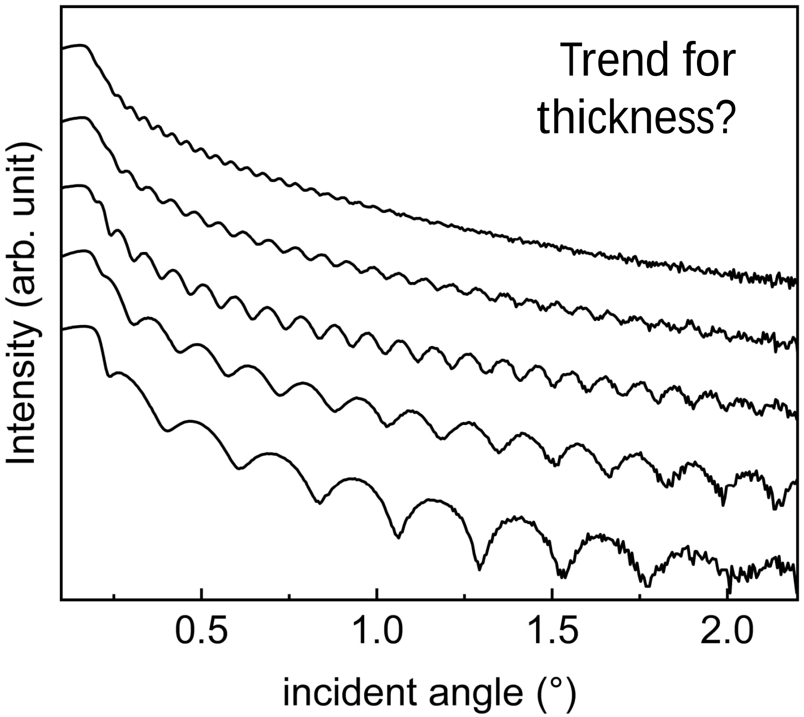


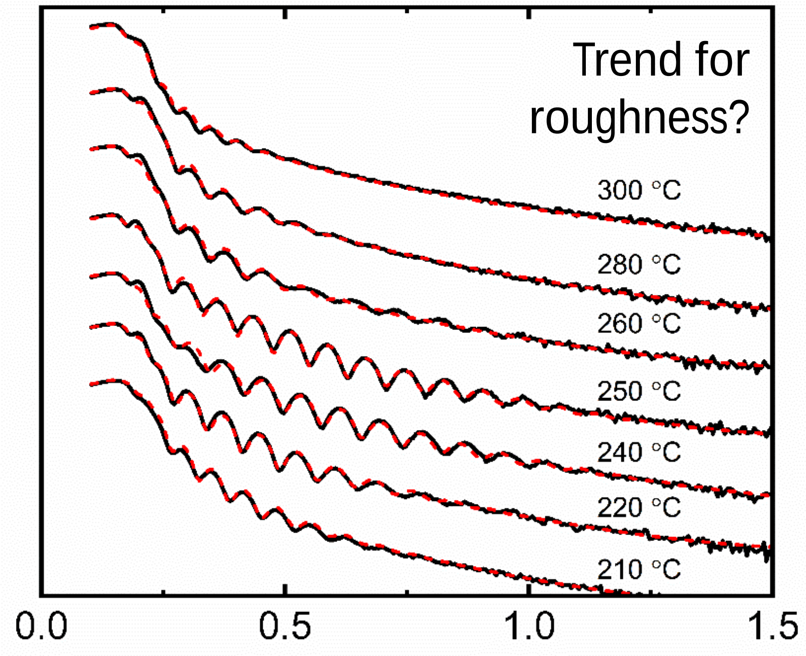
Surface roughness:
Total intensity drop

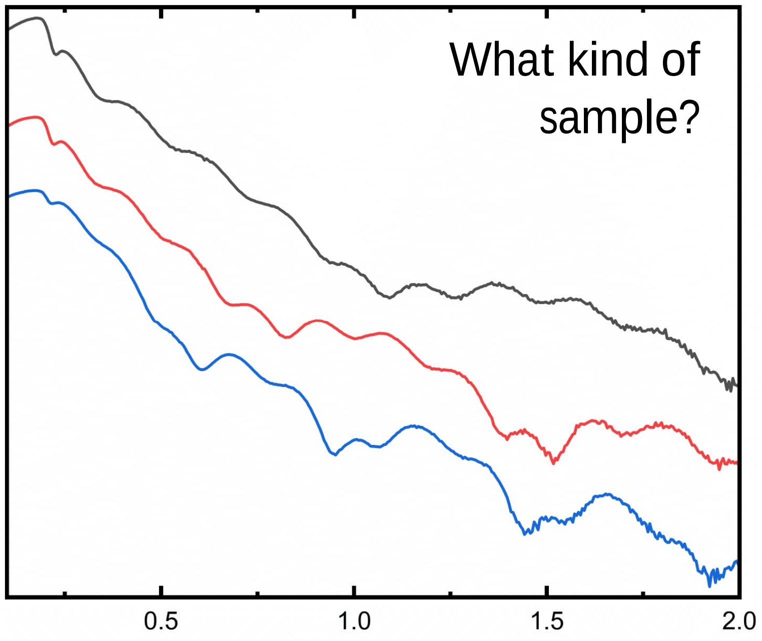


Interface roughness:
Oscillation amplitude drop
→ No clear film-substrate-interface for clean interference (oscillation)

Examples – qualitative interpretation



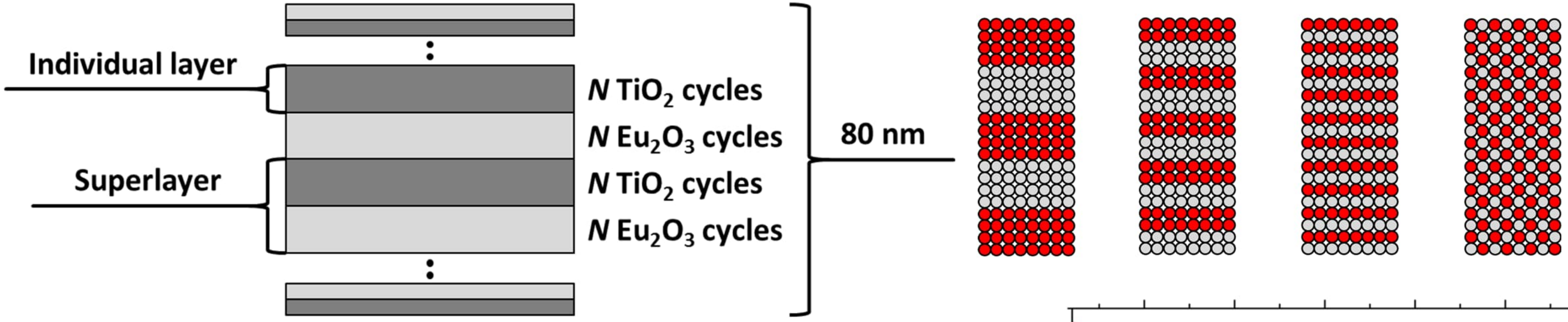


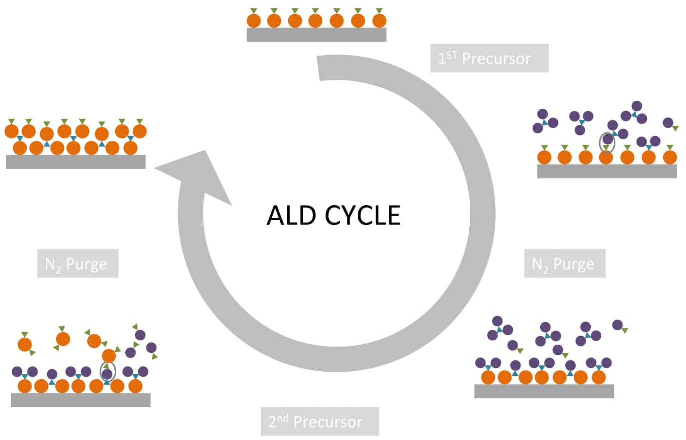


In the Exercise Session we evaluate XRR patterns qualitatively and perform simulations demos to get quantitative values

Superlattices → periodicity in XRR

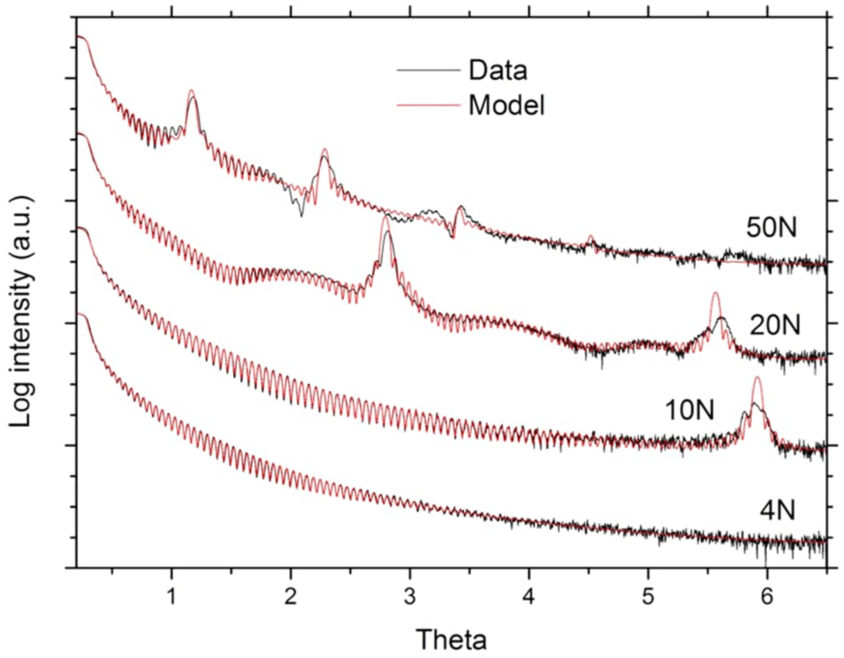
ALD-grown superlattice: Eu_2O_3 and TiO_2 layers grown on top of each other with different frequencies: in the XRR pattern you can see clear (more intense) superlattice peaks.





Superlayer thicknesses:

10N = 7.5 Å
20N = 15.9 Å
50N = 29.1 Å



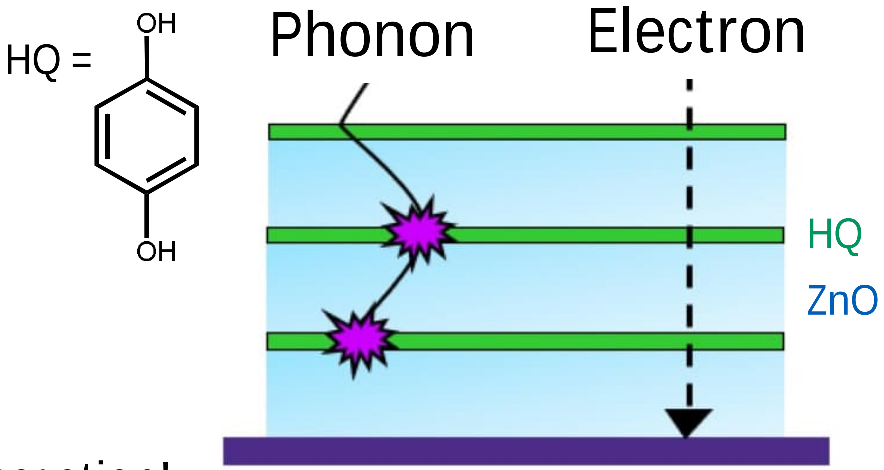
Flexible thermoelectric ZnO:organic

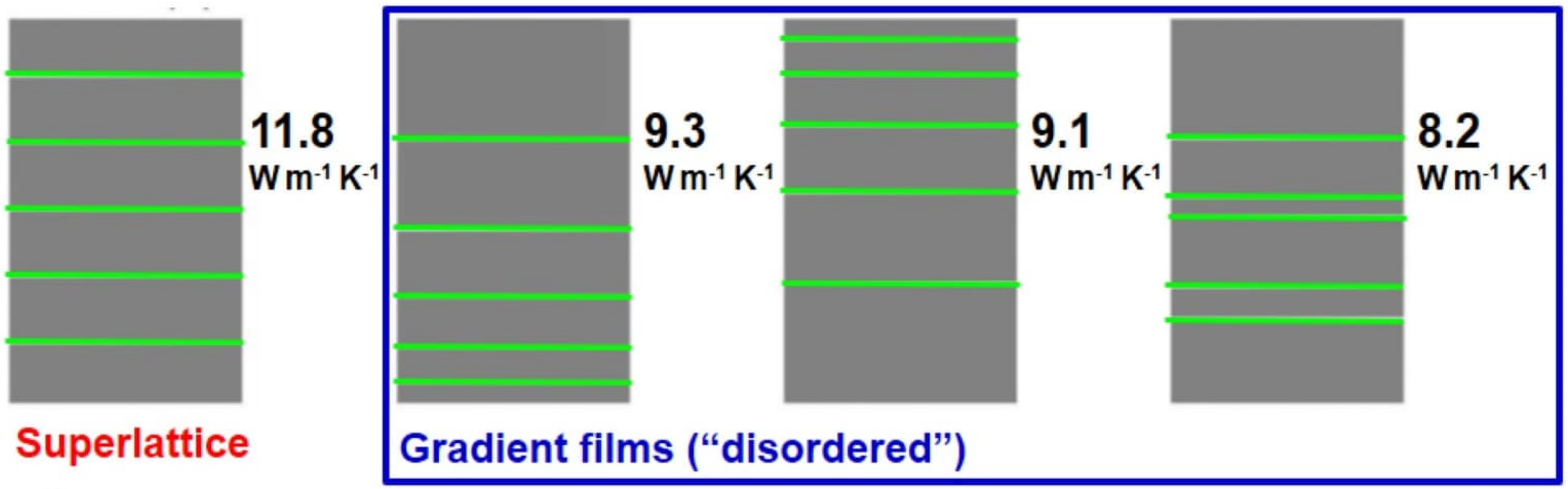
ALD/MLD technique enable arbitrary layer engineering → both periodic superlattices and disordered gradient films

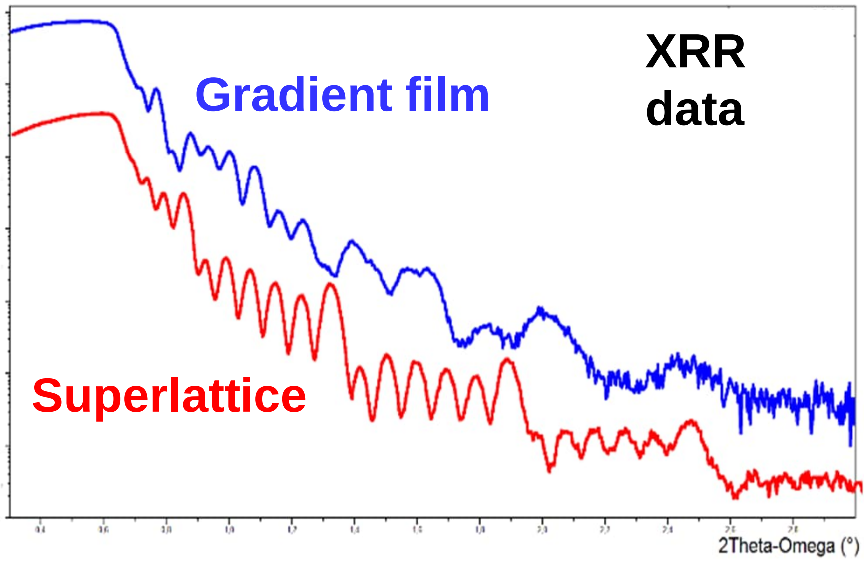
Thermoelectrics: High electrical, low thermal conductivity

ZnO relatively good thermoelectric material but high lattice thermal conductivity

ALD/MLD: Organic monomolecular layers added to hamper the phonon propagation!
XRR: visible SL peaks as an indication of the regular ordered SL structure



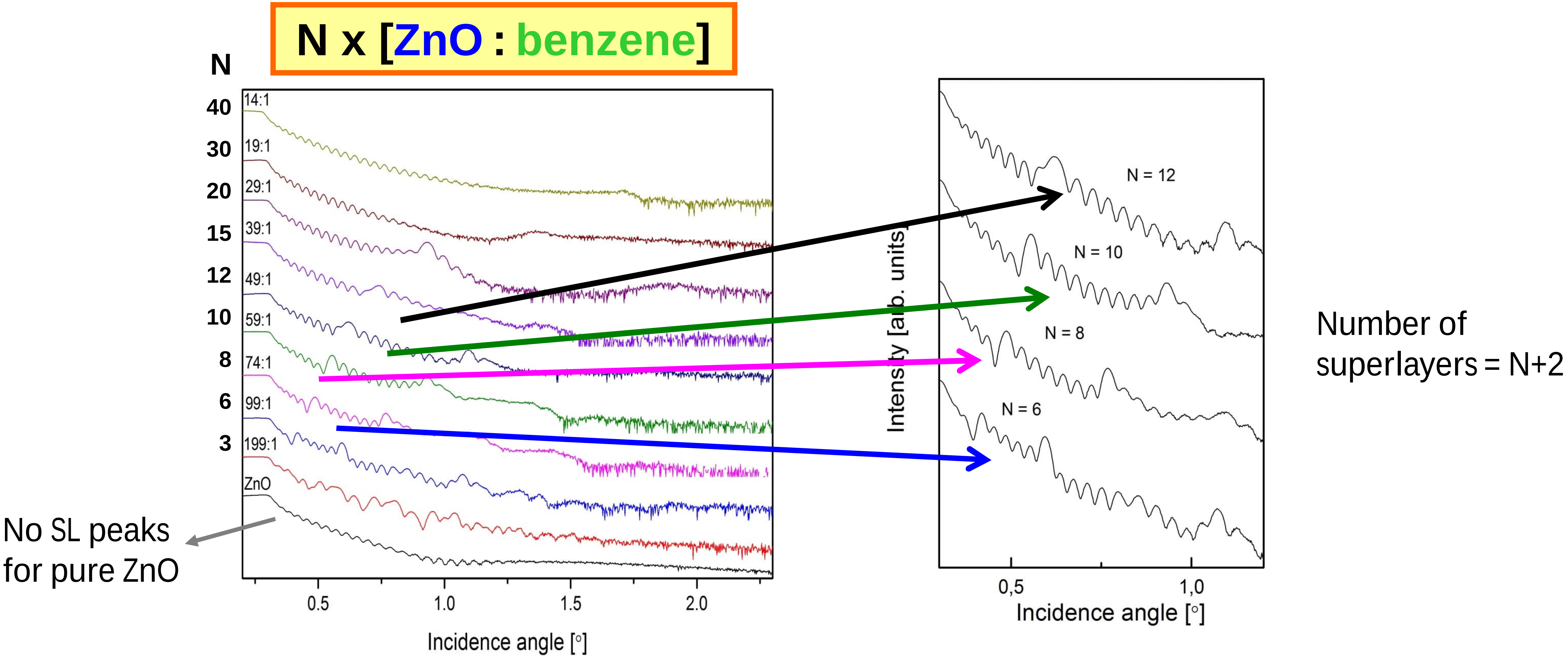




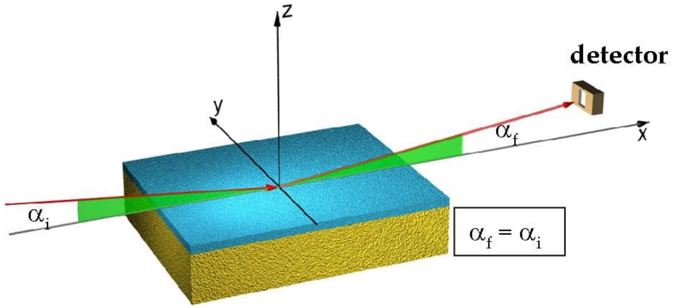
Krahl, F., Giri, A., Tomko, J. A., Tynell, T., Hopkins, P. E. and Karppinen, M. (2018), Adv. Mater. Interfaces, 5, 1701692.
Marin, G., Funahashi, R. and Karppinen, M. (2020), Adv. Eng. Mater., 22, 2000535.

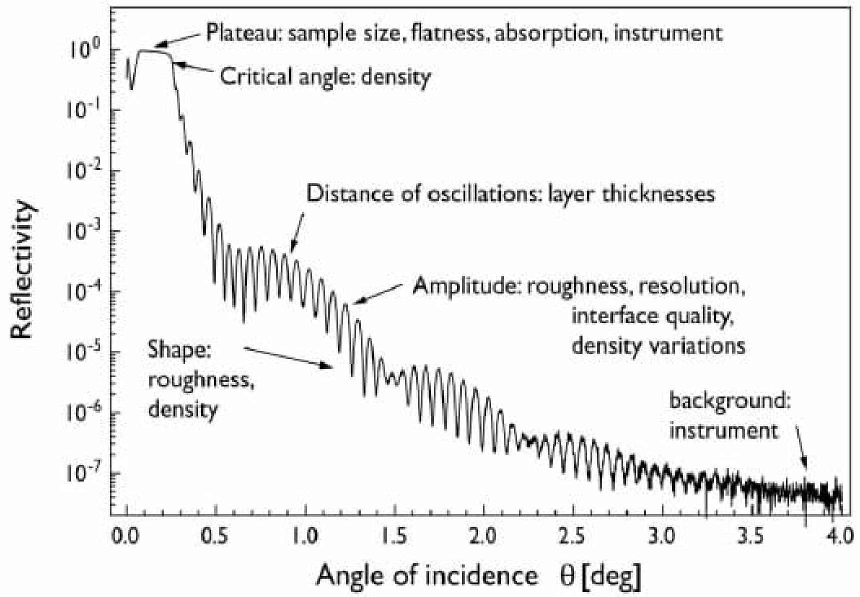
XRR:

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



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





XRR Measurement – Recap

- XRR devise similar (same) to XRD device but the optics are partly different
- INCIDENT ANGLE fixed to the SCATTERING ANGLE
  1) For $\theta_i \leq \theta_c$, sample surface reflects all X-rays (total internal reflection)
  2) When $\theta_i \geq \theta_c$, X-rays start to penetrate to the sample (top layer)
     - θ_c depends on density
  3) When the incident angle is further increased the intensity starts to oscillate (Kiessig fringes)
     - Film thickness, density contract
  4) Decay rate of oscillation amplitude and total intensity depend on interface and surface roughness
- Typical measurement range: few degrees

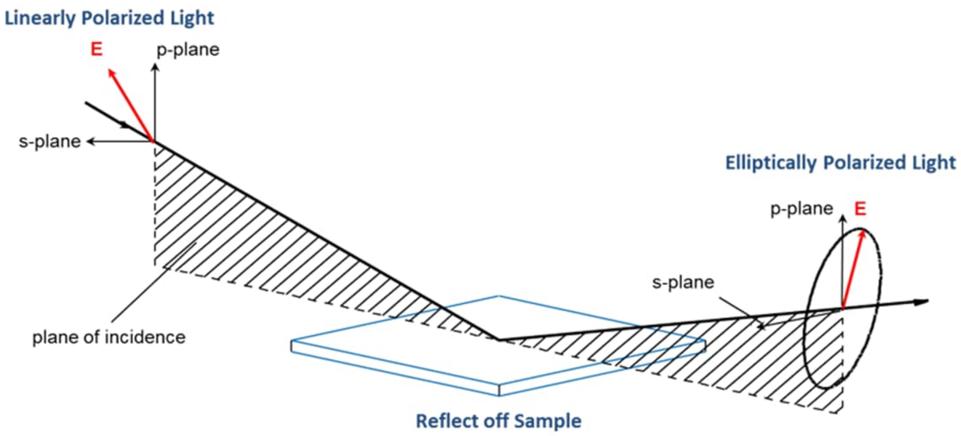
  (with higher angles the background noise level increases considerably)

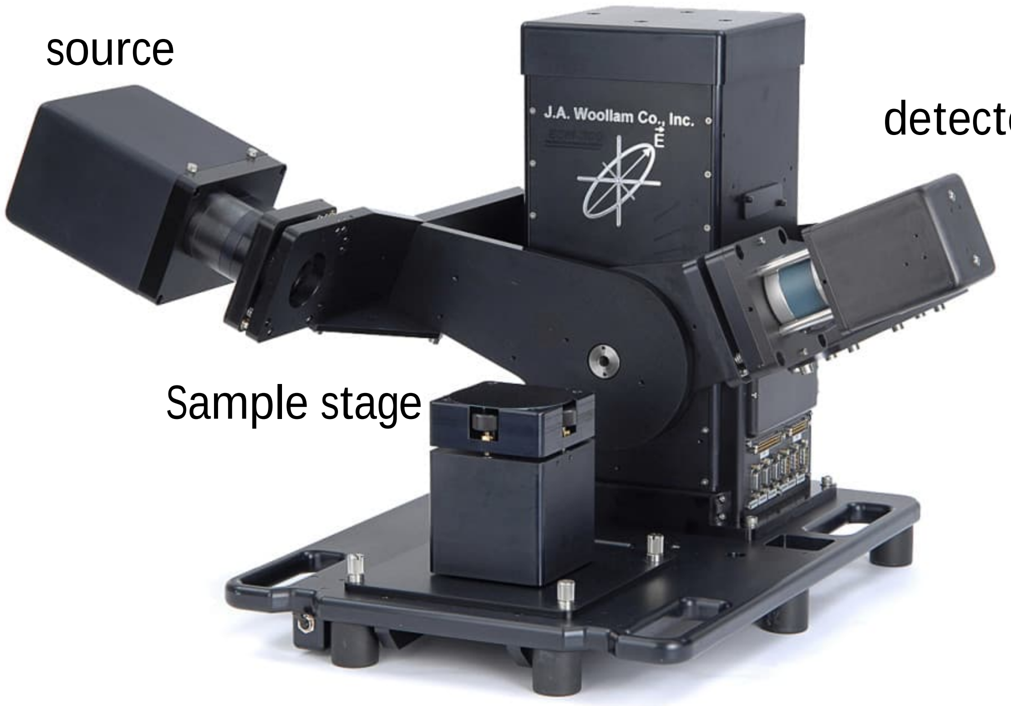
Major limitation of XRR is maximum film thickness (~200 nm)

Any alternative techniques?

Ellipsometer

- From ~1 nm to few µm





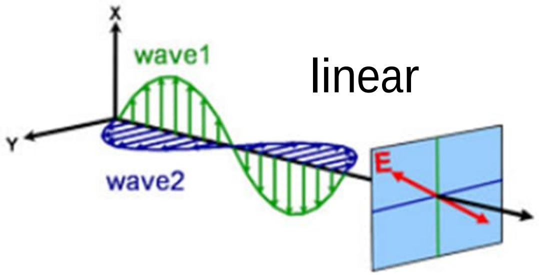
https://www.jawoollam.com/

Measures a chance in light polarization (amplitude & phase difference)

- Wavelength 200–1900 nm (near UV – visible light)

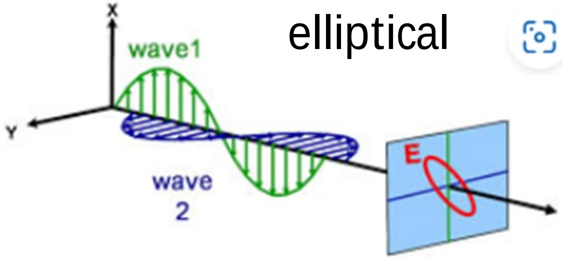
Incident light is linearly (s and p) polarized

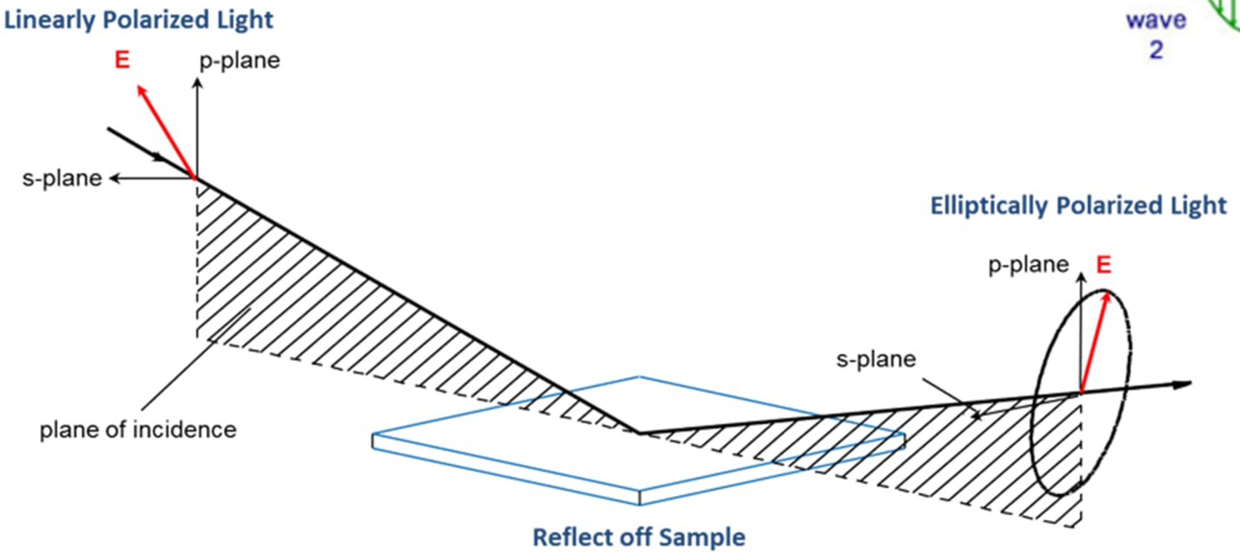
linear



Reflected light is (typically) elliptical
→ Change in polarization

elliptical





Phase difference of s and p plane and amplitude changes for reflected light

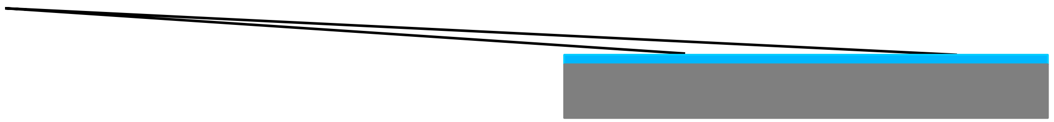
- The change depends on film thickness and optical properties of the material

→ Film thickness, optical properties (refractive index), roughness

Pros over XRR:

- Broad thickness range
- Optical constants
- Excellent mapping capability
    - Small beam diameter (high incident angles, different optics)

XRR: low incident angle → beam spread (~cm)



Cons over XRR:

- Output is not given directly and fitting of the data is often demanding
    - Optical properties of the material should be known
    - Complex model often needed
    - Difficult for new material research
- Does not provide mass density
- Limited to semi-opaque films

Ellipsometer: high incident angle → small beam diameter (~mm)