



**Ondes stationnaires et
diffraction de Kossel
pour l'étude des films minces**

IP²CT
FR2622



Philippe JONNARD

Equipe

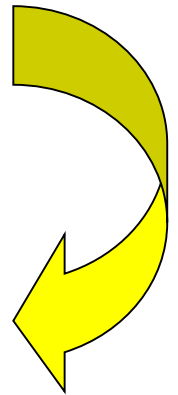
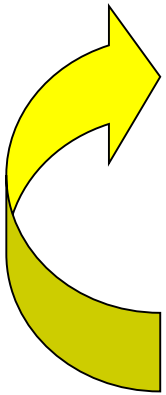
“Interfaces, Multimatériaux, Sources et Optiques X”

Topics

IMSOU team

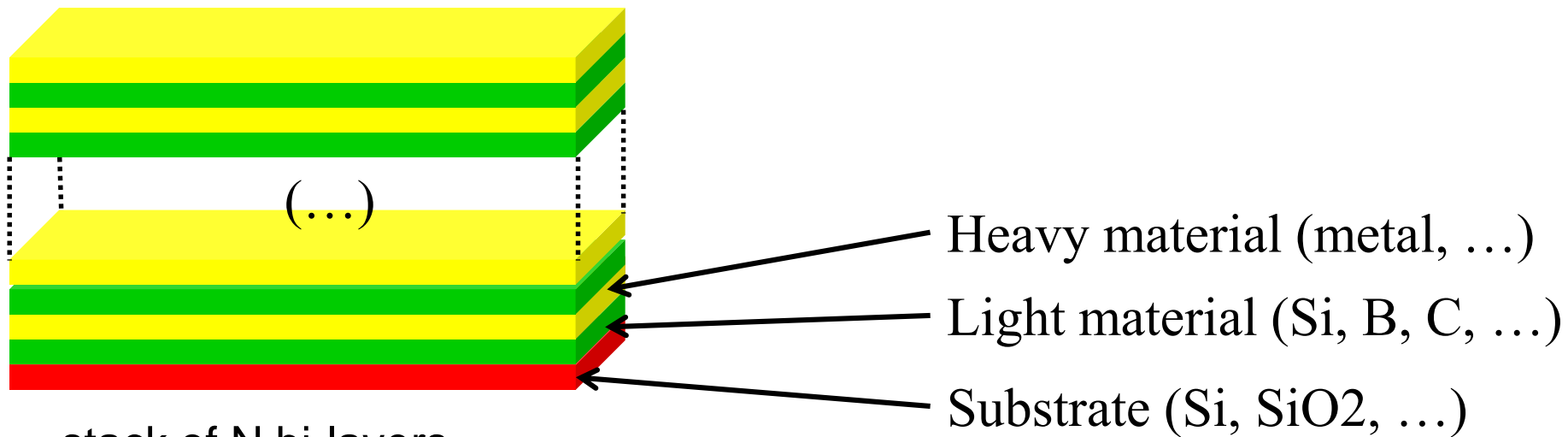
Characterization of
nanometric multimaterials
by x-ray spectroscopy and x-ray optics

Development of
spectroscopic and optical devices
for materials characterization



Periodic multilayers for EUV and X-ray ranges

Extreme UV : 20 – 200 eV 0.6 – 6 nm
Soft x-ray : 200 – 5000 eV 0.25 – 0.6 nm



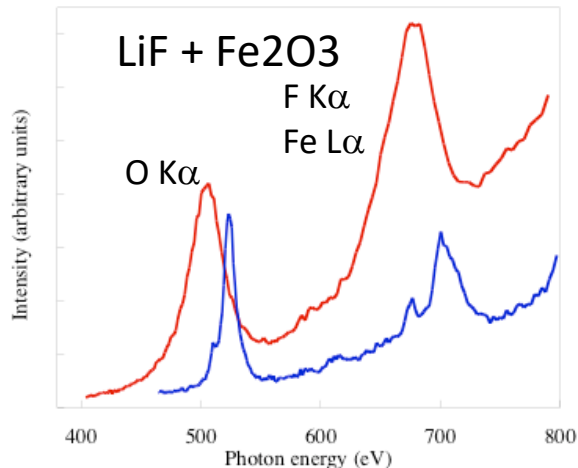
thickness_{light} + thickness_{heavy} = period d of a few nm

↳ can diffract EUV and x-rays

$$\text{Bragg law : } p\lambda = 2d \sin\theta$$

Applications of multilayers

- Solar images from spatial telescopes
- Photolithography @ 13.5 nm
- Optical components for synchrotron beamlines
- Optical components for new x-ray sources (x-ray laser, high harmonic generation, ...)
- Optics for diffraction apparatus



X-ray emission spectroscopy

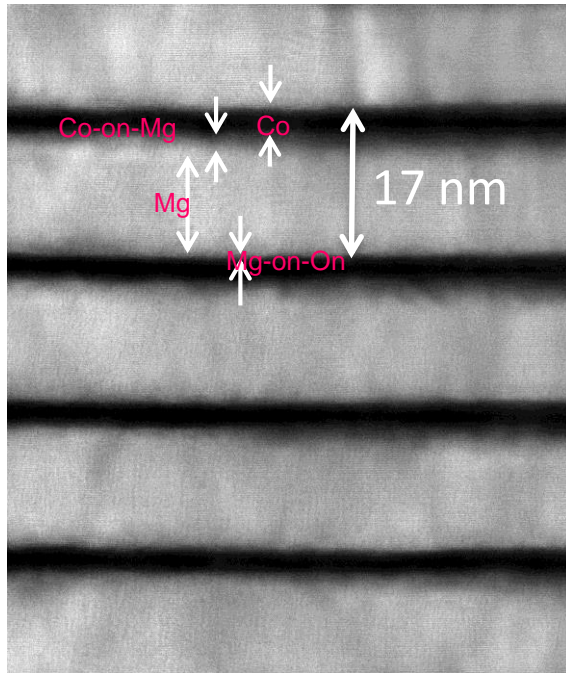


Imaging at a given wavelength

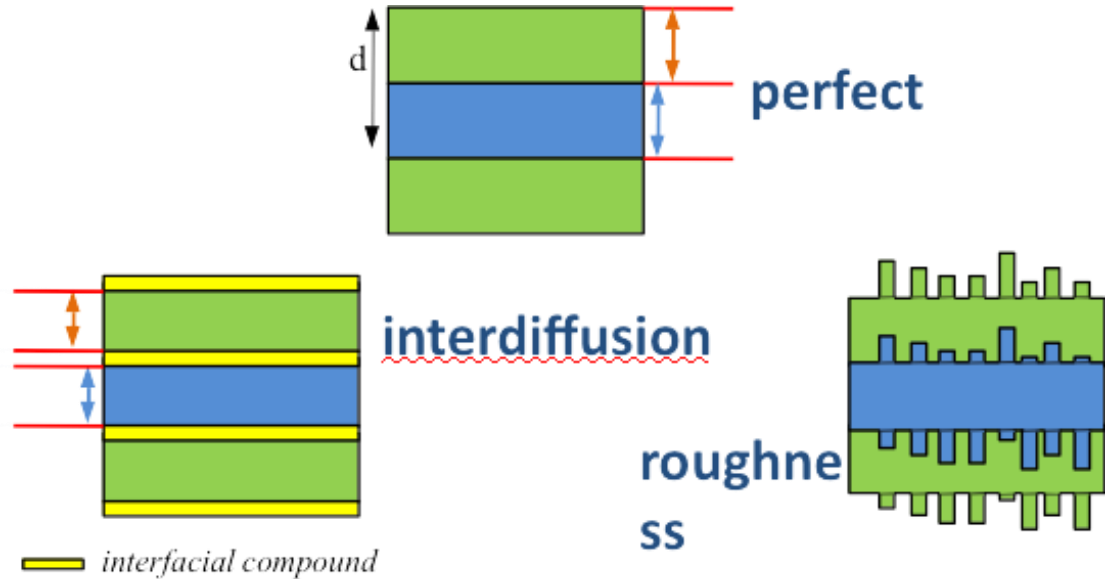


Photolithography
@ 13.5 nm, 6.x nm

Motivation and challenges



Co
Mg
Co
Mg
Co
Mg

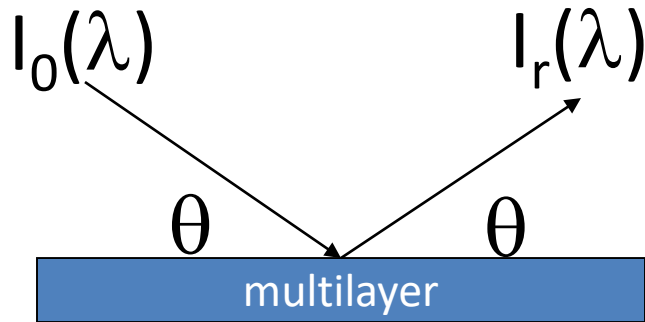


| | Visible $\lambda=500\text{nm}$ | EUV $\lambda=30.4\text{nm}$ |
|----------|-----------------------------------|--------------------------------|
| d | $\sim 125\text{nm}$ | Co_2.6nm/Mg_13.6nm |
| σ | $\sim 10\text{ nm}$ | $\sim 0.5\text{-}0.8\text{nm}$ |

R multiplied by **DW factor**
 $\exp(-2[2\pi\sigma \sin\theta / \lambda]^2)$

Interface is the largest challenge for EUV multilayer!

X-ray reflectivity



$$R(\theta) = I_r(\lambda) / I_0(\lambda)$$

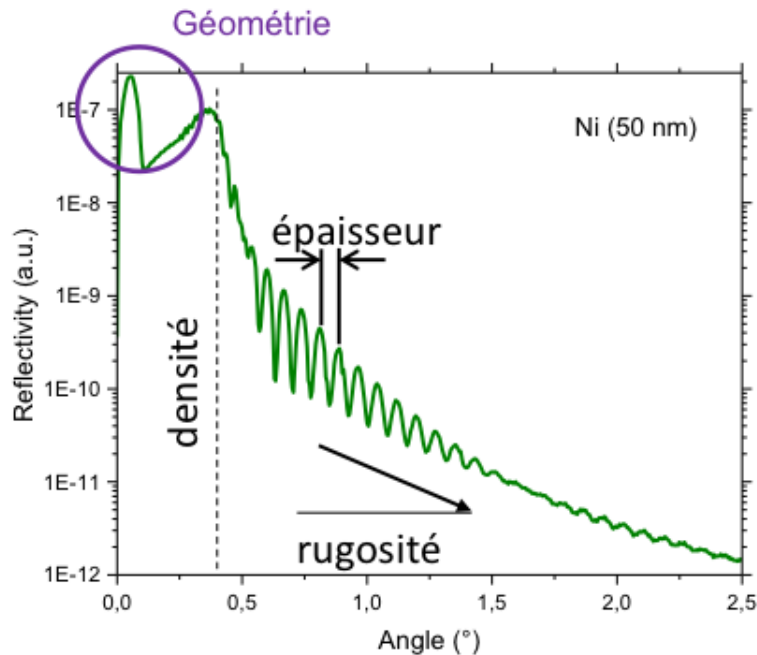
$$R(\lambda) = I_r(\theta) / I_0(\theta)$$

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

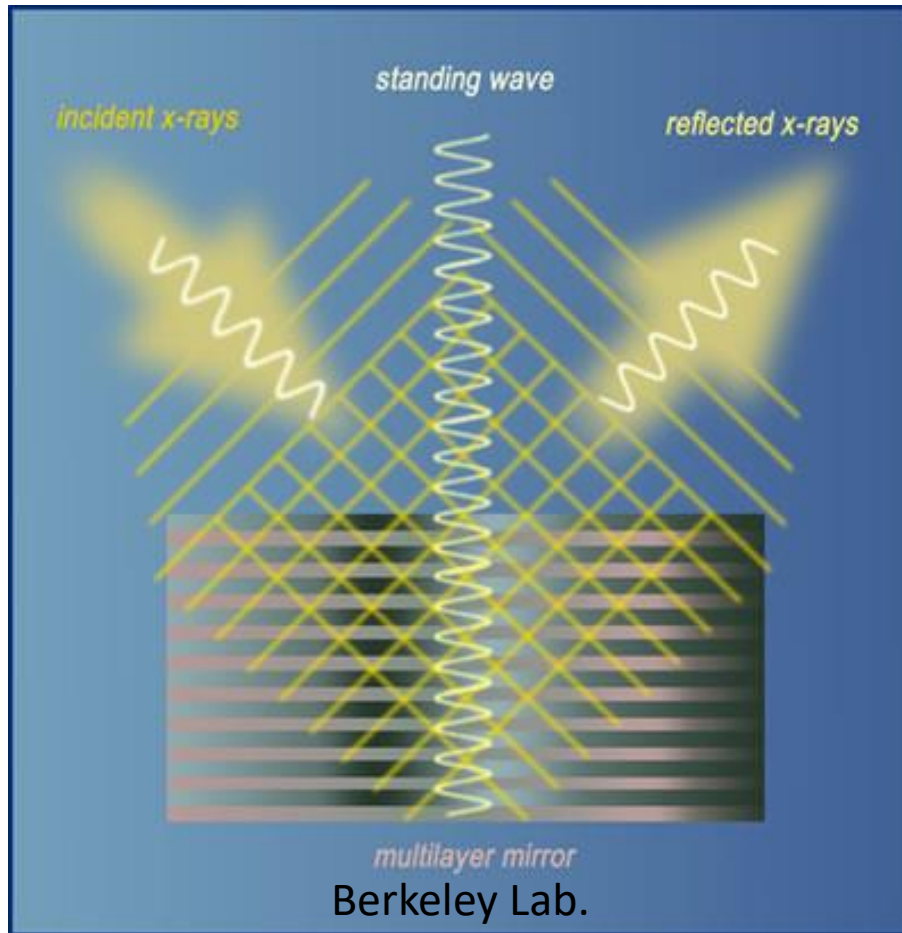
Bragg law

Determination of parameters
of the stack

- thickness
- roughness
- density / optical index
of the various layers



X-ray standing waves



In (or close to) **Bragg conditions**

- a strong standing wave develops inside and outside the multilayer
- having the period of the multilayer

Generally used

- In **hard** x-ray range
- In **glancing incidence**
- With crystal or
- With multilayer (set of **bilayers**)

To probe

- thin layer on **top of the multilayer**
- **Interfaces of the multilayer** itself

By using

- Fluorescence or photoelectrons

What we do

- In **soft** x-ray range
- In **glancing incidence and exit**
- With multilayer (set of **bilayers or trilayers**)

To probe

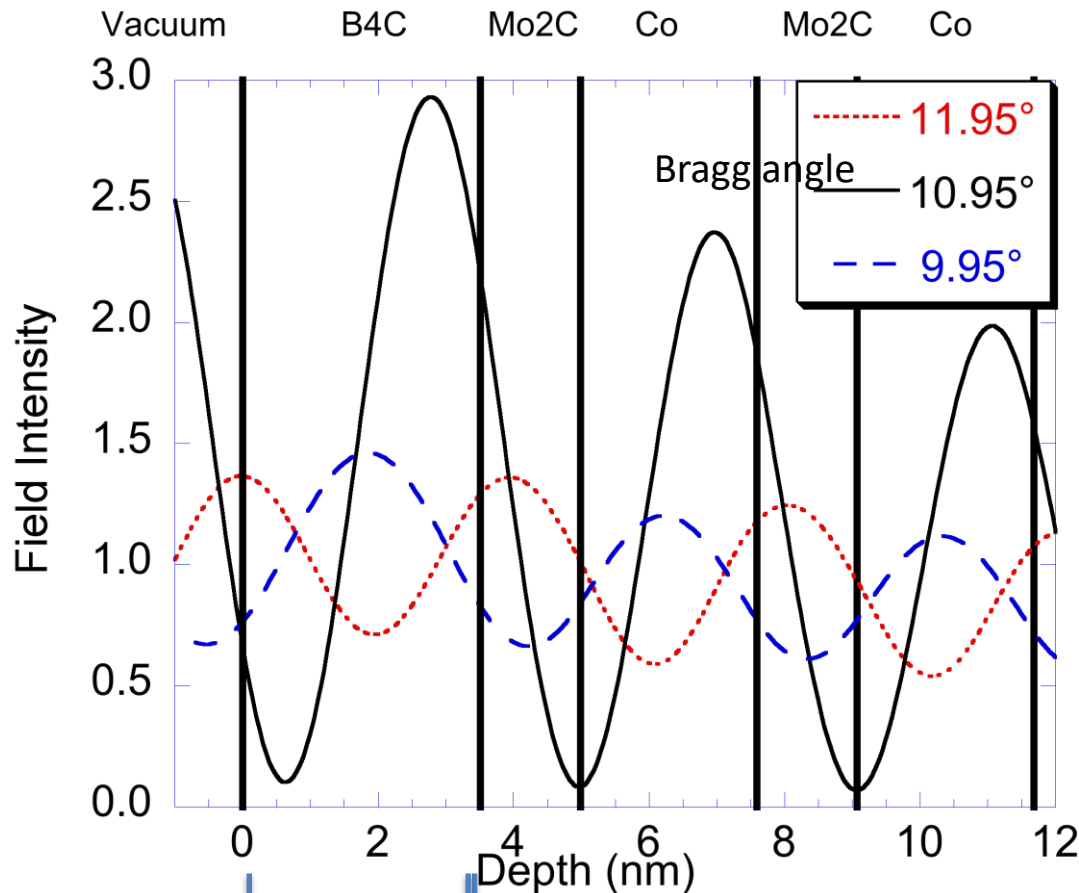
- **Interfaces of the multilayer itself**

By using

- **X-ray fluorescence**

X-ray standing waves

Depth distribution of the electric field



Rotate sample
(change the wavelength)
Change incident or detection angle
↓
Shift of the nodes and anti-nodes

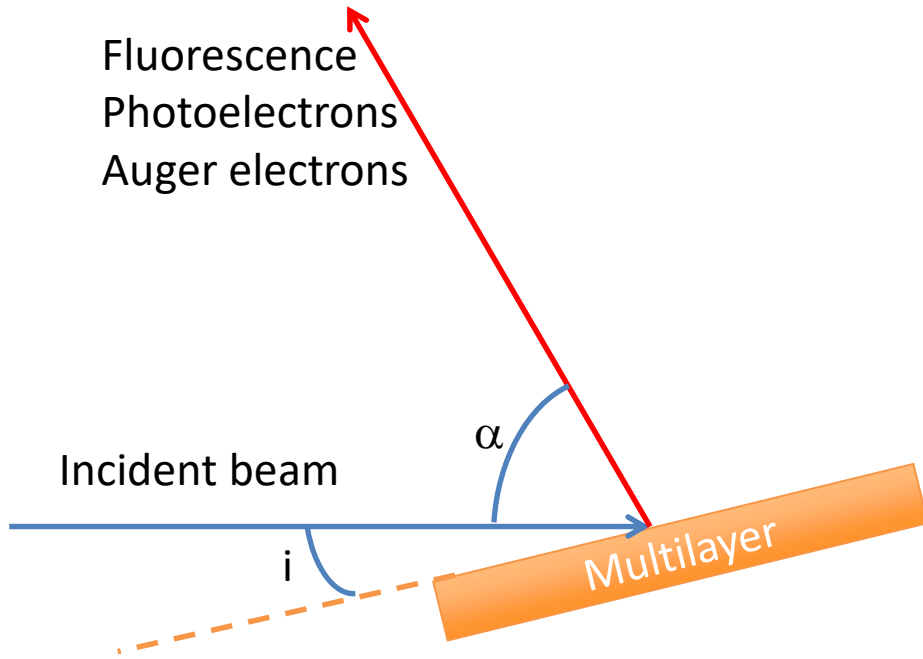
Analysis by

- XPS
- XRF
- AES

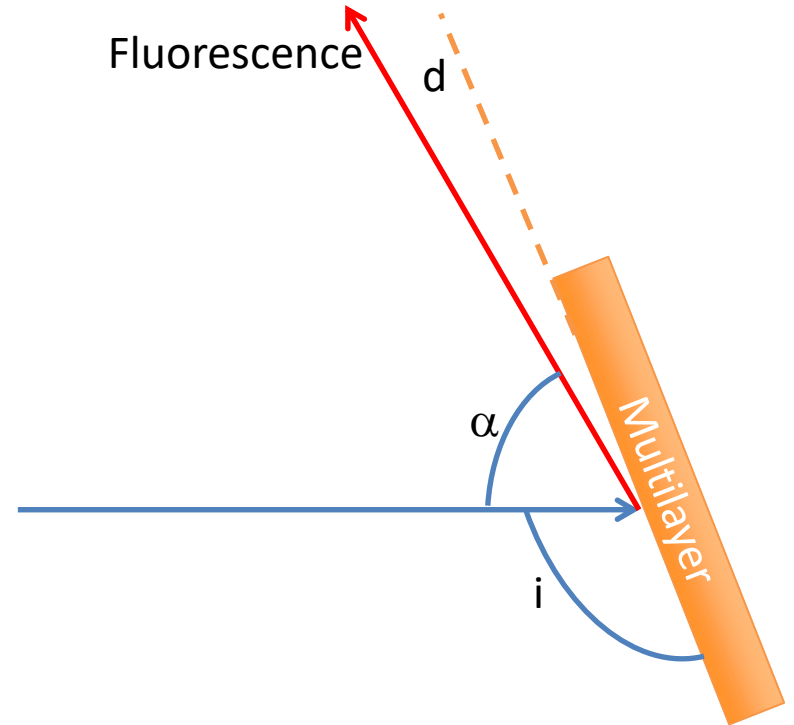
of a

- Multilayer
- Superficial material

Two XSW modes

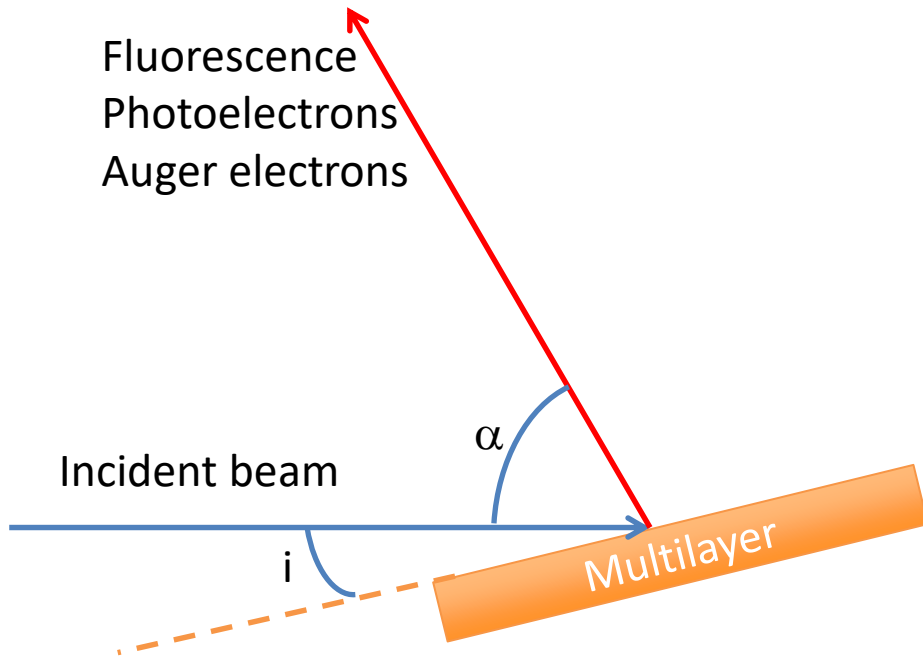


Glancing incidence mode
"Standard" or GI



Glancing exit mode
"Kossel" or GE

Two XSW modes



Glancing incidence mode

“Standard” or GI

Incident beam = x-ray beam

Requires synchrotron

x-ray tube

Geometry to be fulfilled

Generally very grazing

Detected beam

No special geometry requirement

Large solid angle of detection possible

Two XSW modes

Incident beam = any ionizing beam

X-rays

Electrons

Ions

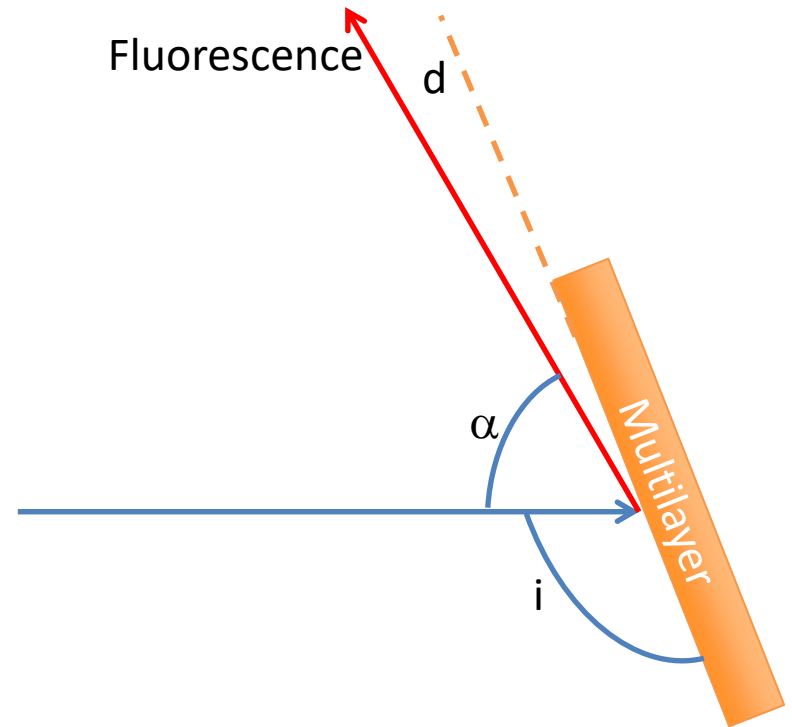
No geometry requirement

**Detected beam =
characteristic x-rays**

Geometry requirement

Generally very grazing

Small solid angle of detection



Glancing exit mode

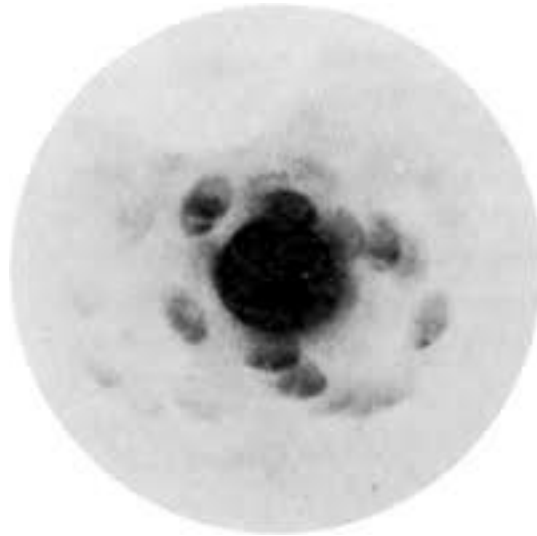
“Kossel” or GE

A bit of history



M. Von Laue

Nobel prize 1914 for his discovery of the x-ray diffraction by crystals



First x-ray diffraction pattern

Hydrated copper sulfate

P1 triclinic

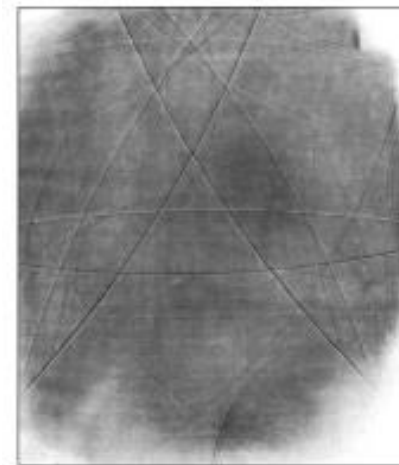
1912: von Laue, Friedrich, Knipping



W. Kossel

1935

Diffraction of the fluorescence produced within the crystal by the crystal itself



Multilayer

Si substrate /

[Mg (5.1nm) / Co (2.6nm)]x30 /

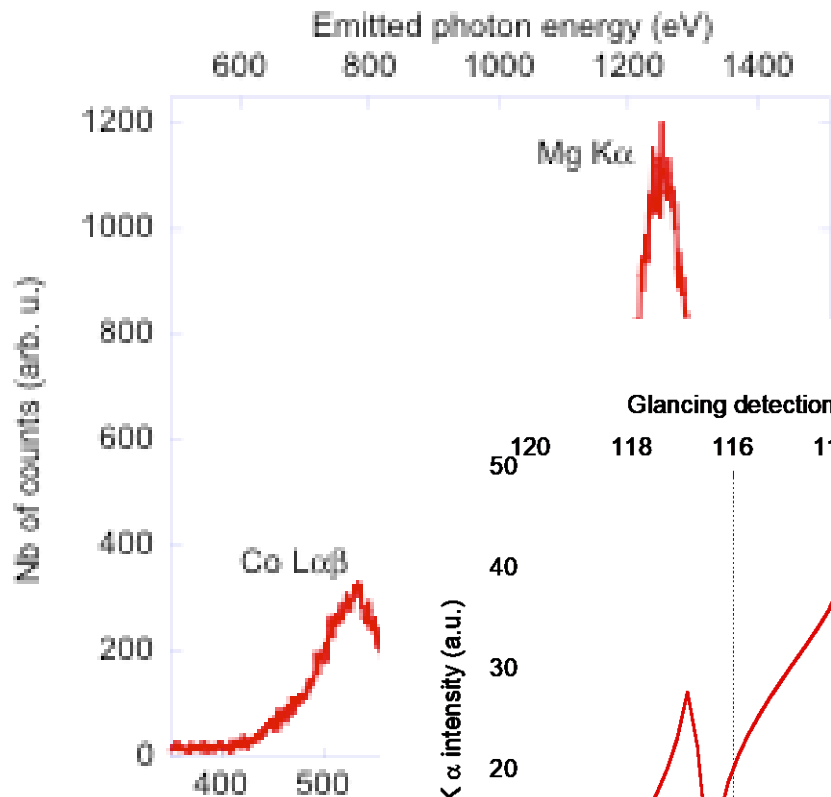
B4C (3.5nm) capping layer

Mg/Co XSW - XRF

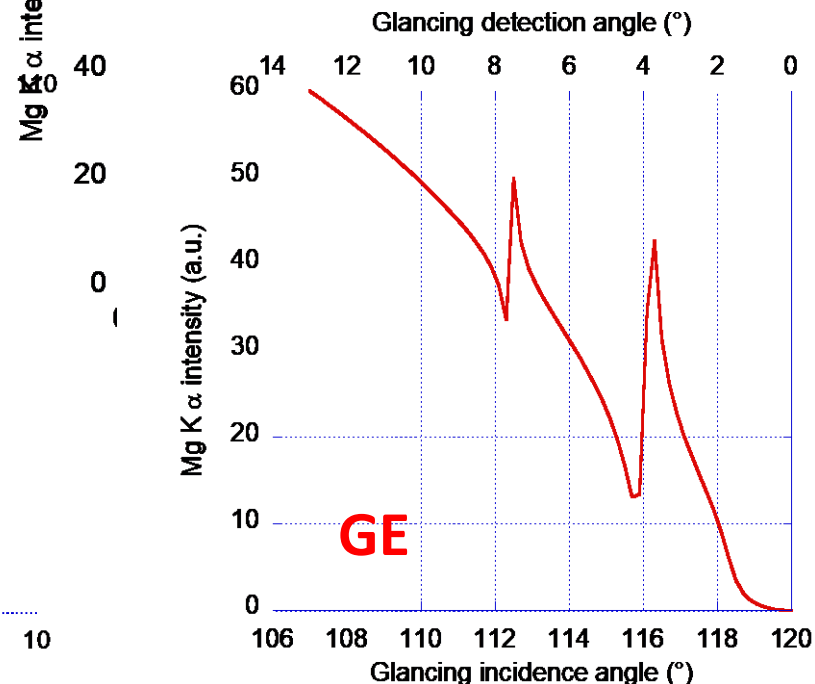
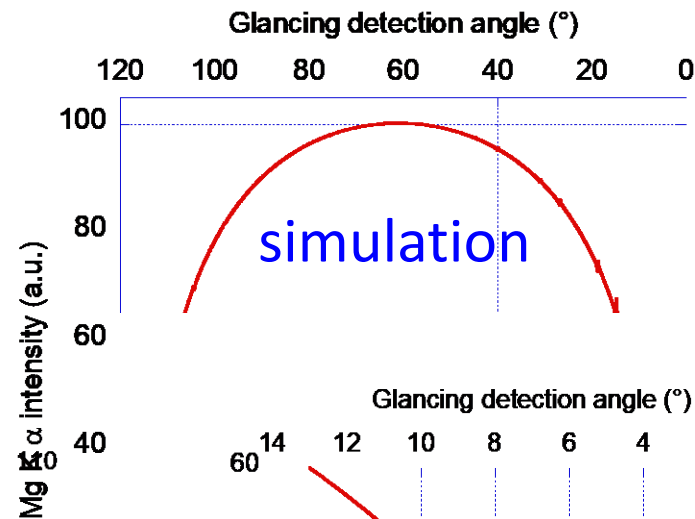
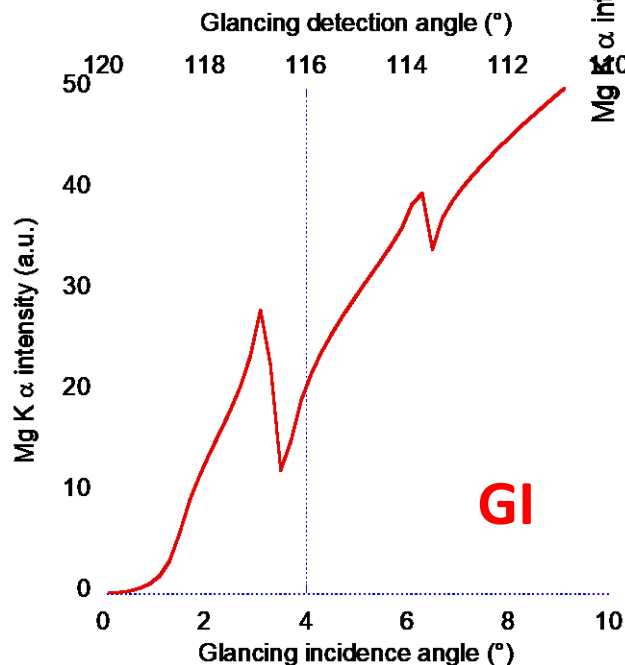
Incident radiation 1500eV; 0.827nm

Mg K α emission 1253.6eV; 0.989nm

60° between incident and detection directions



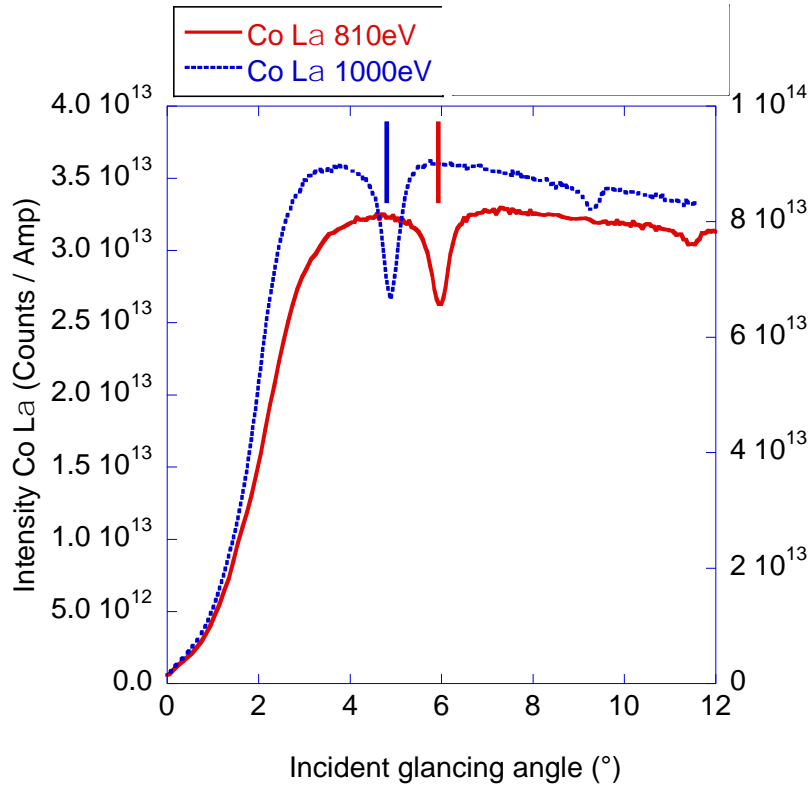
X-ray em



Fluorescence of Mg/Co multilayer

Si substrate / [Mg (5.1nm) / Co (2.6nm)]x30 / B4C (3.5nm)

"Classic" - GIF mode

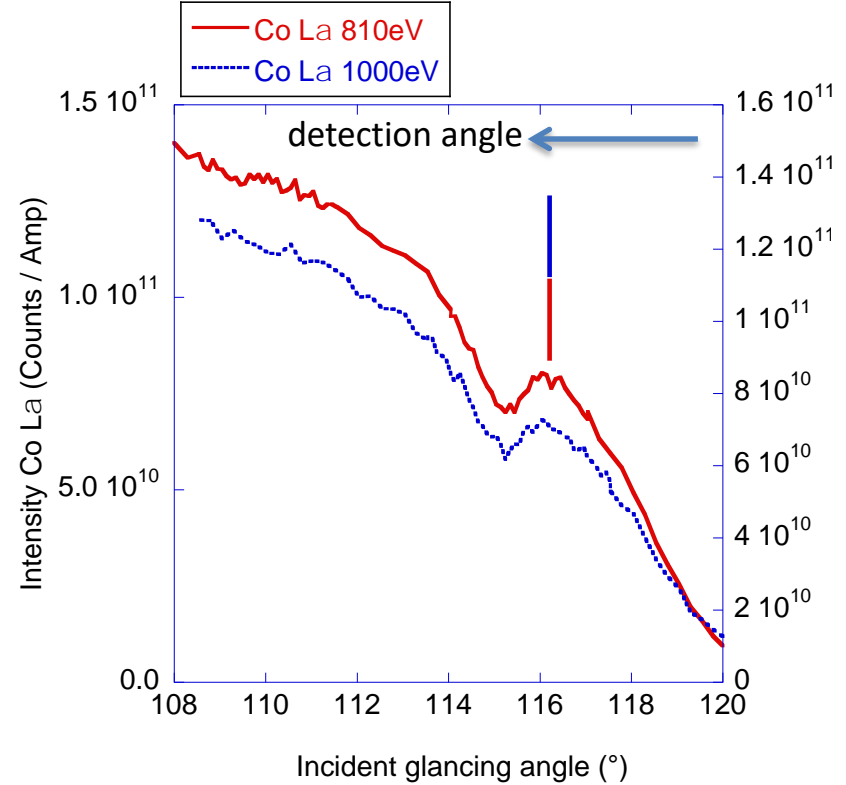


Features appear at Bragg angle of **incident** radiation



Move with energy of incident radiation

"Kossel" - GEF mode



Features appear at Bragg angle of **emitted** radiation



Do not move with energy of incident radiation

Introduction of Zr into Mg/Co stack

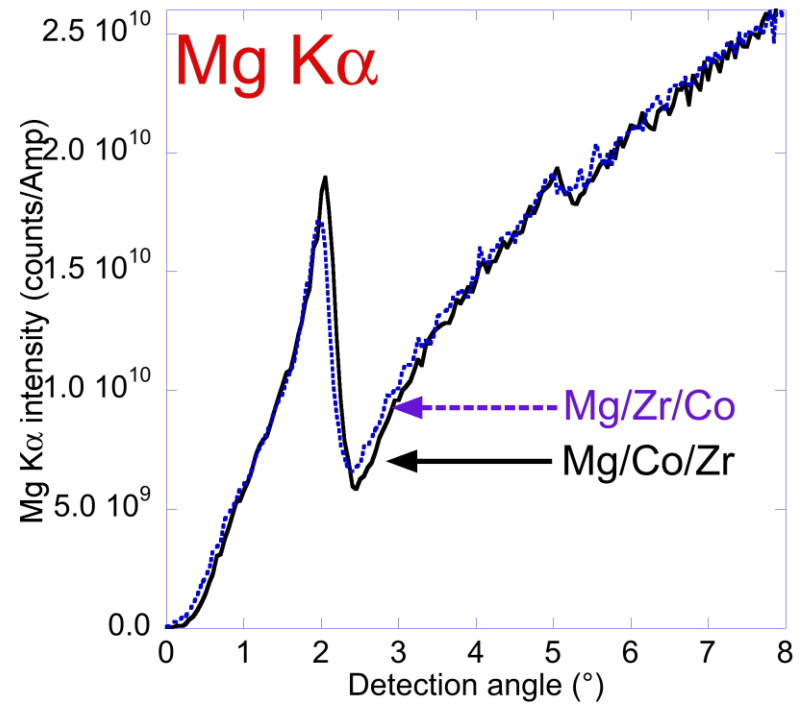
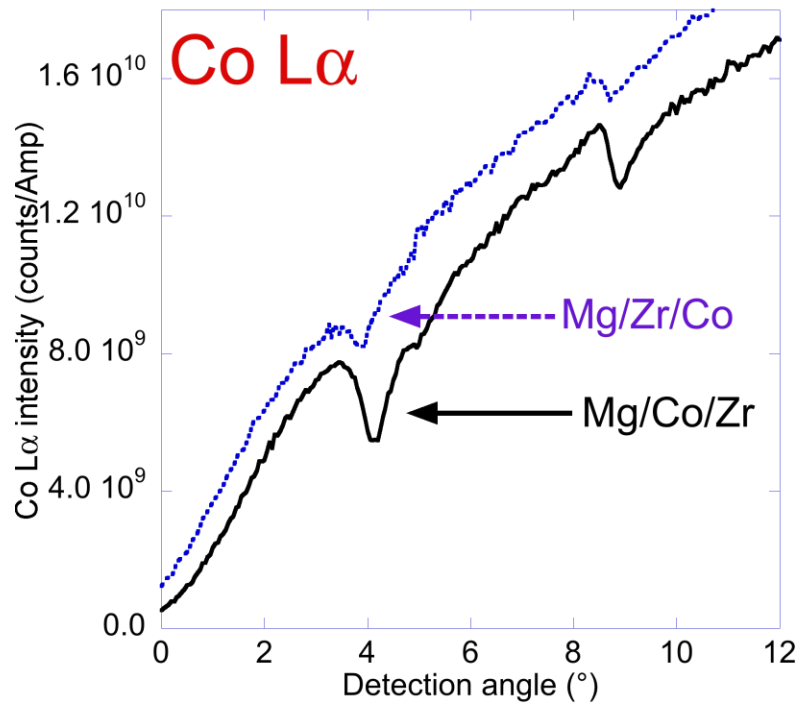
- Makes the stack stable upon annealing
- Improves the reflectivity (optimization on the optical path within the stack)

Si substrate / [Mg (5.45nm) / Co (2.55nm) / Zr (1.5nm)]x30 / B4C (3.5nm)
Si substrate / [Mg (5.45nm) / Zr (1.5nm) / Co (2.55nm)]x30 / B4C (3.5nm)

Two different orders of the layers

GE measurements – Mg-Co-Zr

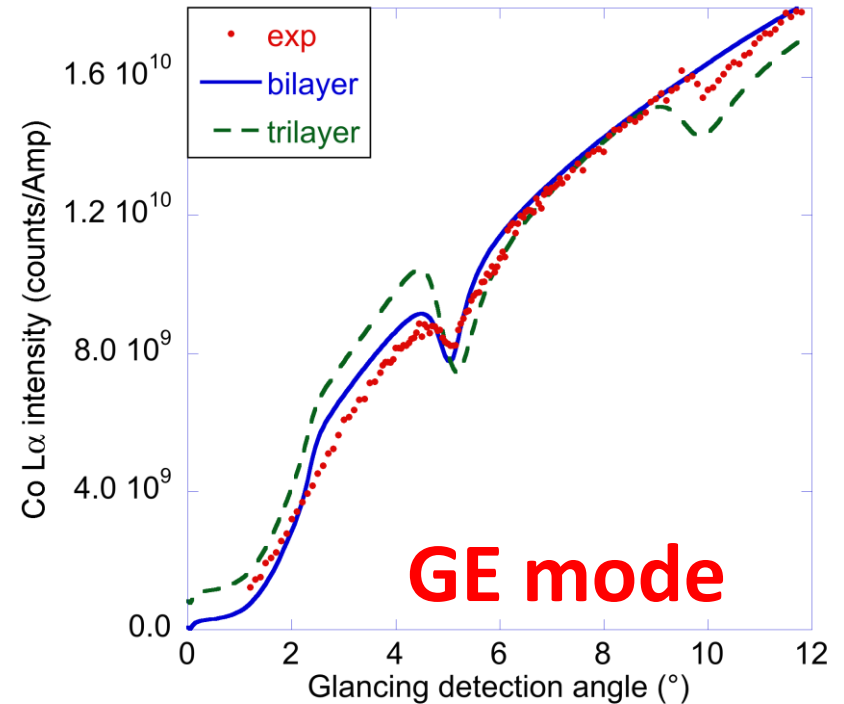
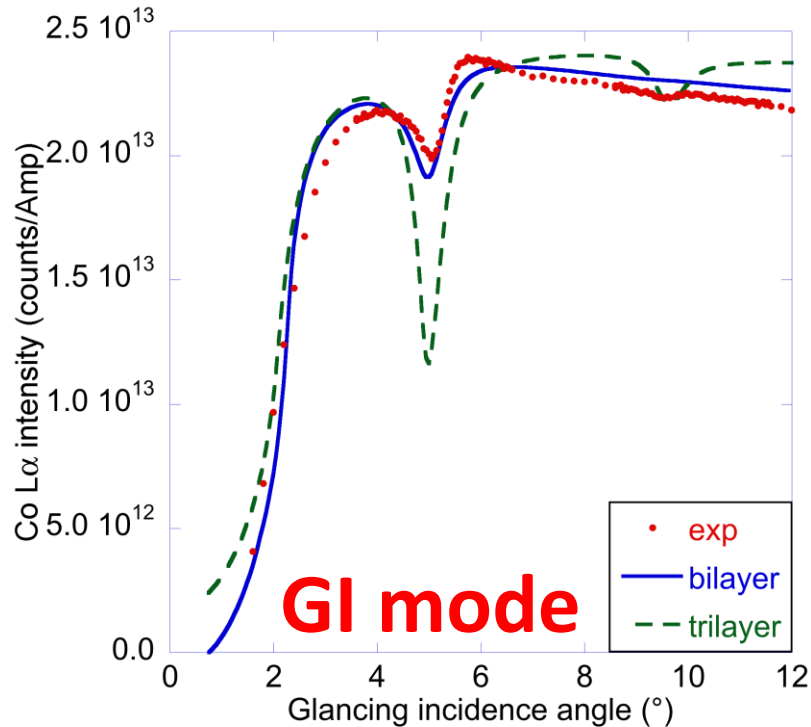
Different contrasts of the features for Co L emission depending on the sample



Same behavior in GI mode

Simulations – Mg-Co-Zr

Mg/Zr/Co – Co L emission



- Mg/Zr/Co described as Mg/Co₄Zr
- Mg/Co/Zr trilayer with nominal parameters

Mg-Co-Zr interfaces

From XRR, NMR, XES, XSW-XRF

- **Sharp Zr-on-Co interfaces** in Mg/Co/Zr
- **Mixing at Co-on-Zr interfaces** in Mg/Zr/Co

Surface free energy

- Co 2.0 J.m^{-2}
- Zr 1.6 J.m^{-2}



Asymmetric behavior of
Zr-on-Co and Co-on-Zr interfaces

Pd/Y based periodic multilayers

● Problem: the original design has bad optical performance

- Grazing incident X-ray reflectometry (Cu K radiation 8048 eV)

Low reflection, bad periodicity

- Severe interdiffusion between Pd and Y layers.

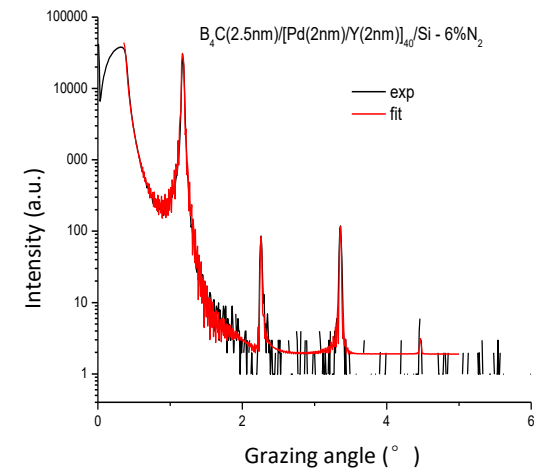
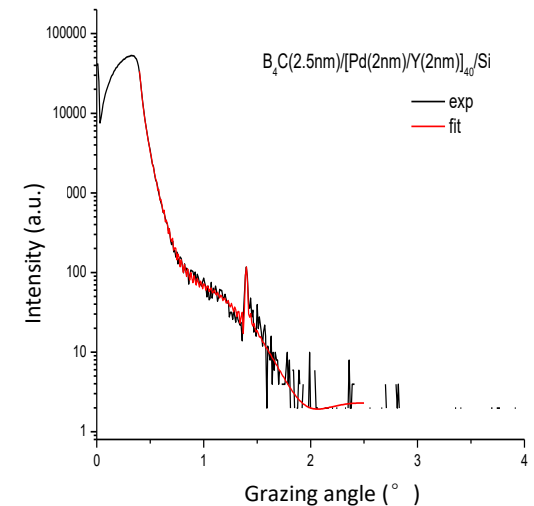
● Solution: Derivative systems

- N₂ in the sputtering gas [1].

0% 2% 6%

- B₄C barrier layers [2].

- **Pd-on-Y interfaces**
- **Y-on Pd interfaces**
- **all interfaces**

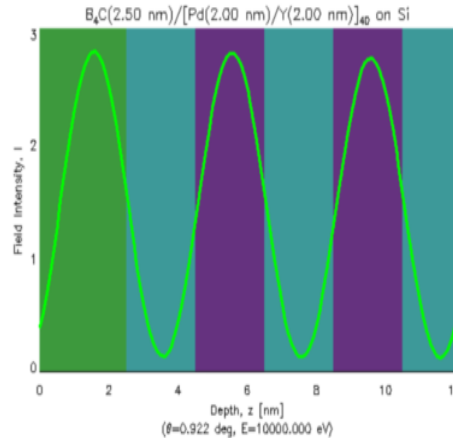


[1] Xu *et al.*, "Enhancement of soft X-ray reflectivity and interface stability in nitridated Pd/Y multilayer mirrors," *Opt. Express*. 23, 33018 (2015).

[2] Prasciolu *et al.*, "Thermal stability studies of short period Sc/Cr and Sc/B₄C/Cr multilayers," *Appl. Opt.* 53(10), 2126 (2014).

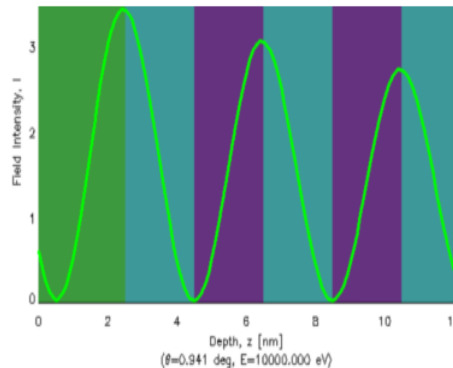
Combine PIXE with Kossel diffraction

$\theta < \theta_{\text{Bragg}}$

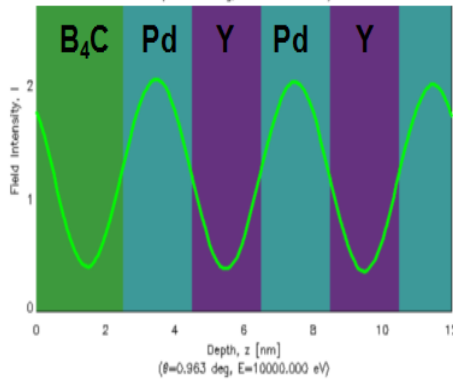


$$D = \frac{\lambda}{2 \sin \theta} = \frac{2\pi}{Q}$$

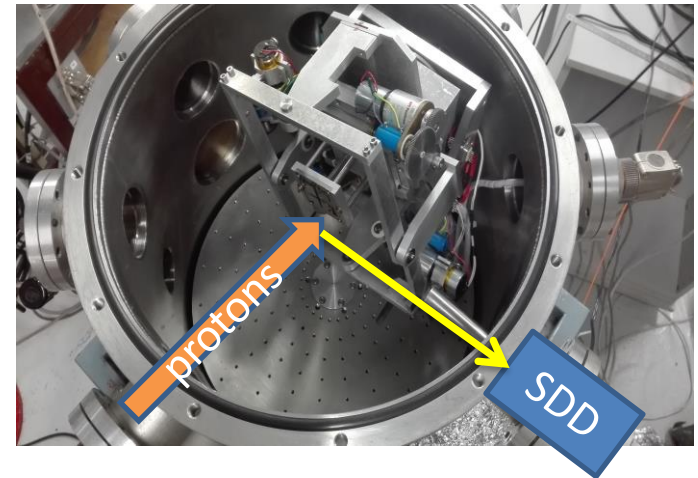
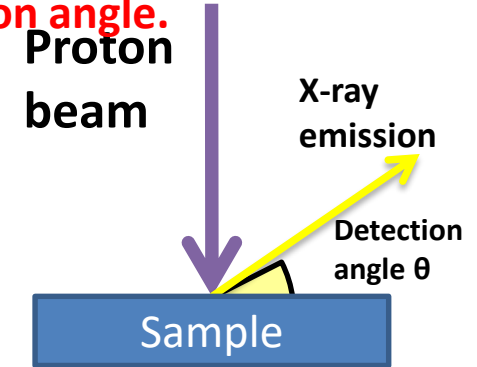
$\theta = \theta_{\text{Bragg}}$



$\theta > \theta_{\text{Bragg}}$



Measurement of X-ray emission intensity as a function of the detection angle.



X-ray color camera

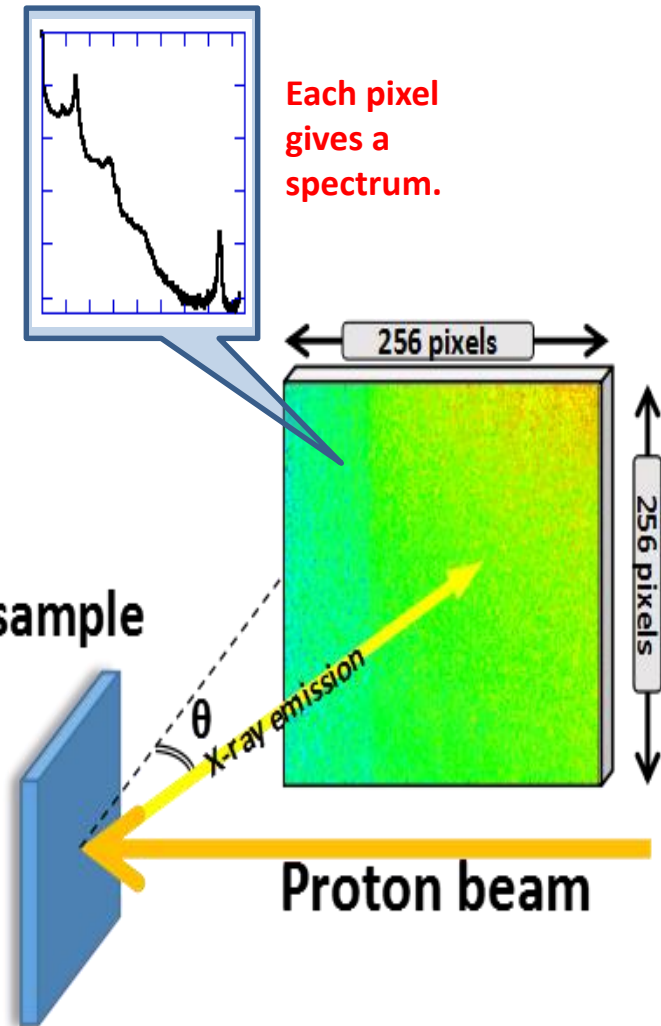
- Advantage: spatially resolved.

- Measurement of X-ray emission intensity in a squared area of about 13 x 13 mm.
- Native: 1024 x 1024 sensor array with 13 x 13 μm pixels.
- Our selection: 256 x 256 of 52 x 52 μm .

>>> compromise of angular/energy resolution

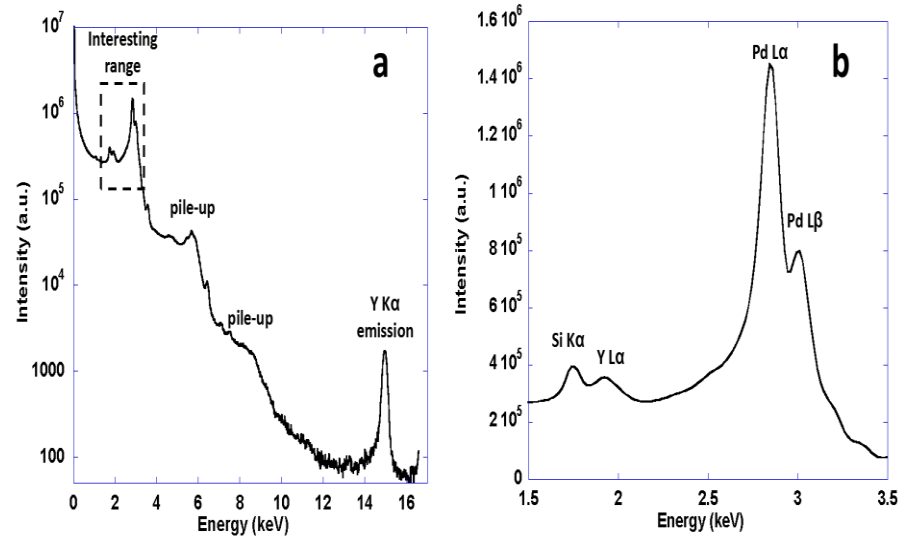
- No need to scan the angle.
- We place a 200 μm beryllium film in front of the camera to filter the scattered protons. Protection of the camera.
- Acquisition time significantly reduced compared to SDD.

Days to 2 hours >>>potential of in-situ measurements
(annealing test, oxidation test)



X-ray emission spectrum

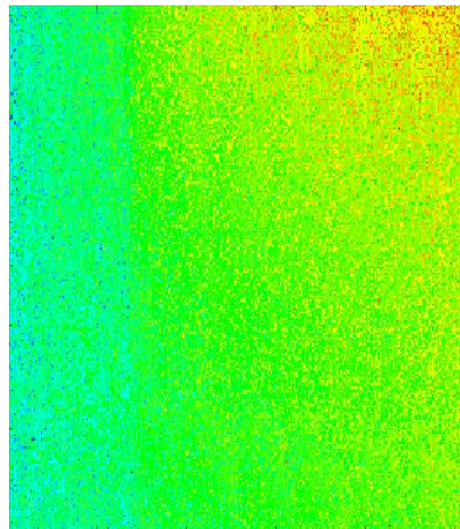
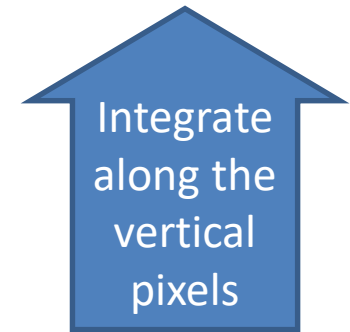
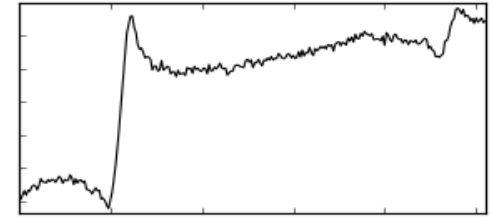
- $B_4C(2.5 \text{ nm})/[Pd(2 \text{ nm})/B_4C(2 \text{ nm})/Y(2 \text{ nm})]_{x40}/Si$
- Energy resolution is about 150 eV at 5.9 keV (Mn $K\alpha$).
- Pd $L\alpha$ $L\beta$, Y $L\alpha$ $K\alpha$, Si $K\alpha$ can be observed
- Pile up effect due to multiple photons detection
- Energy calibration of the spectrum is carried out with Pd $L\alpha$ peak (2.838 keV) and Y $K\alpha$ peak (14.958 keV)
 - Y $K\alpha$ has too low intensity.
 - Y $L\alpha$, Si $K\alpha$ are in the low efficiency part of the X-ray camera.
 - Pd $L\beta$ does not bring additional information
 - **We measure Pd $L\alpha$ emission**



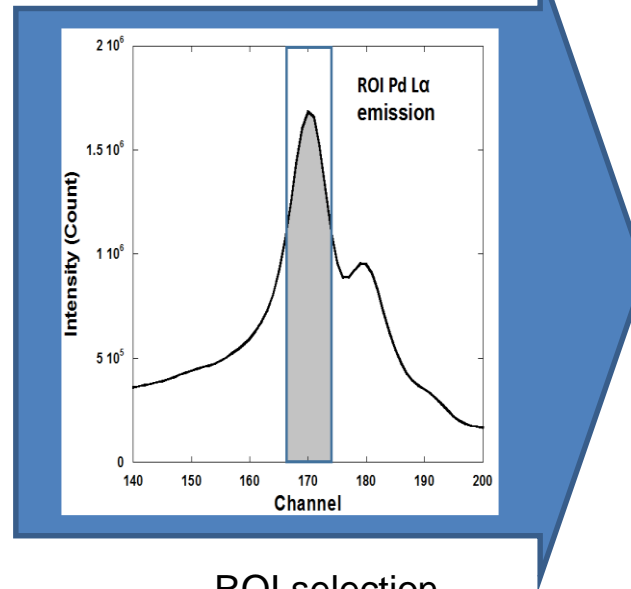
X-ray spectrum of Pd(2 nm)/ B_4C (2 nm)/Y(2 nm) multilayer:
a) overview (log scale)
b) zoomed range of interest (linear scale).

Kossel curves

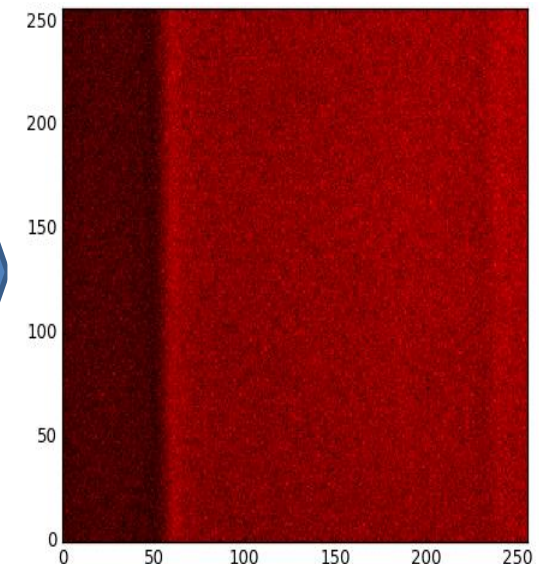
- The original image obtained by X-ray color camera contains the intensity of emitted photons of all energies.
- Kossel curve: the angular distribution of the characteristic X-ray emission.
- To get the Kossel curve of Pd L α emission, we need 3 steps:
 1. Select region of interest (ROI) on the spectrum.
 2. “Filter” the original image by applying ROI.
 3. Integrate the “filtered” image along the vertical pixels.



Distribution of X-ray emission



ROI selection



Distribution of Pd L α

Calibration of detection angle

- Pixel of the detector - grazing exit angle

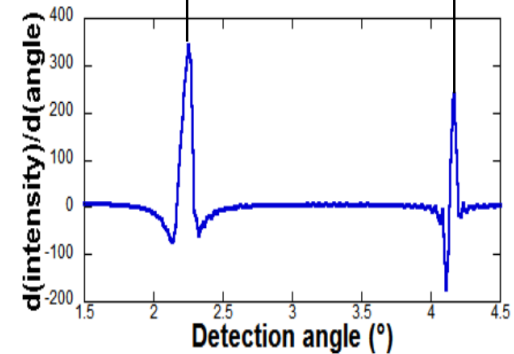
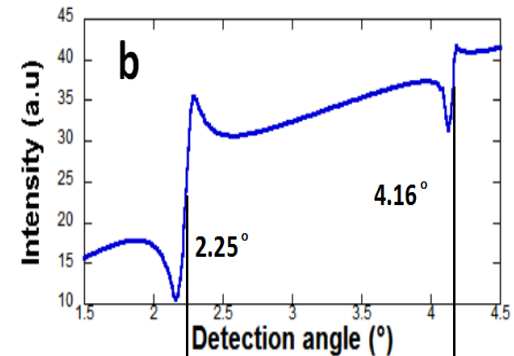
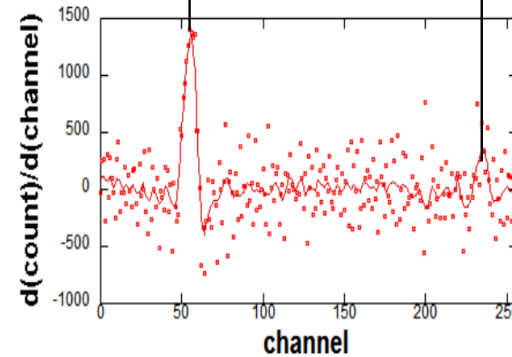
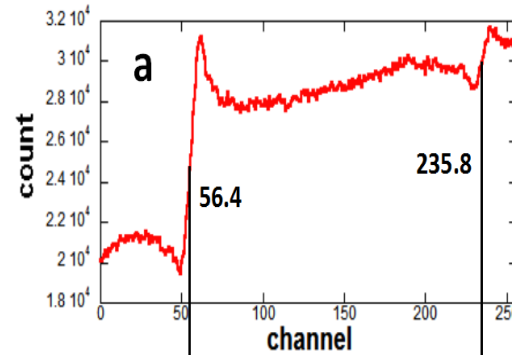
- 4-layer sample:
 $B_4C(2.5 \text{ nm})/[B_4C(1 \text{ nm})/Pd(2 \text{ nm})/B_4C(1 \text{ nm})/Y(2 \text{ nm})]_{x40}/Si$

- 1st and 2nd order of Kossel oscillation

- a) experimental curve in channel (pixel)

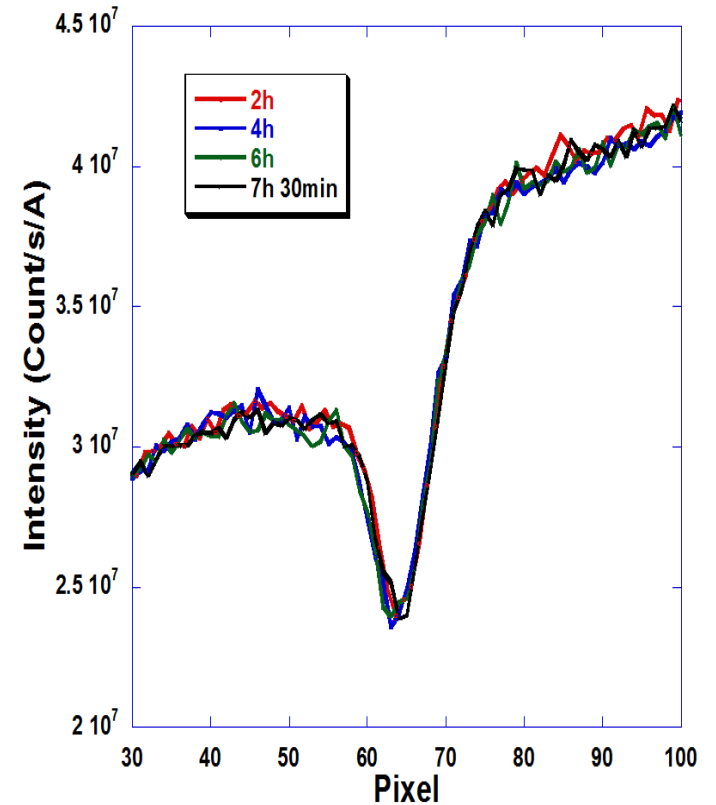
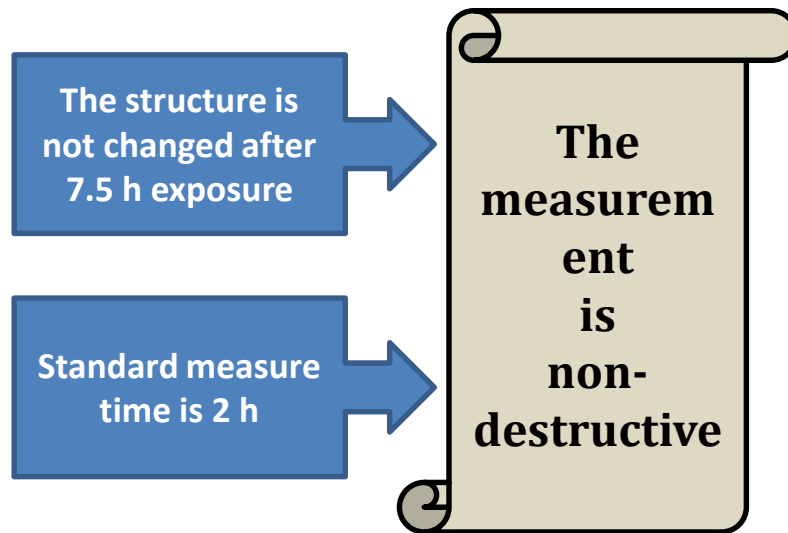
- b) simulated curve in angle (degree)

- Precise values obtained from the derivatives of the curves



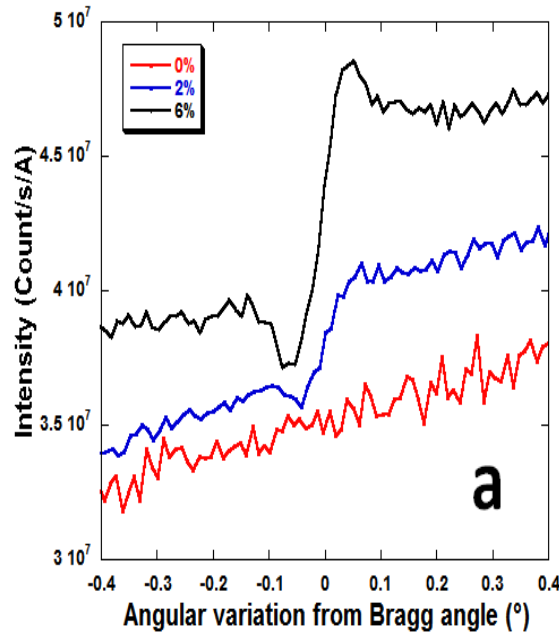
Non-destructive test

- $B_4C(2.5 \text{ nm})/[Pd(2 \text{ nm})/B_4C(2 \text{ nm})/Y(2 \text{ nm})]_{x40}/Si$
- Exposure under proton beam for 7.5 hours
- Kossel curve maintains its shape

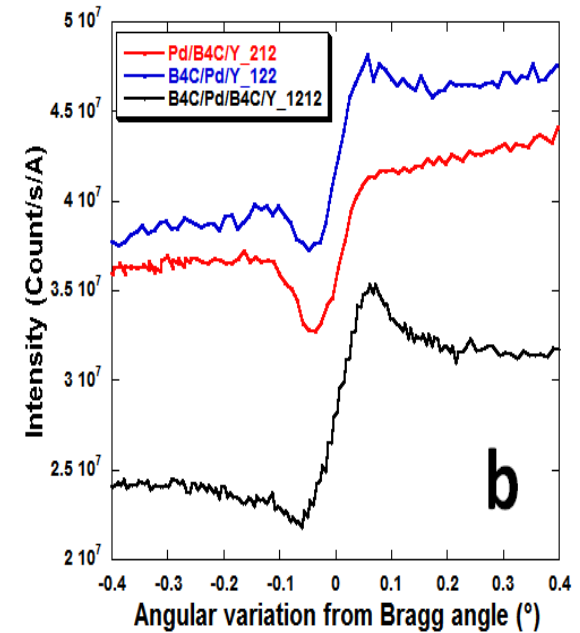


Kossel curves of Pd La emission

- 2-hour acquisition time. Curve statistics can be further improved by increasing the acquisition time.
- Angles are adjusted to the Bragg angle, which is in most cases located in the center of the Kossel oscillation.
- The periodicity of the originally designed Pd/Y multilayer is totally compromised.
- Nitrogen reduces the interdiffusion.
- Kossel features can be distinguished for samples with different B_4C barrier layers. **Structural sensitivity.**



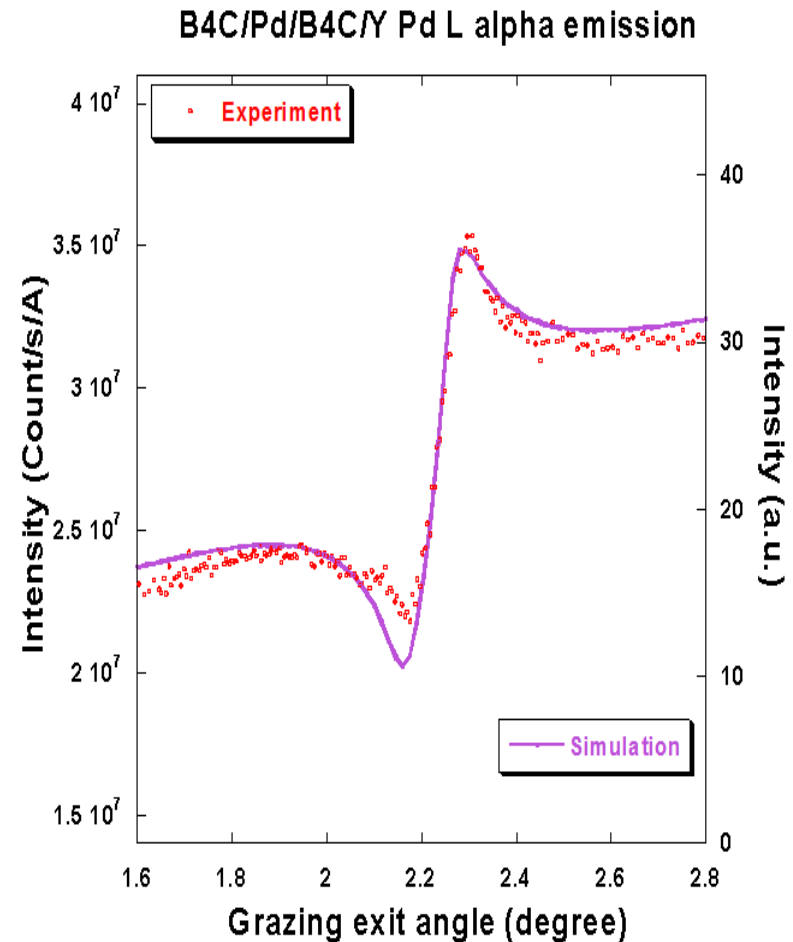
Kossel curves of the series of samples:
a) Deposited with nitrogen in the sputtering gas.



Kossel curves of the series of samples:
b) With B_4C barrier layers. The notation gives multilayer structure and layer thickness respectively.

Simulation

- Simulation of the PIXE-Kossel curve.
- Code for XRF-Kossel curve.
- Approach.
- Uniform ionization.
- Still not perfect due to background.
- Improvement needed.



MERCI DE VOTRE ATTENTION

- Jean-Michel André
- Karine Le Guen
- Vita Ilakovac
- Yanyan Yuan
- Meiyi Wu
- Jiaping Zhang
- Christopher Pendenque
- SAFIR plateforme
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Palaiseau
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Strasbourg
- Tongji University
Shanghai
- BEAR beamline
Trieste