Ondes stationnaires combinées à l'émission X ou à la photoémission X pour l'étude de films minces

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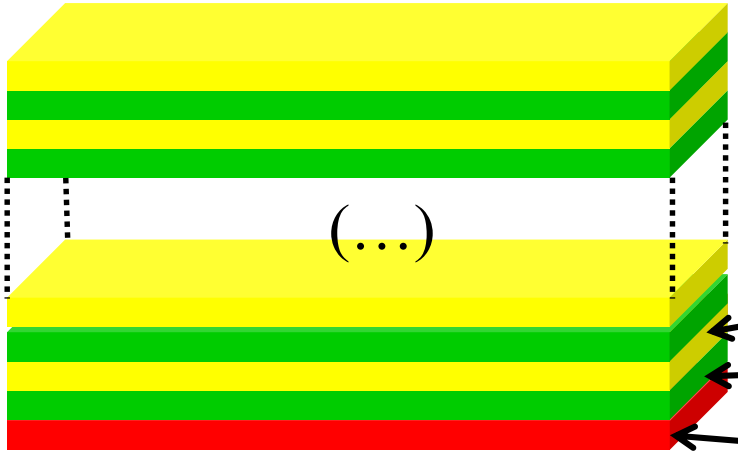
Séminaire de l'Institut des Matériaux Jean Rouxel, Nantes, 4 avril 2019

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



Heavy material (metal, …)

Light material (Si, B, C, …)

Substrate (Si, SiO2, …)

stack of N bi-layers

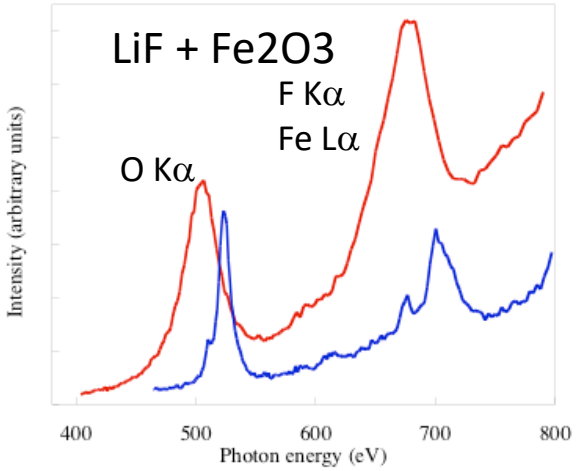
thickness_light + thickness_heavy = period d of a few nm

↳ can diffract EUV and x-rays

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

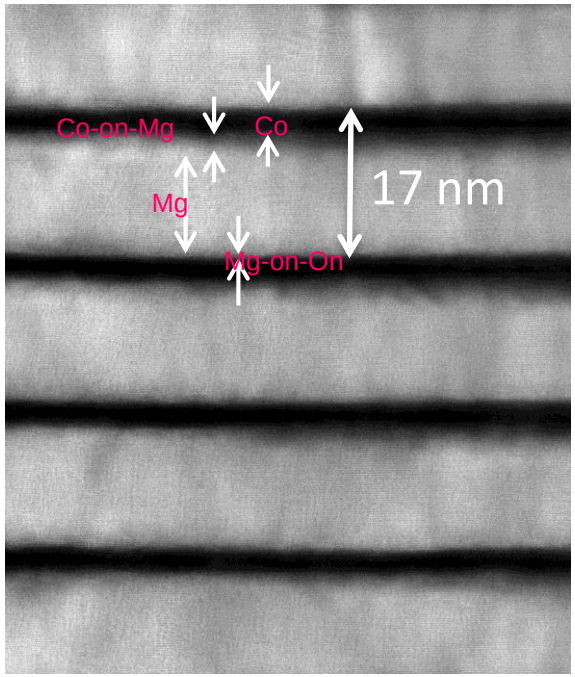


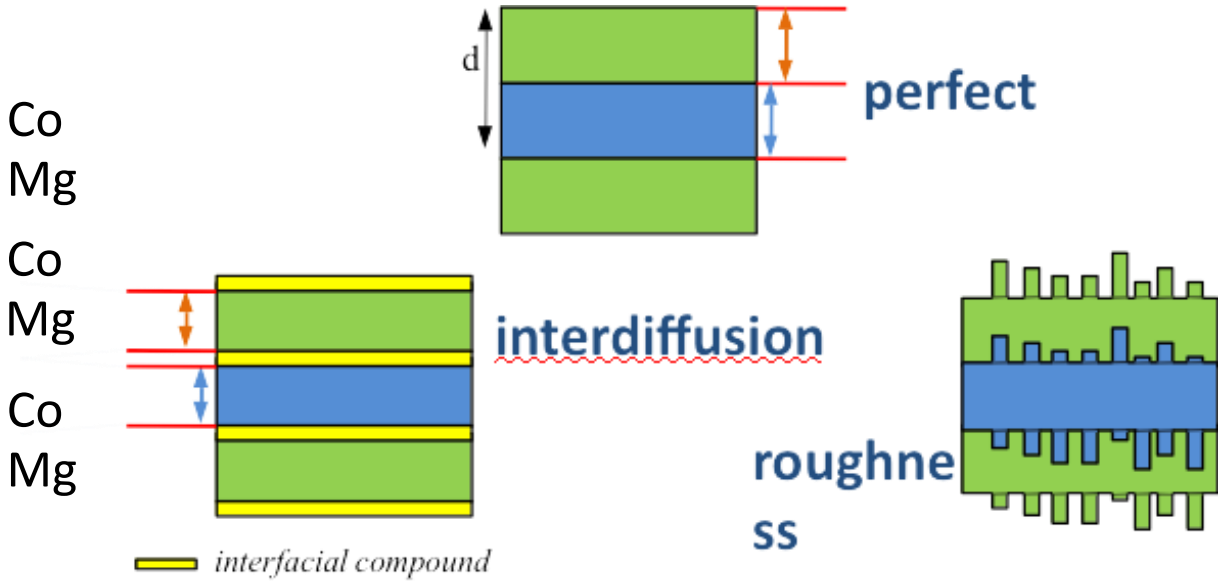
X-ray emission spectroscopy

Imaging at a given wavelength

Photolithography
@ 13.5 nm, 6.x nm

Motivation and challenges





	Visible λ=500nm	EUV λ=30.4nm
d	~125nm	Co_2.6nm/Mg_13.6nm
σ	~10 nm	~0.5-0.8nm

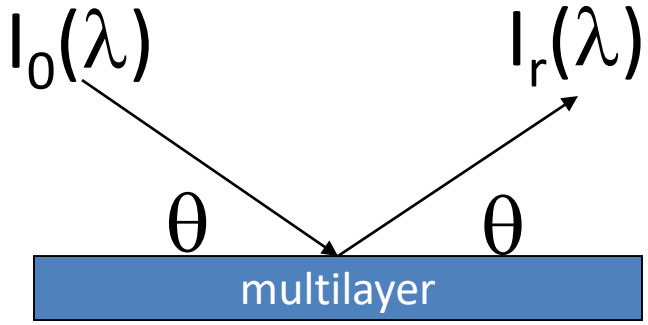
R multiplied by DW factor

$\mathbf{\exp(-2[2\pi\sigma \sin\theta / \lambda]^2)}$

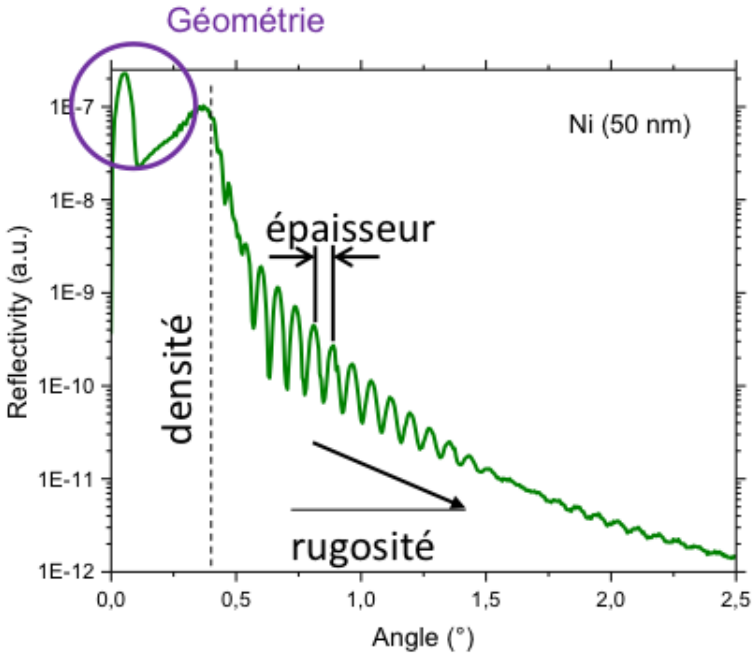
$\mathbf{\exp(-2[\pi\ \sigma/d]^2)}$

Interface is the largest challenge for EUV multilayer!

X-ray reflectivity



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



Determination of parameters of the stack

- thickness
- roughness
- density / optical index

of the various layers

- Les ondes stationnaires (XSW)
- XSW – XRF: Co/Mg/Zr
- XSW – HAXPES: Pd/Y/B4C
- Kossel – XRF: Pd/Y/B4C

- Les ondes stationnaires (XSW)
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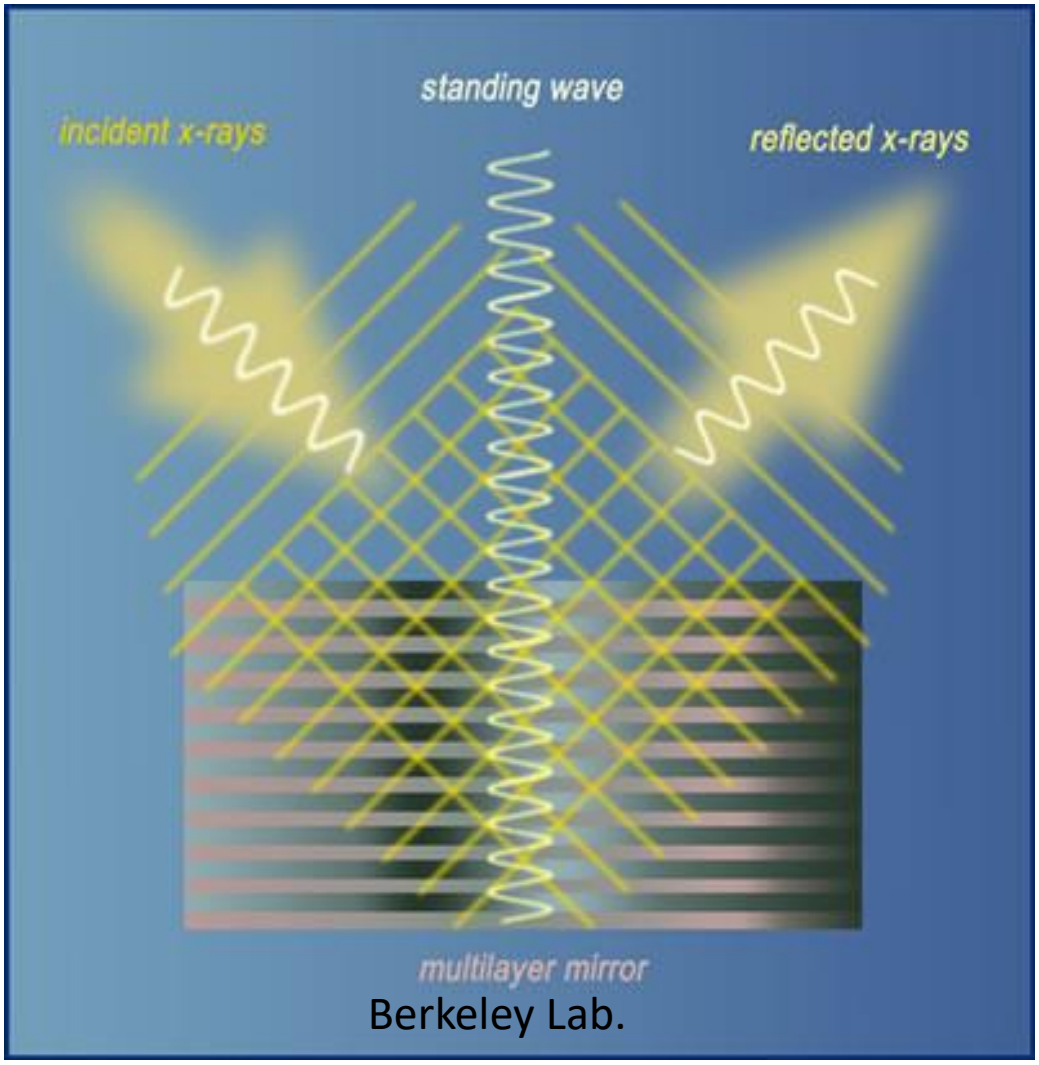
X-ray standing waves



Berkeley Lab.

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

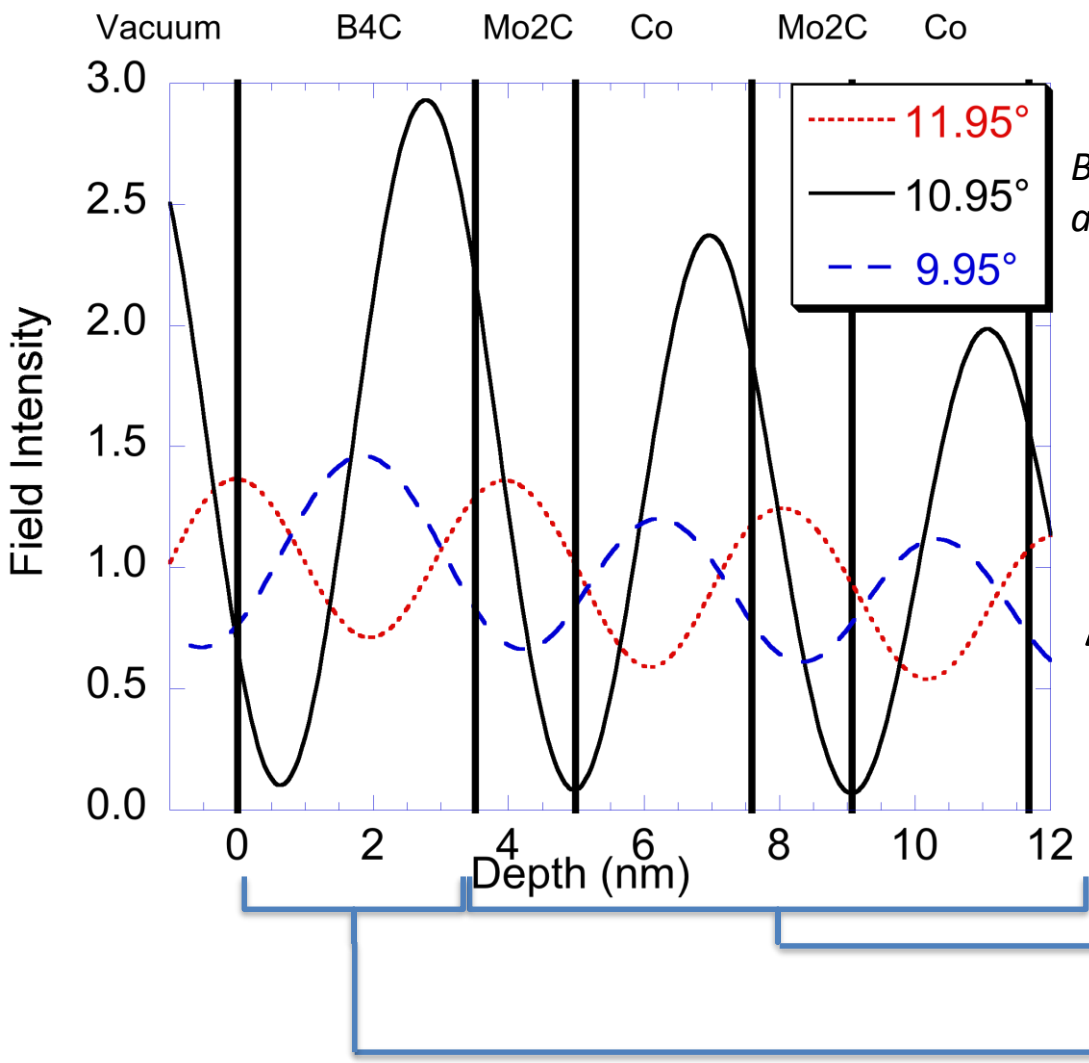
- Fluorescence or photoelectrons

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

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

X-ray standing waves

Depth distribution of the electric field



Co/Mo2C d = 4 nm

E = 780 eV (1.6 nm)

Rotate sample

(change the wavelength)

Change incident or detection angle

⬇

Shift of the nodes and anti-nodes

Analysis by XPS

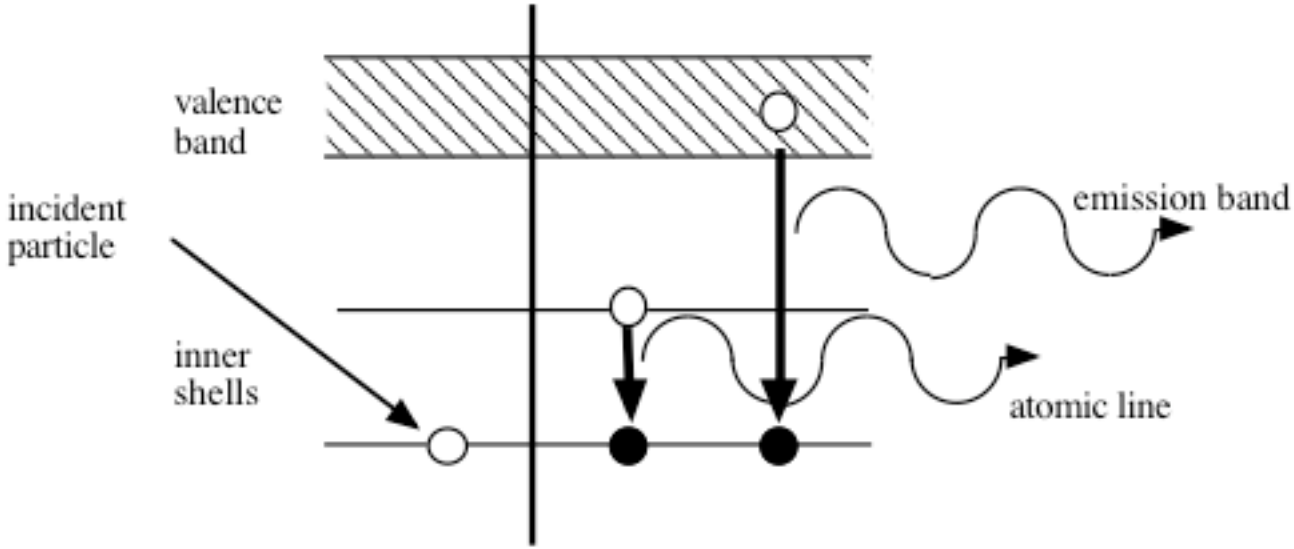
XRF

AES

of a Multilayer

Superficial material

X-ray emission spectroscopy



Observation of the energy distribution of the emitted radiation

Information about the chemical state of the emitting element

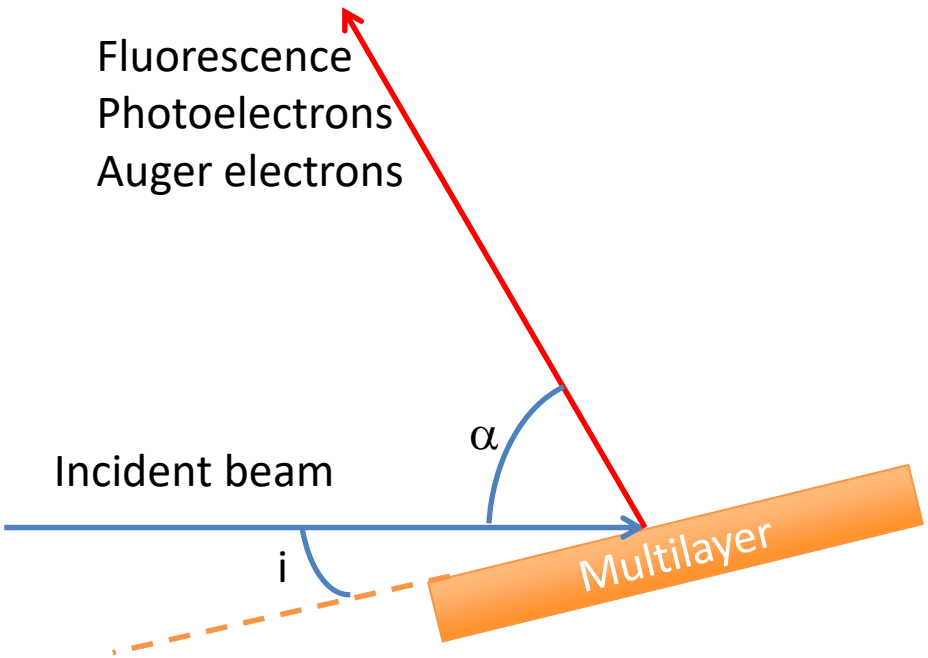
Incoming beam

- **Electrons**
- **Particles**
- **X-rays**

Detection / dispersion

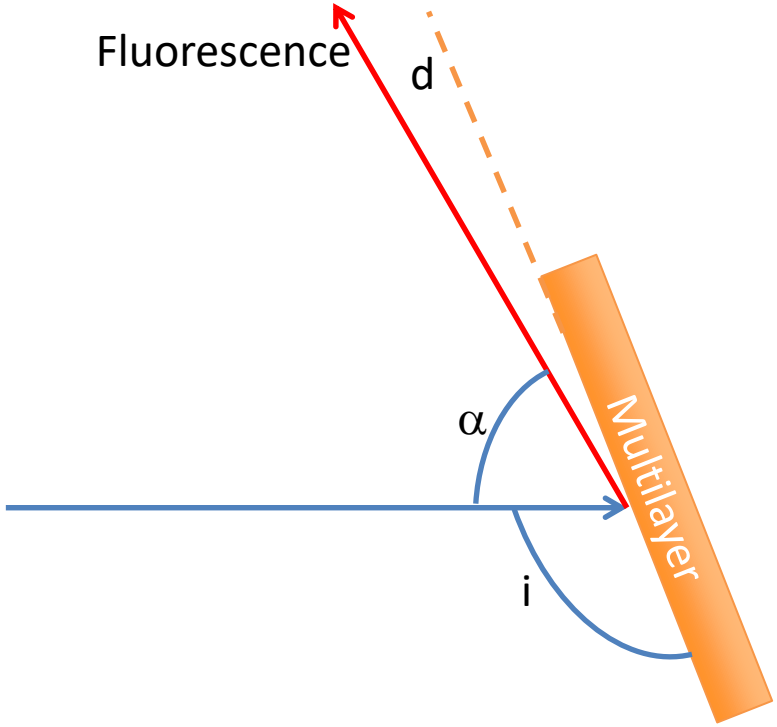
- **WDS : crystal spectrometer**
- **EDS : Si(Li), SDD, bolometer**
  energy dispersive CCD camera

Two XSW modes



Glancing incidence mode

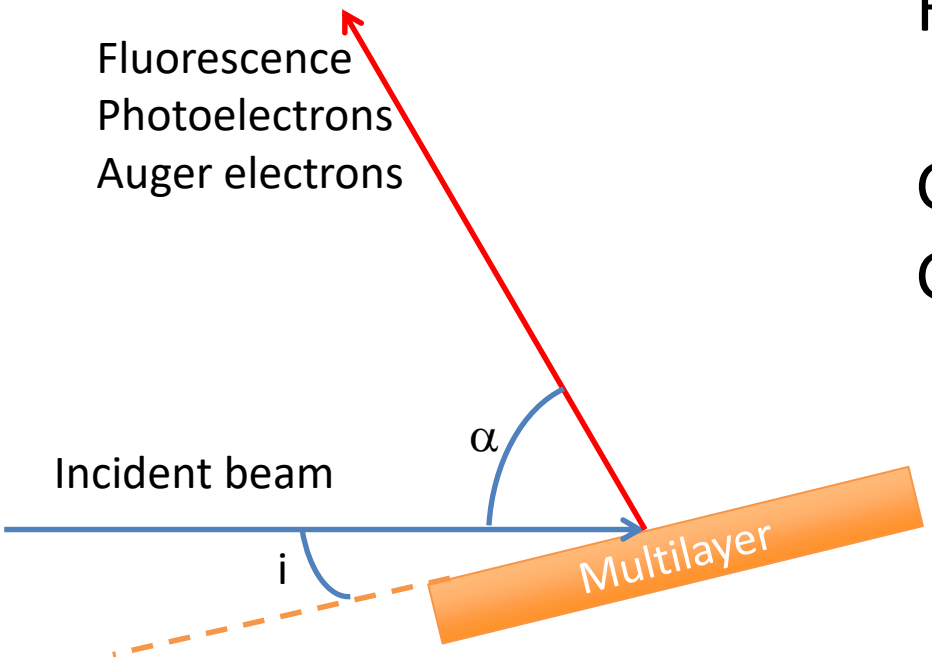
“Standard” or GI



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

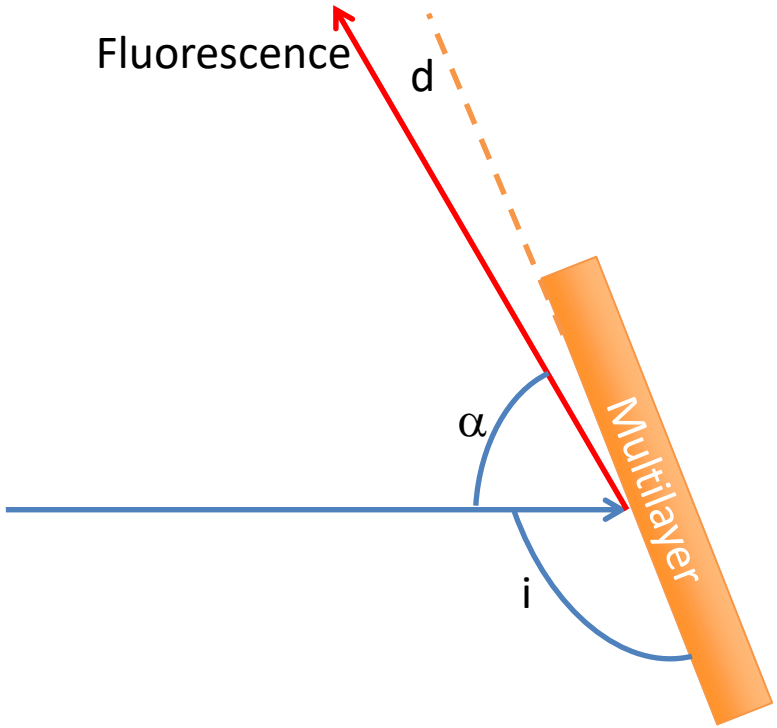
No geometry requirement

Detected beam = characteristic x-rays

Geometry requirement

Generally very grazing

Small solid angle of detection



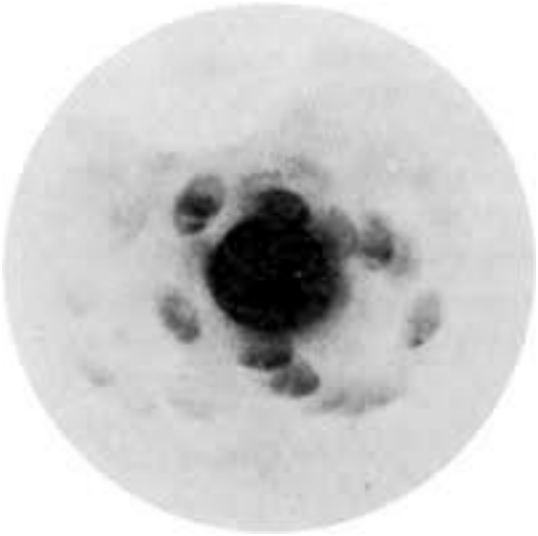
Glancing exit mode

"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

$P\bar{1}$ triclinic

1912: von Laue, Friedrich, Knipping

W. Kossel

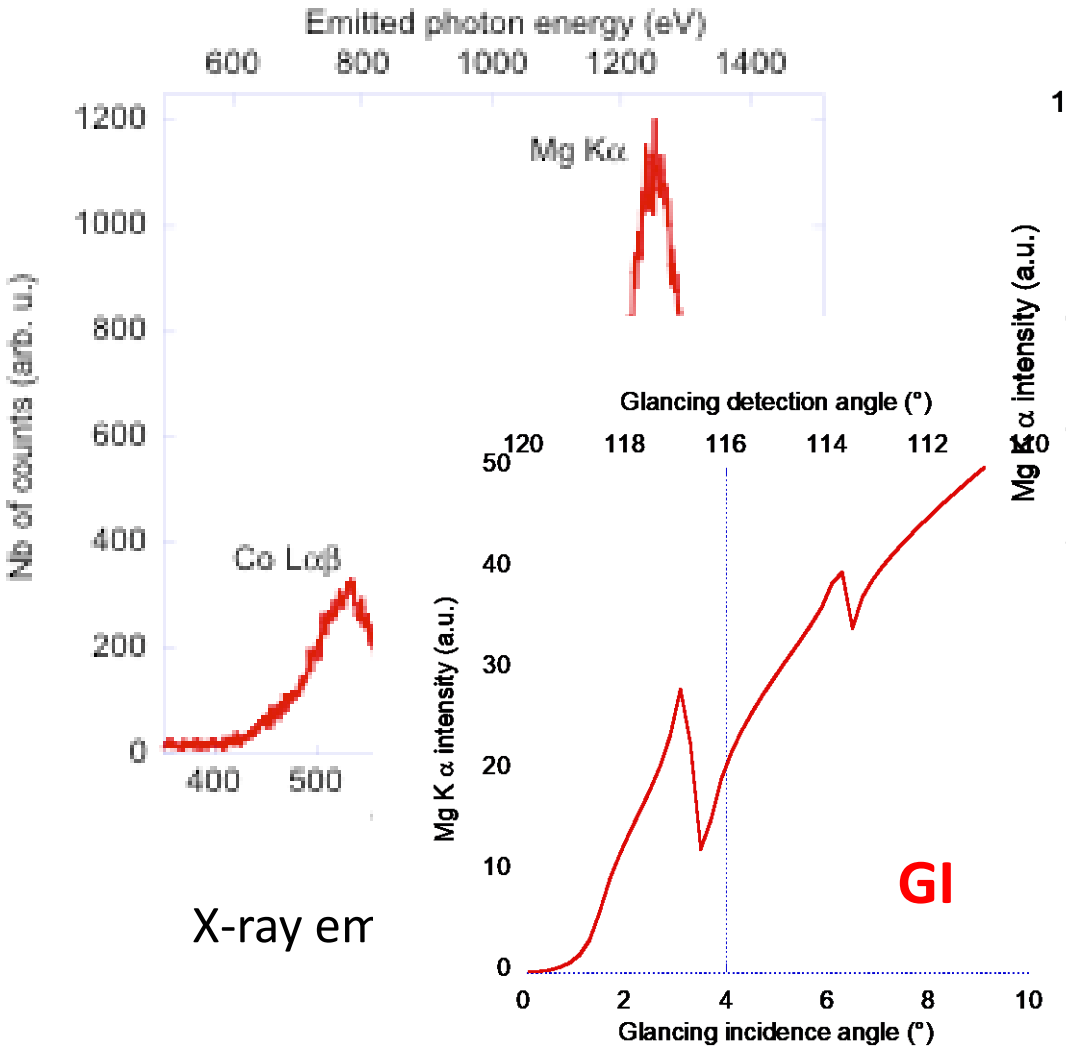
1935

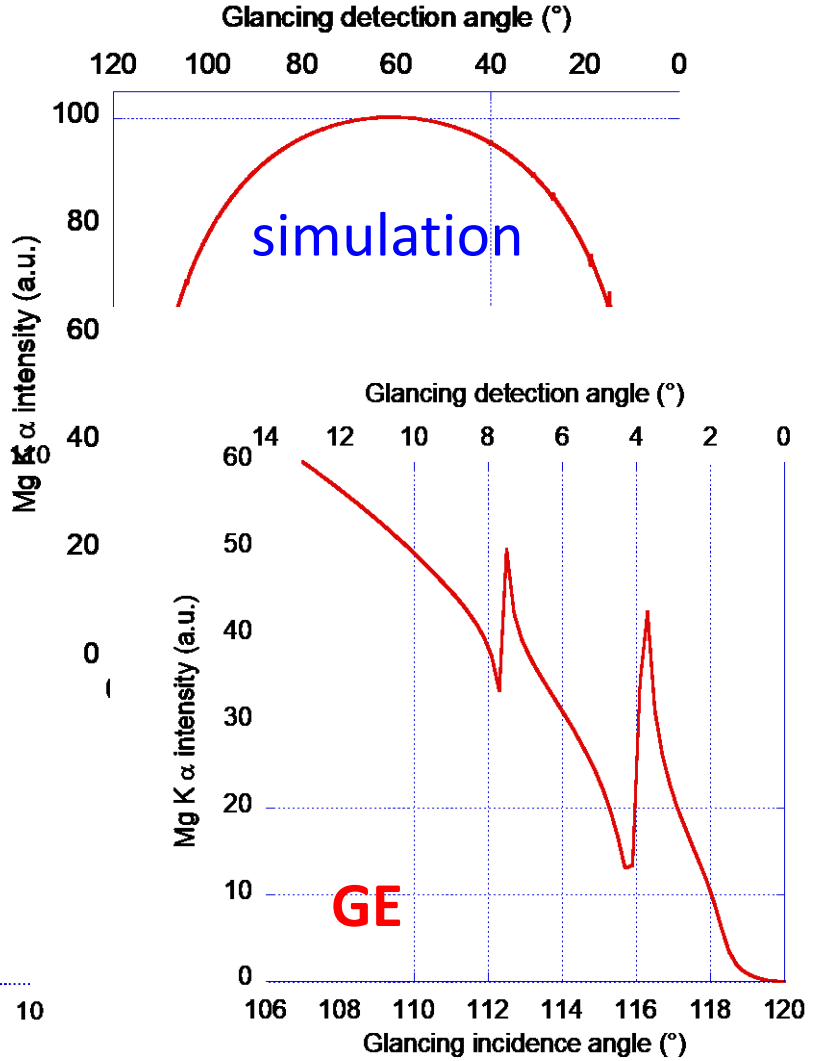
Diffraction of the fluorescence produced within the crystal by the crystal itself

Mg/Co XSW - XRF

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

Incident radiation 1500eV; 0.827nm
Mg Kα emission 1253.6eV; 0.989nm
60° between incident and detection directions

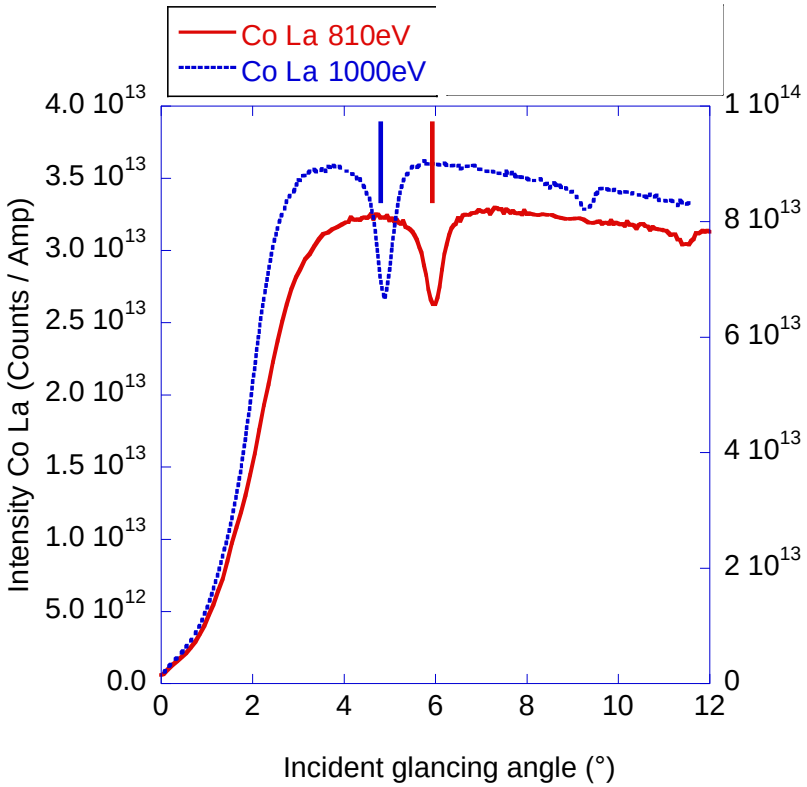




Fluorescence of Mg/Co multilayer

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

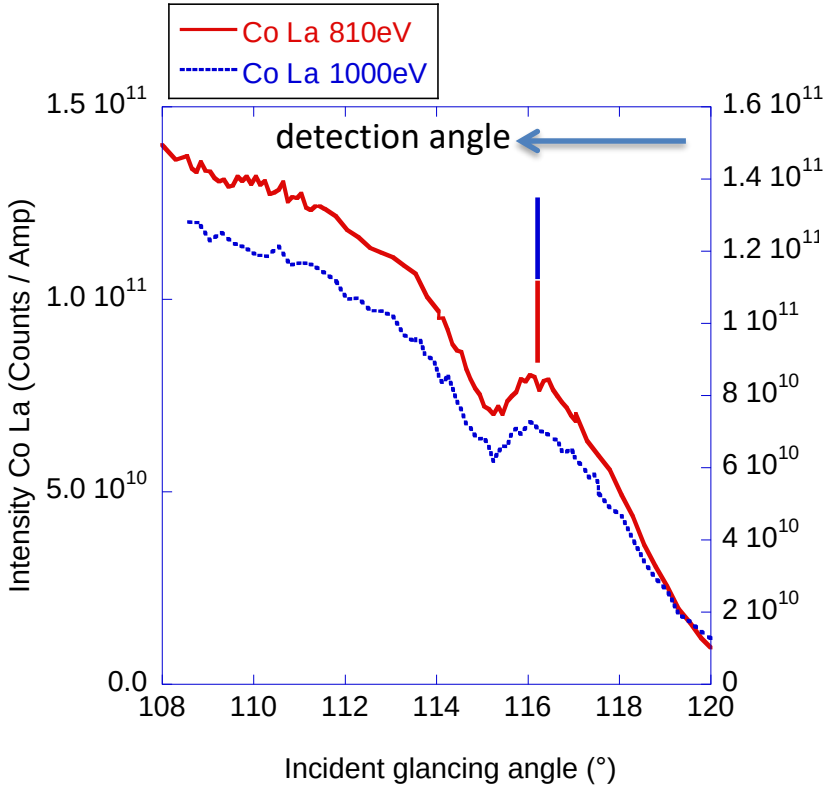
"Classic" - GIF mode



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

Move with energy of incident radiation

"Kossel" - GEF mode



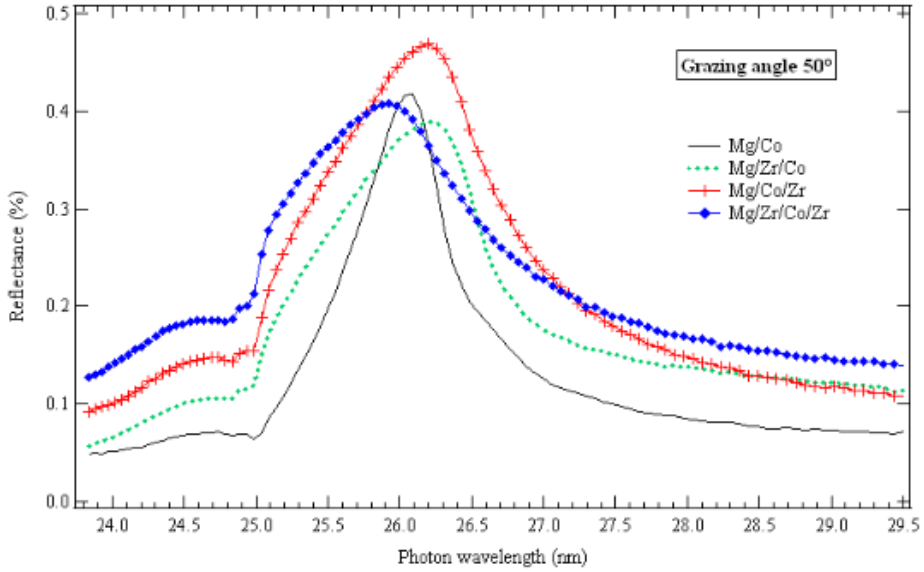
Features appear at Bragg angle of **emitted** radiation

Do not move with energy of incident radiation

- Les ondes stationnaires (XSW)
- XSW – XRF: Co/Mg/Zr
- XSW – HAXPES: Pd/Y/B4C
- Kossel – XRF: Pd/Y/B4C

Introduction of Zr into Mg/Co stack

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

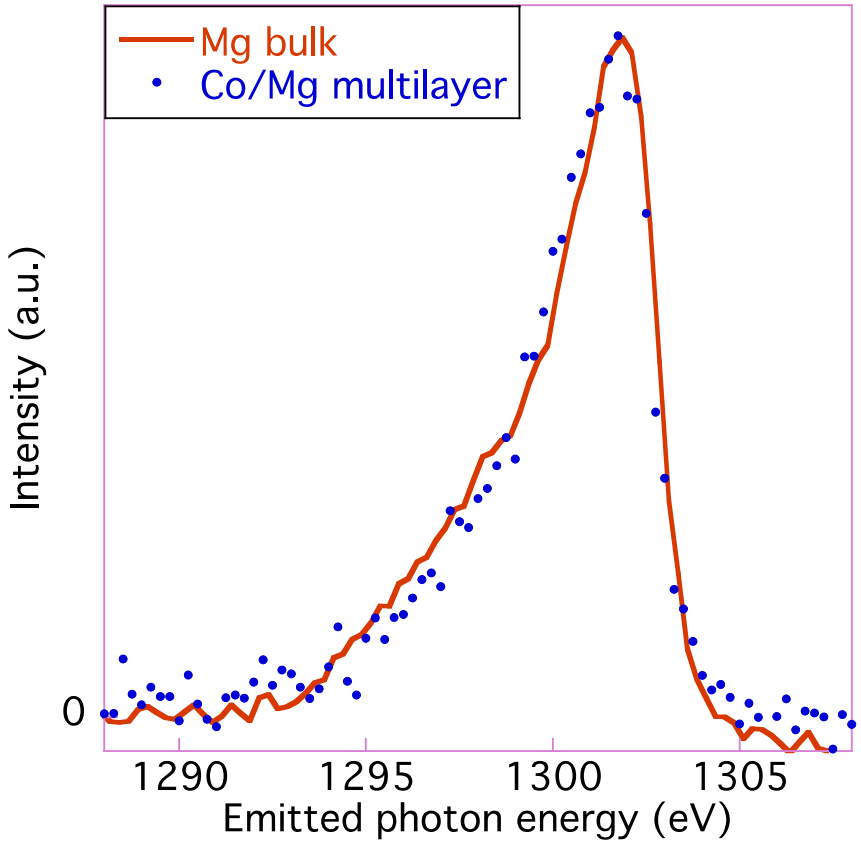


Reflectivity measurement
at the application wavelength
26 nm (50 eV)

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

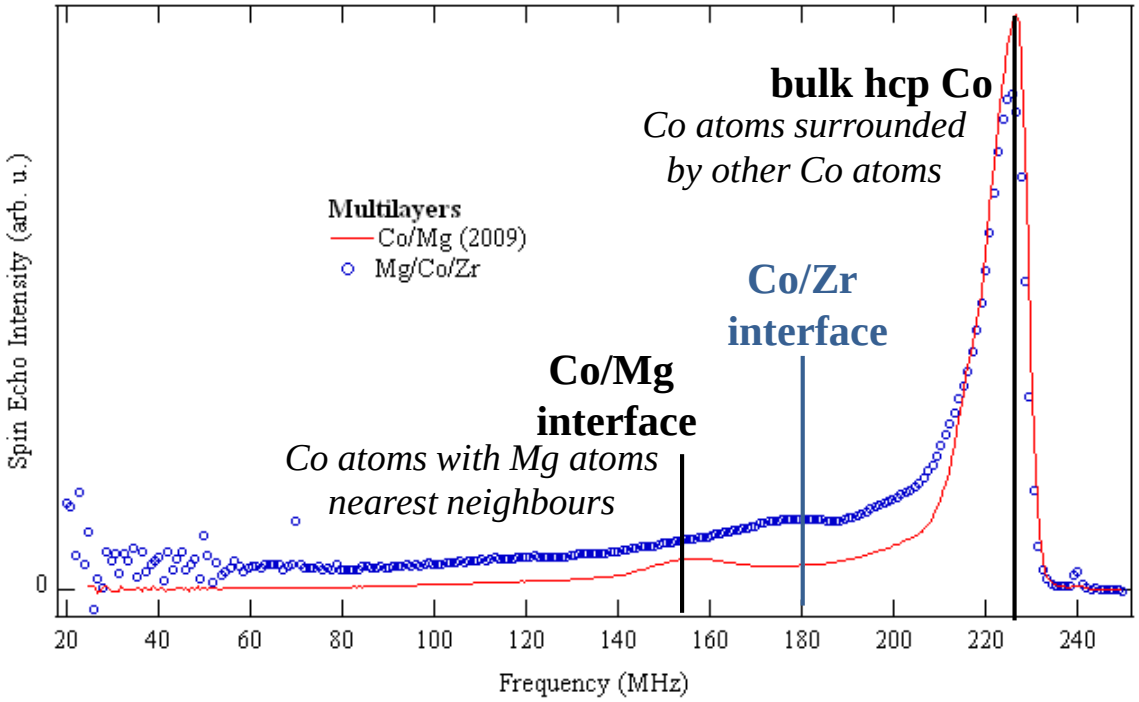
X-ray emission spectrosocpy



- Mg atoms as in pure Mg
- No interaction between Mg and Co layers

NMR spectroscopy

Probe of the nearest neighbour local structure around the Co atoms

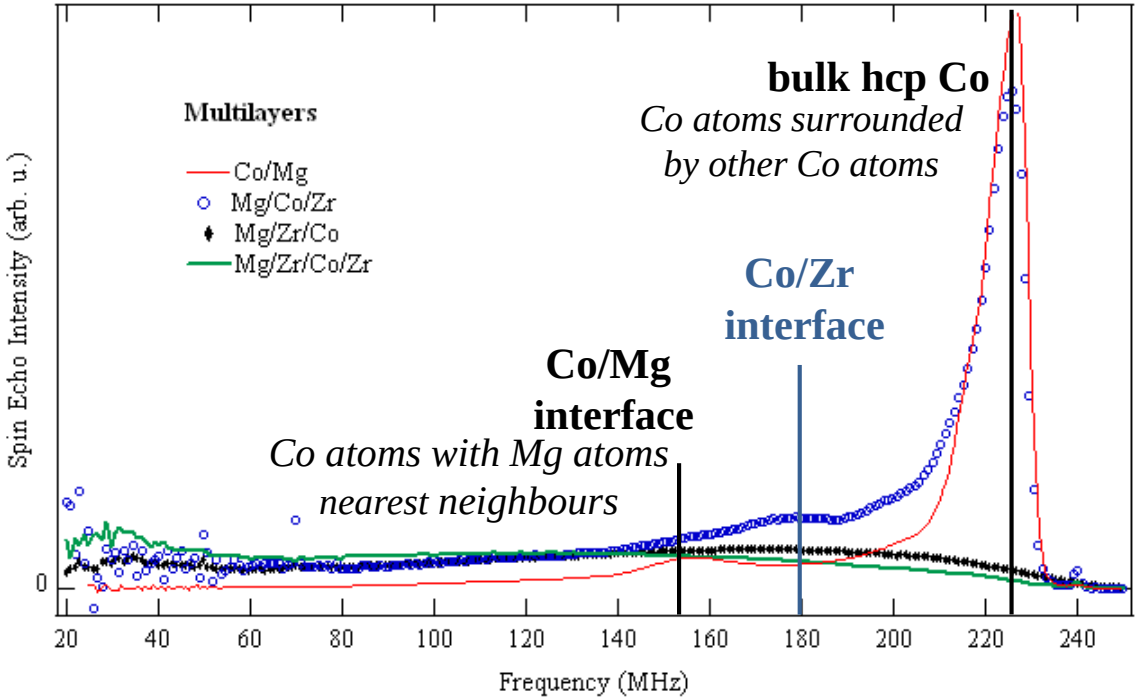


Mg/Co and **Mg/Co/Zr**

well-defined layers and interfaces

NMR spectroscopy (3)

Probe of the nearest neighbour local structure around the Co atoms



Mg/Co and **Mg/Co/Zr**
well-defined layers and interfaces

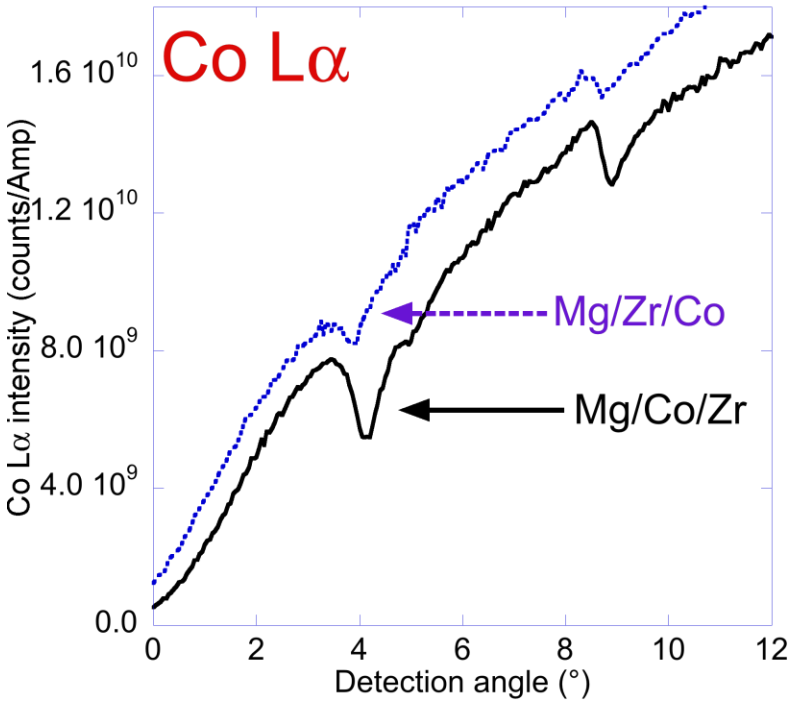
Mg/Zr/Co and **Mg/Zr/Co/Zr**
strong intermixing between Co and Zr

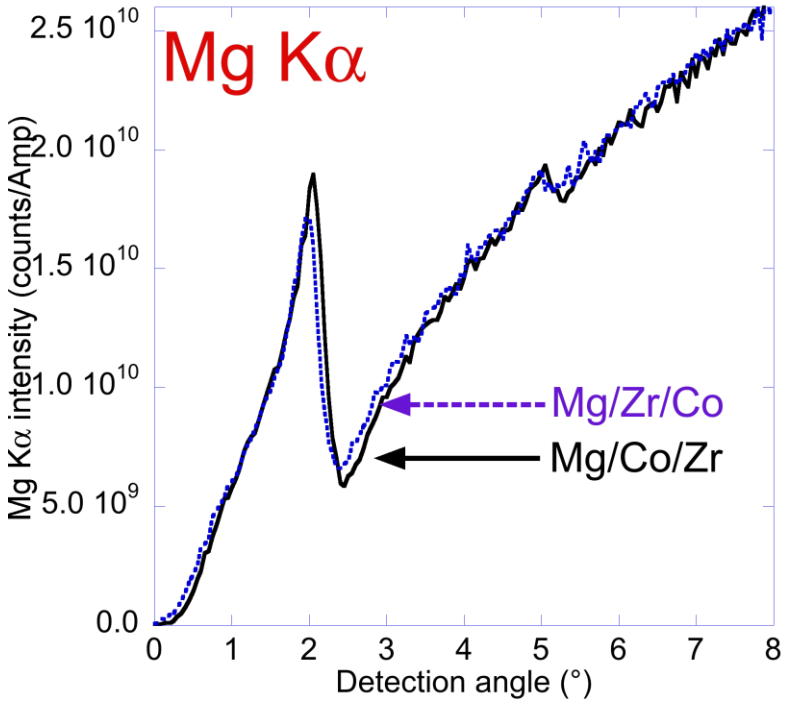
Mg/Co and **Mg/Co/Zr** **only geometrical roughness**

Mg/Zr/Co and **Mg/Zr/Co/Zr** **reaction between Co and Zr**

GE measurements – Mg-Co-Zr

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

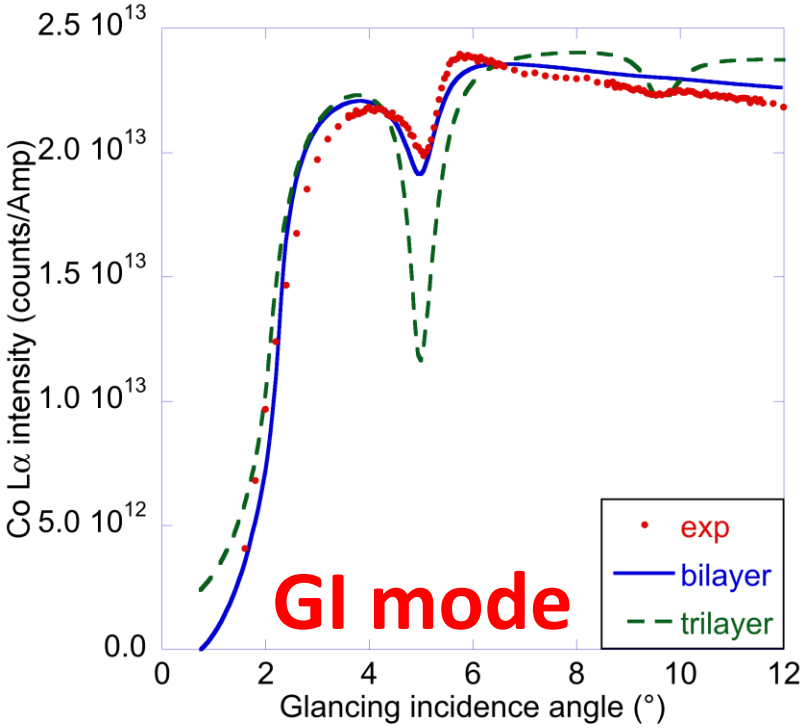


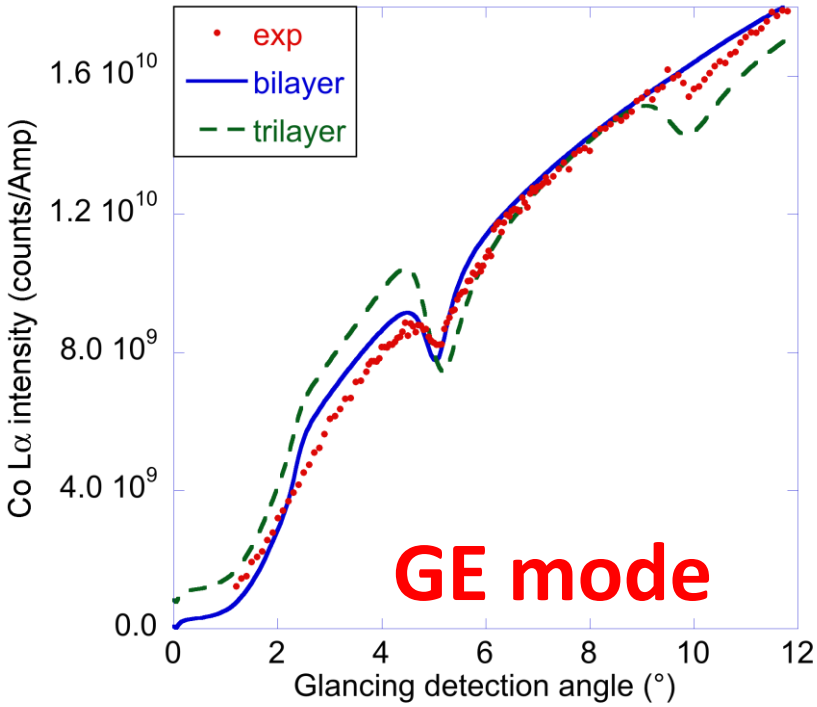


Same behavior in **GI mode**

Simulations – Mg-Co-Zr

Mg/Zr/Co – **Co L emission**





- **Mg/Zr/Co trilayer described as Mg/Co_4Zr bilayer**
  - **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 $J.m^{-2}$

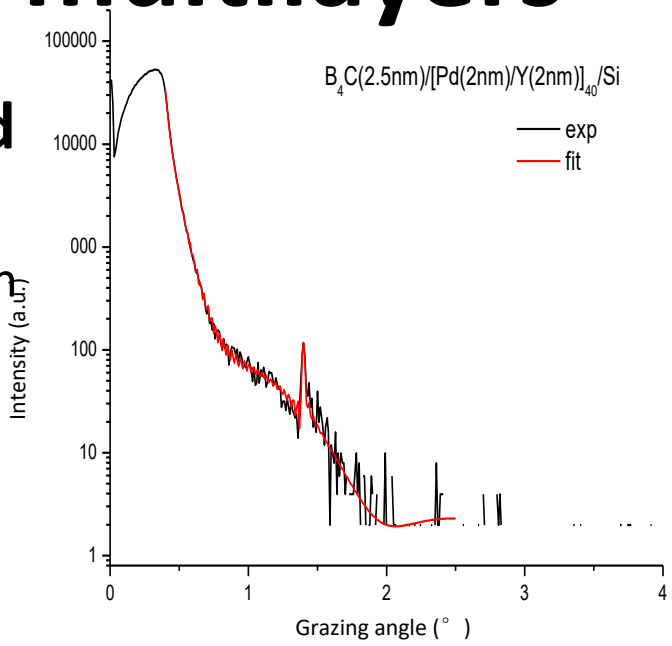
Asymmetric behavior of
Zr-on-Co and Co-on-Zr interfaces

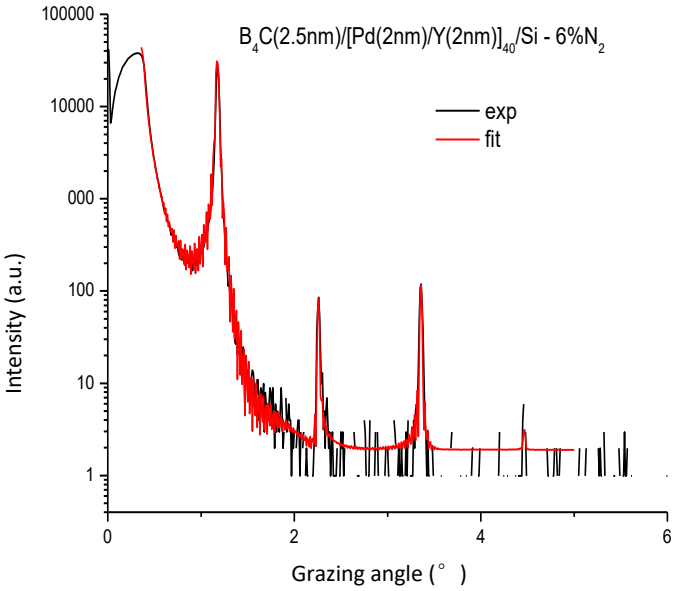
- Les ondes stationnaires (XSW)
- XSW – XRF: Co/Mg/Zr
- XSW – HAXPES: Pd/Y/B4C
- Kossel – XRF: Pd/Y/B4C

Pd/Y based periodic multilayers

- **Problem: the original design has bad optial performance**
  - X-ray reflectometry @ 8048 eV - Cu K radiation
    Low reflectance, bad periodicity
  - Severe interdiffusion between Pd and Y layers.

- **Solution: Derivative systems**
  Interface engineering
  - N_2 in the sputtering gas
    0% 2% 6%
  - B_4C barrier layers at
    Pd-on-Y interfaces
    Y-on Pd interfaces
    all interfaces

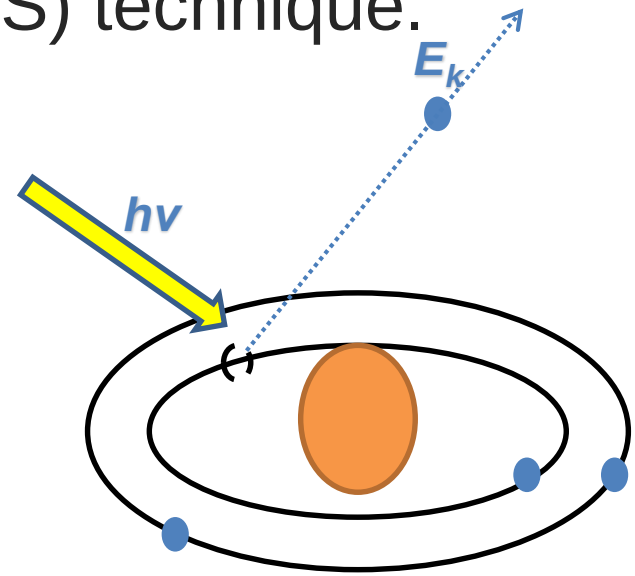




Methodology: HAXPES

- An extension of conventional X-ray Photoelectron Spectroscopy (XPS) technique.

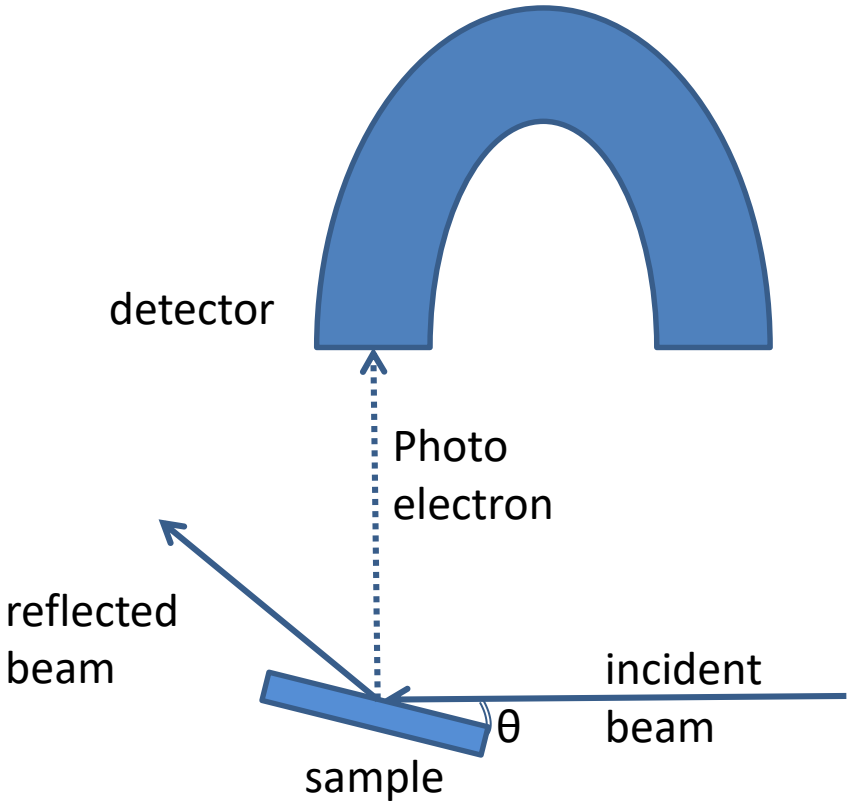
$$h\nu = E_b + \phi_{spectrometer} + E_k$$



- Higher incident photon energy.
  - Longer inelastic mean free path. Probed depth increases.
  - 10 keV => 22 nm (about 5-6 periods, bulk sensitive)
  - 3 keV => 9 nm (about 2 periods, surface sensitive)

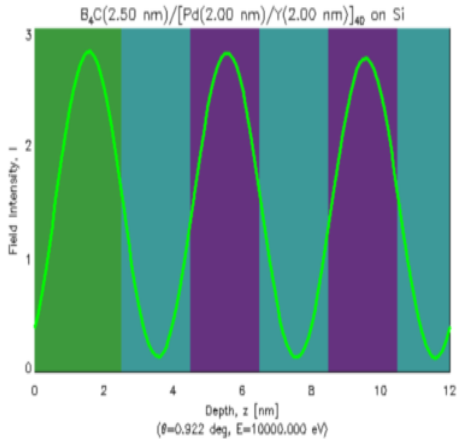
- GALAXIES beamline in SOLEIL Synchrotron.
  - High brilliance monochromatic x-ray source.
  - Small cross section due to high energy.

Methodology: combine HAXPES with XSW

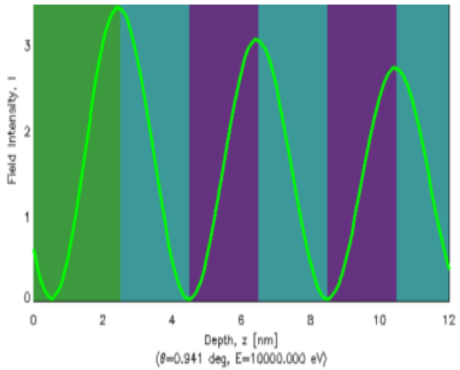


$$D = \frac{\lambda}{2\sin\theta} = \frac{2\pi}{Q}$$

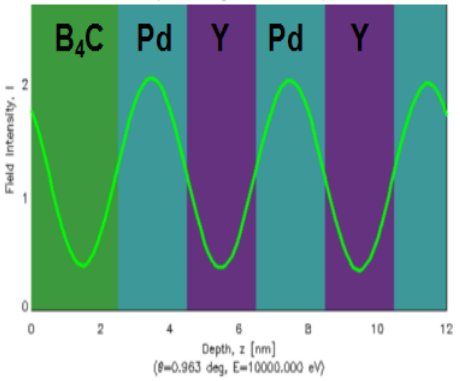
$\theta_i < \theta_{Bragg}$



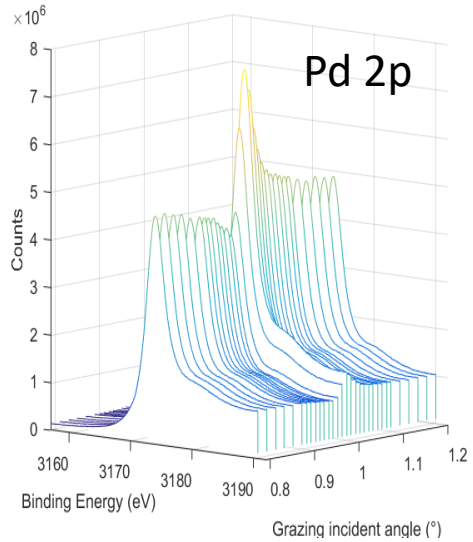
$\theta_i = \theta_{Bragg}$

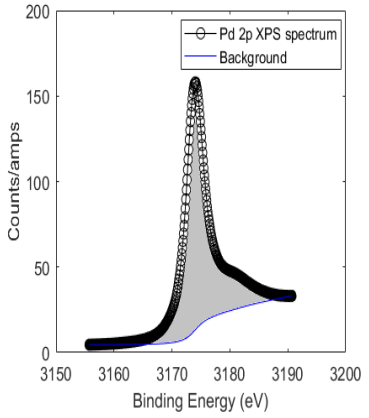


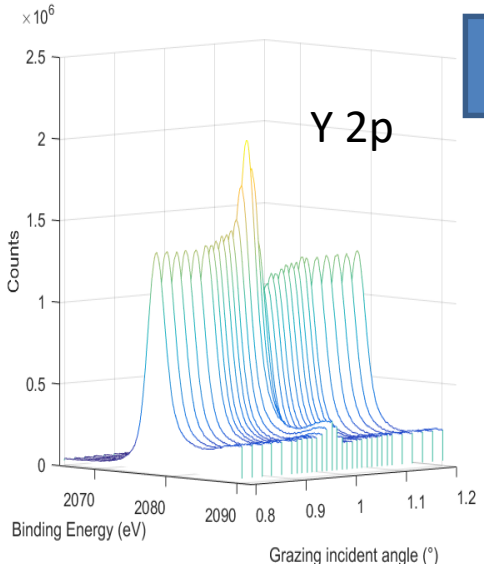
$\theta_i > \theta_{Bragg}$



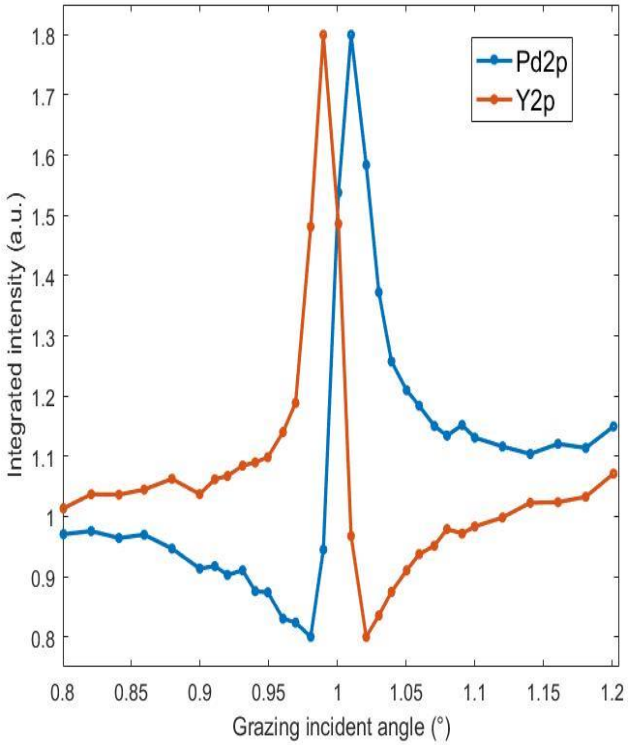
From HAXPES spectra to XSW curves





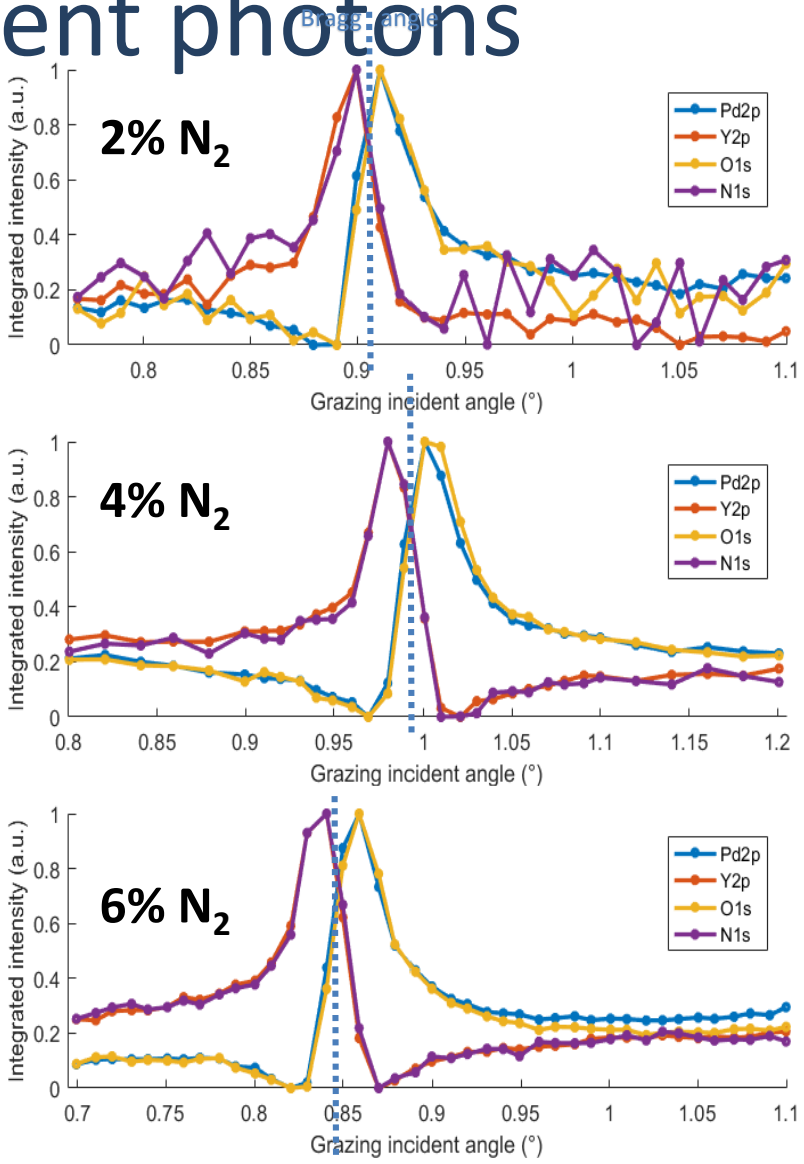


Integrate the peak considering a Shirley background.



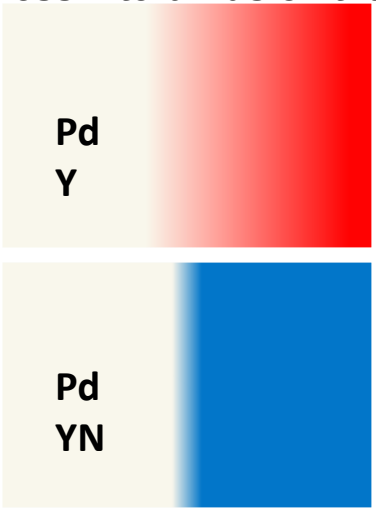
Result: XSW curves measured with 10 keV incident photons

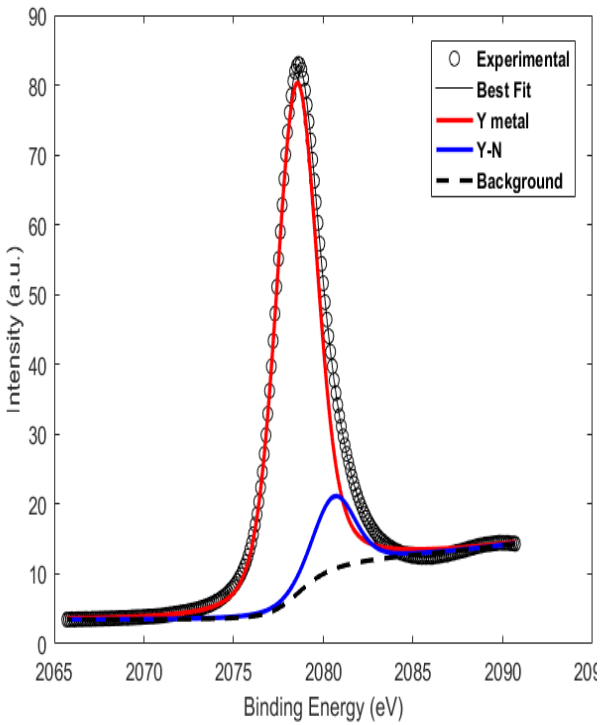
- **Bulk sensitive.**
- **XSW curves, extracted from photoemission spectra, of the Pd/Y multilayers prepared with 2, 4, 6 and 8% of N_2 respectively measured with a 10 keV incident photon energy.**
- **Elemental information in the stacks. Chemical selectivity.**
  Pd & O **Y & N**

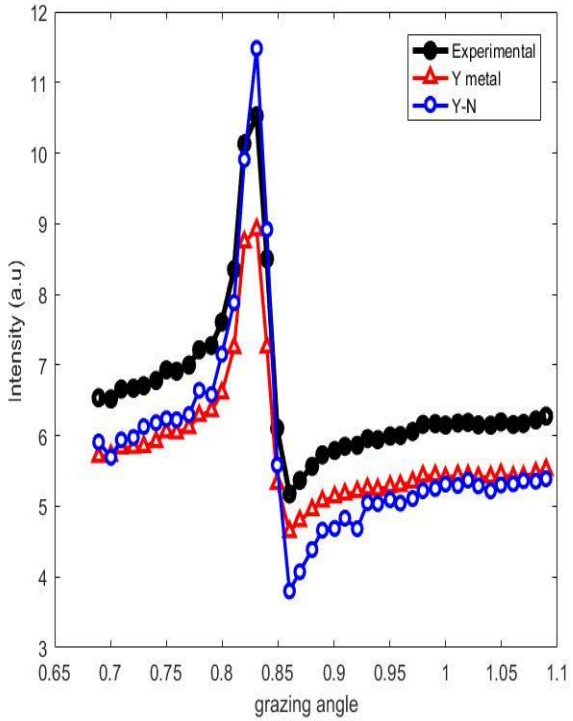


Decomposition of Y 2p3/2 spectra

- **Distribution of chemical states.**
- **4-peak model was used to fit the spectra, only 2 peaks are necessary.**
- **Only Y metal and YN are presented in the Y layers.**
- **According to the XSW curve contrast, YN has less interdiffusion than Y.**



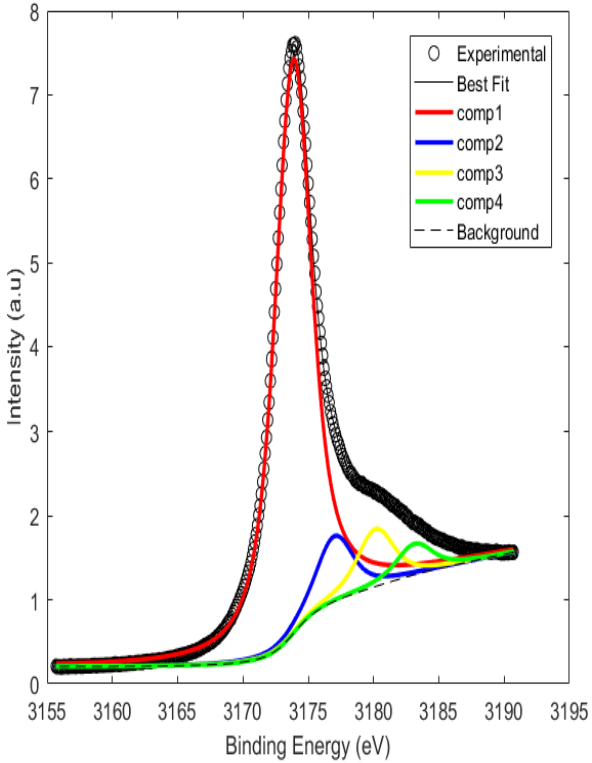


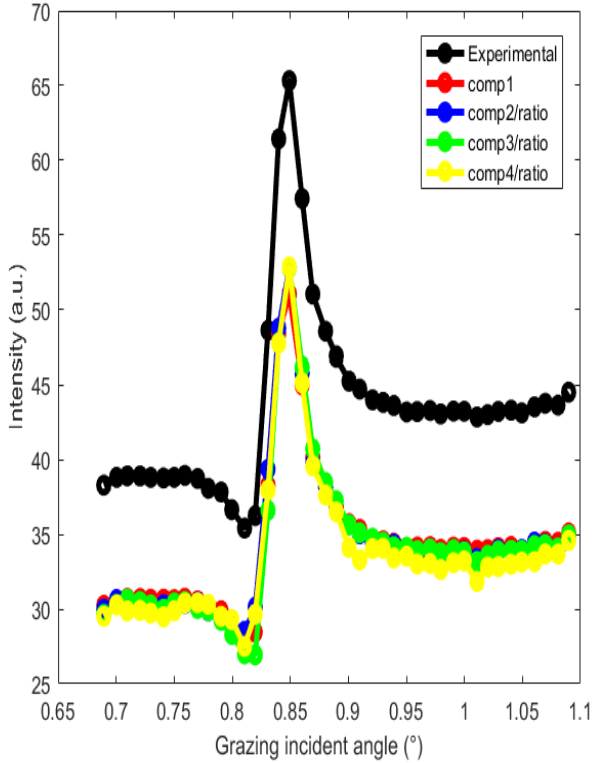


Y $2p_{3/2}$ photoemission spectrum of the sample with 6% nitrogen in the sputtering gas (left), and the XSW curves corresponding to the sub-peaks (right).

Decomposition of Pd 2p3/2 spectra

- **Distribution of different chemical states.**
- **XSW curves are normalized with the ratio compared to the main sub-peak.**
- **Multiple components have the same XSW curve.**
- **Homogeneous distribution of Pd and its oxides? No.**
- **Shake up satellite peaks**
- **=> oxide peak too close to metal peak.**

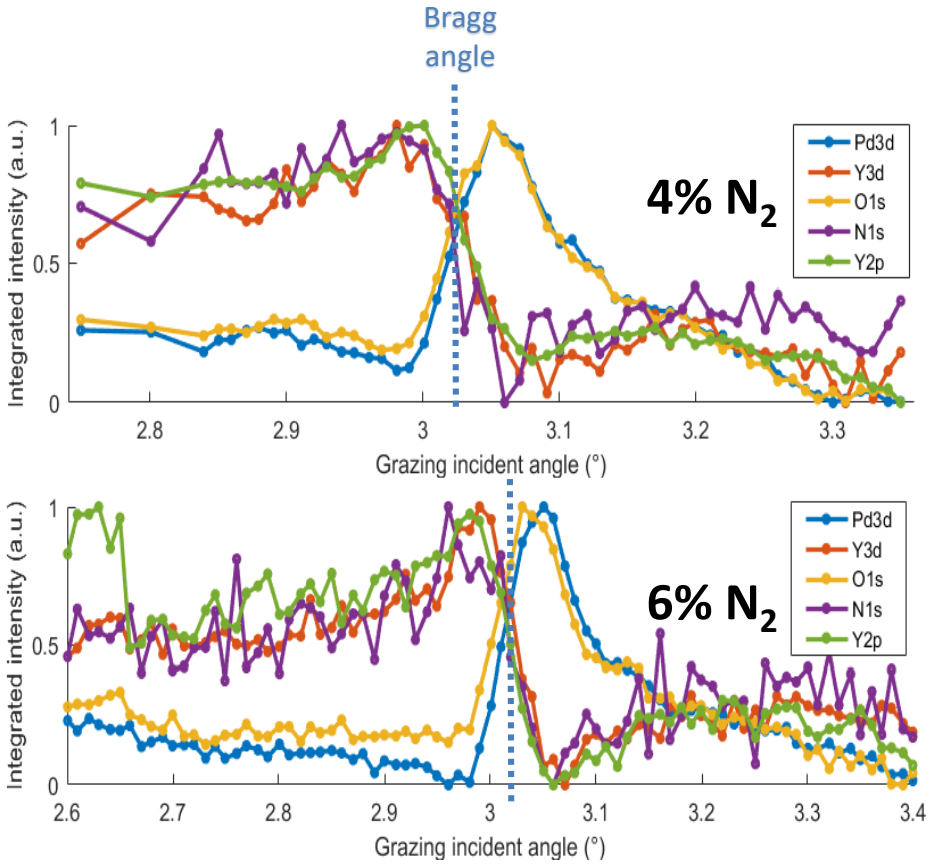




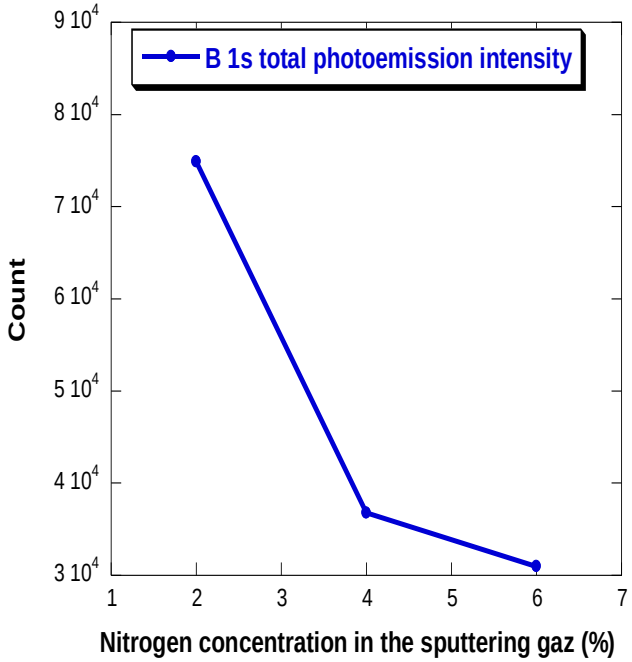
Pd $2p_{3/2}$ photoemission spectrum of the sample with 6% nitrogen in the sputtering gas (left), and the XSW curves corresponding to the sub-peaks (right).

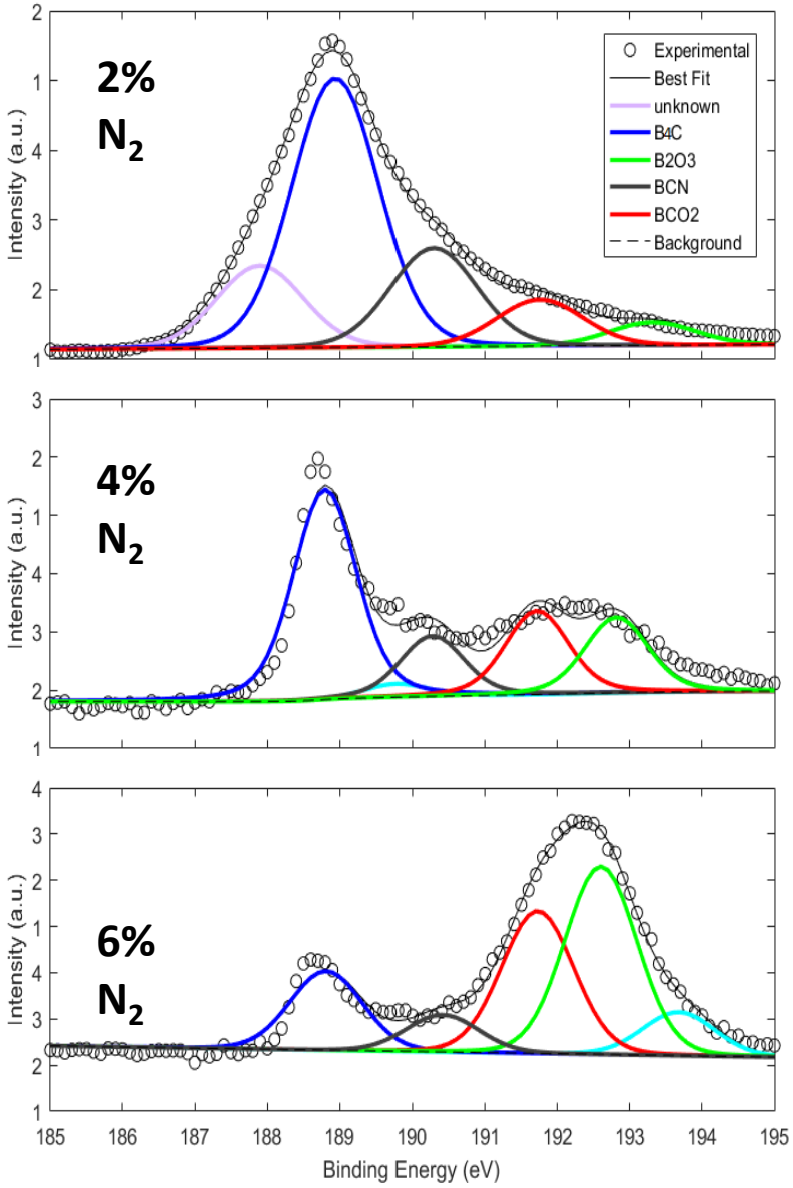
Result: XSW curves measured with 3 keV incident photons

- **Surface sensitive.**
- **XSW curves, extracted from photoemission spectra, of the Pd/Y multilayers prepared with 2, 4 and 6% of N_2 respectively measured with a 3 keV incident photon energy.**
- **2% data unreliable due to instrumental problem.**
- **Elemental information in the stacks. Chemical selectivity.**
  Pd & O **Y & N**



Decomposition of B 1s spectra

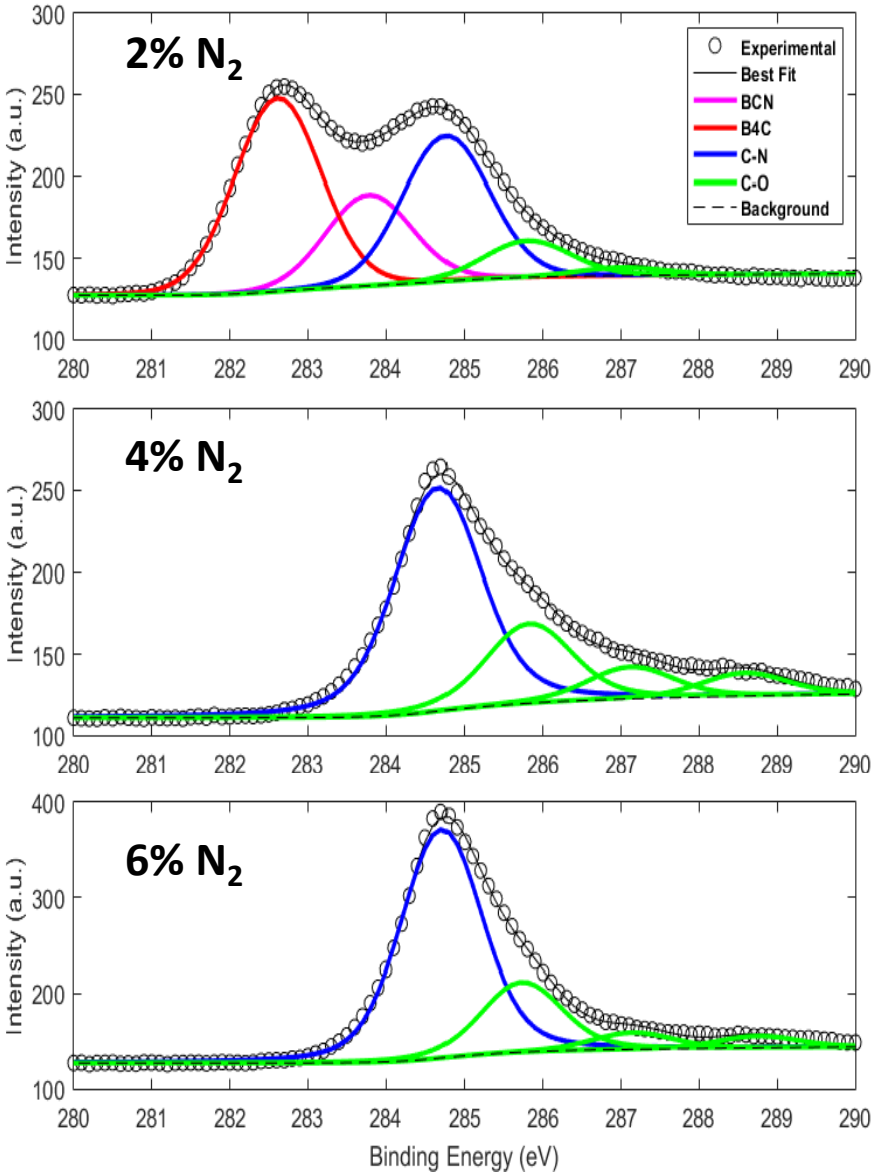




- B 1s total photoemission intensity decreases.
- B_4C component decreases.
- Cap material loss.

Decomposition of C 1s spectra

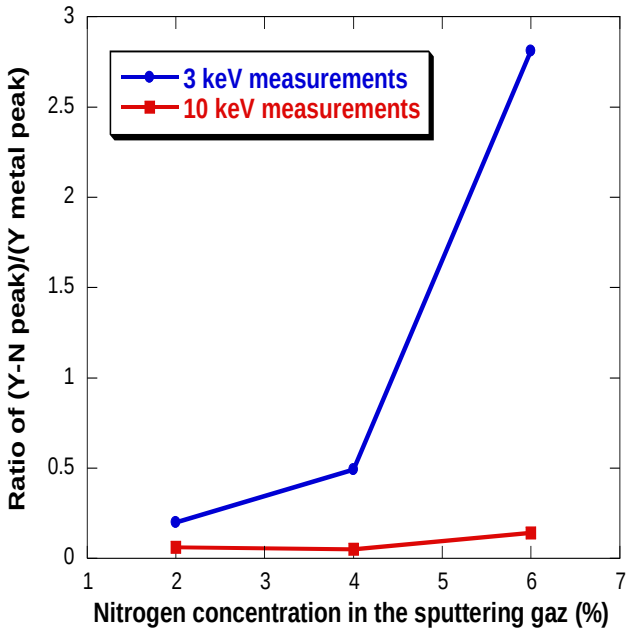
- B_4C component almost entirely disappears.
- Contamination becomes dominant.
- Cap material loss confirmed.
- Due to change of deposition rate.

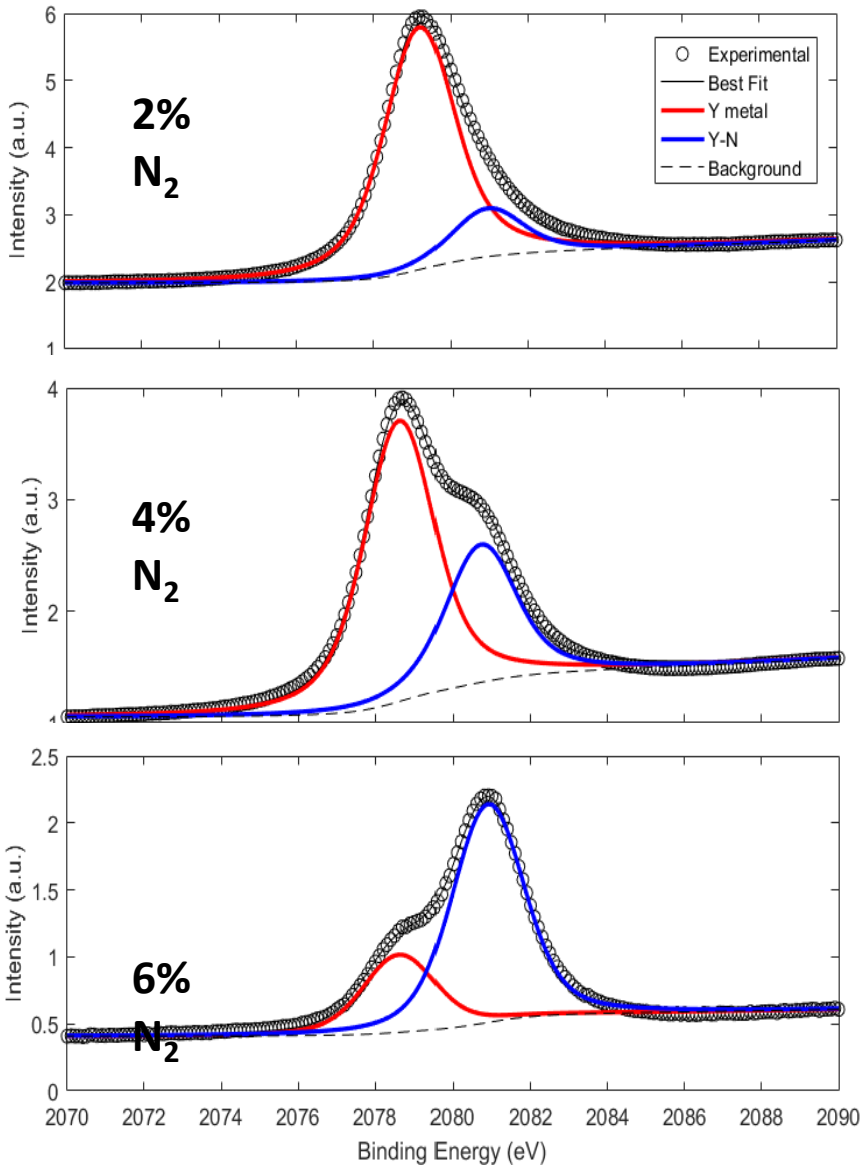


Wang *et al.* "Nitridated Pd/B4C multilayer mirrors for soft X-ray region: internal structure and aging effects," Opt. Express. 25, 7749 (2017).

Decomposition of Y 2p3/2 spectra

- Unexpected variation of YN concentration which only happens on the surface.





- The effect of X-ray standing wave enhancement is clearly observed.
- The information of elemental distribution is obtained indicating a chemical selectivity among the elements:

  Y ♡ N Pd ♡ O
- Only Y metal and YN are presented in the Y layers. The formation of YN improves the optic performance of the multilayers.
- There is B_4C cap material loss when we add nitrogen in the sputtering gas due to the change of deposition rate.

- Les ondes stationnaires (XSW)
- XSW – XRF: Co/Mg/Zr
- XSW – HAXPES: Pd/Y/B4C
- Kossel – XRF: Pd/Y/B4C

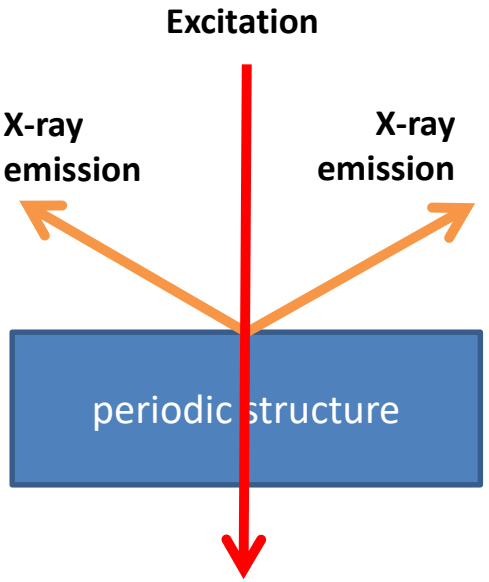
Particle Induced X-ray Emission

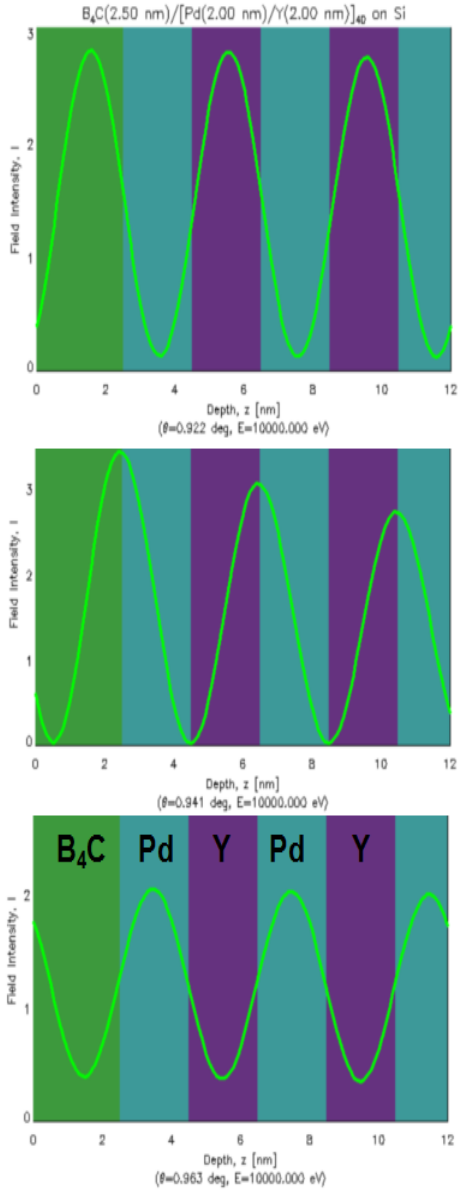
- Particle Induced X-ray Emission (PIXE)
  - Ionization: particle generated core hole
  - X-ray emission (fluorescence)
- SAFIR platform in SU
  - Système d'Analyse par Faisceaux d'Ions Rapides
    (Analysis System using fast ions)
  - Van de Graaff accelerator of positive ions
  - 2 MeV proton beam, ionization of Pd L shell
- Advantages of protons
  - Low scattering
  - Low Bremsstrahlung
  - Low energy loss (0.5% after penetrating the multilayer)
  - Uniform ionization cross section

Van de Graaff accelerator in SAFIR

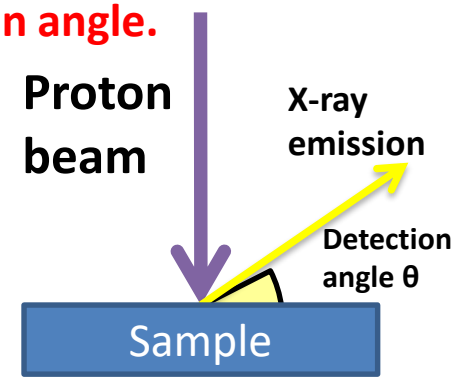
Combine PIXE with Kossel diffraction

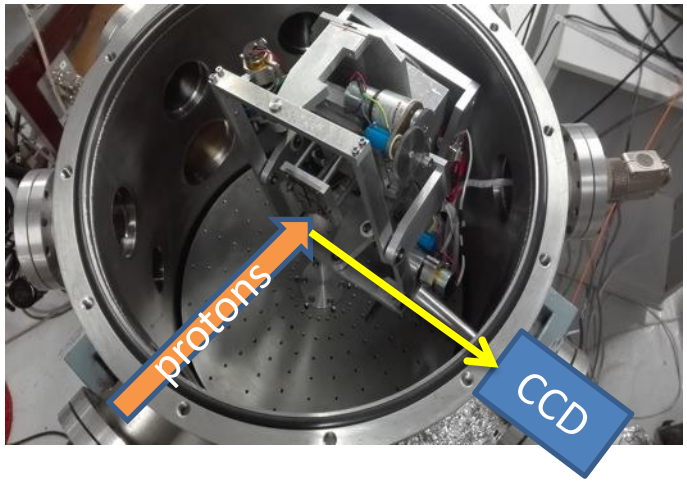
$$D = \frac{\lambda}{2\sin\theta} = \frac{2\pi}{Q}$$



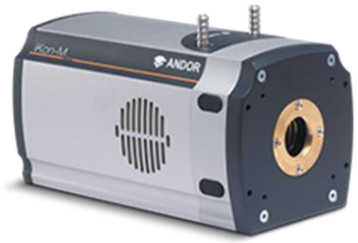


Measurement of X-ray emission intensity as a function of the detection angle.





Energy dispersive CCD



Andor Ikon-M CCD

~150 eV resolution @5.9 keV

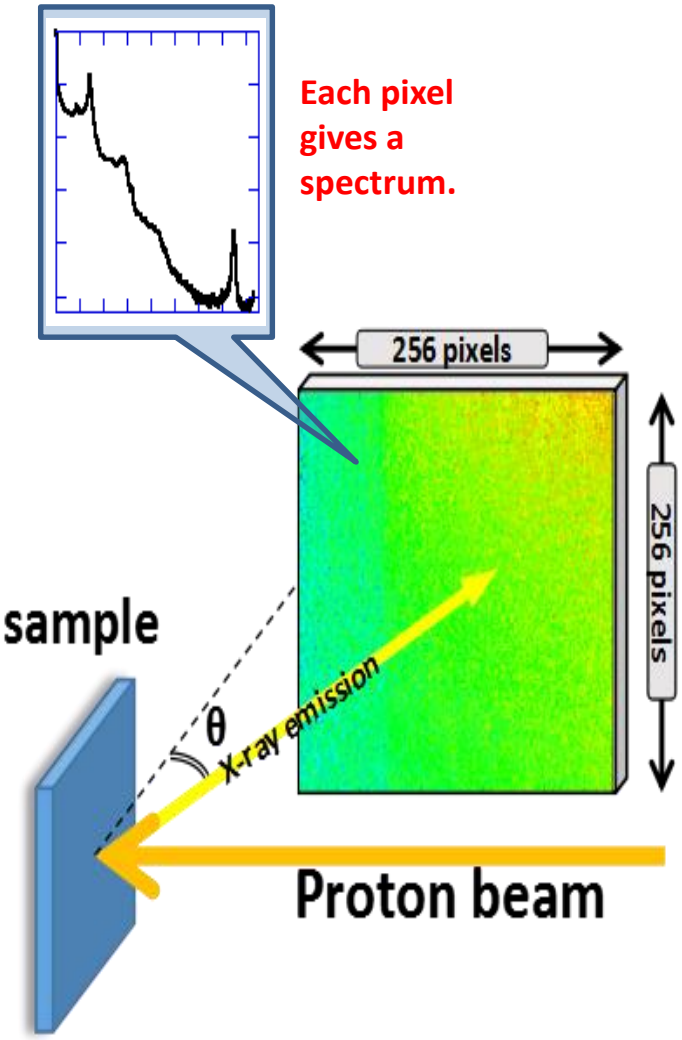
- Advantage: spatially resolved
  - Measurement of X-ray emission intensity in a squared area of about 13 x 13 mm
  - Native: 1024 x 1024 sensor array with 13 x 13 µm pixels
  - Our selection: 256 x 256 pixels of 52 x 52 µm

>>> 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

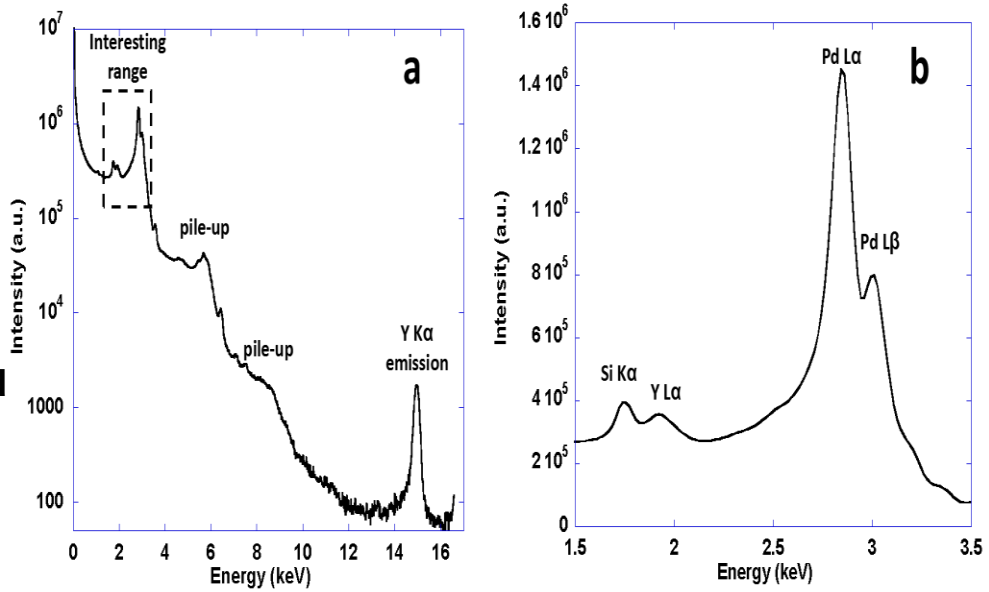
- Acquisition time significantly reduced compared to SDD

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



X-ray emission spectrum

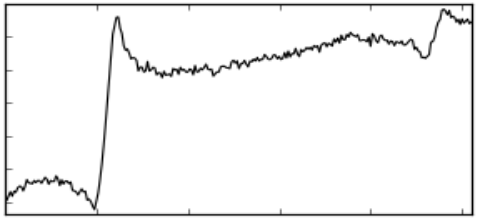
- B_4C(2.5 nm)/[Pd(2 nm)/B_4C(2nm)/Y(2nm)]$_{x40}$/Si
- Energy resolution is about 150 eV at 5.9 keV (Mn Kα).
- Pd Lα Lβ, Y Lα Kα, Si Kα can be observed
- Pile up effect due to multiple photons detection
- Energy calibration of the spectrum is carried out with
  Pd Lα (2.838 keV) and Y Kα (14.958 keV)



- Y Kα has too low intensity.
- Y Lα, Si Kα are in the low efficiency part of the X-ray camera.
- Pd Lβ does not bring additional infomation
- **We measure Pd Lα emission**

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

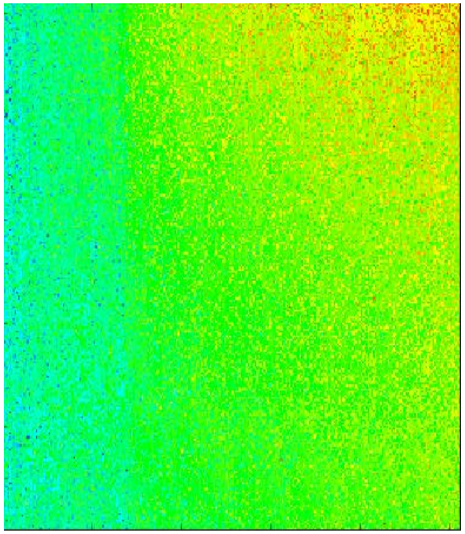
Kossel curves



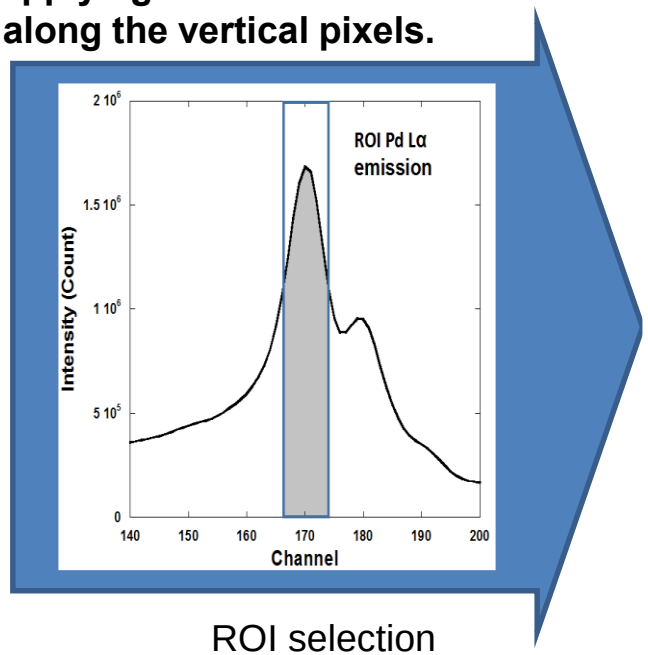
- **The original image obtained by X-ray color camera contains the intensity of emitted photons of all energies.**
- **Kossel curve: the angular distribution of the characteristic X-ray emission.**
- **Too get the Kossel curve of Pd Lα emission, we need 3 steps:**

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.**

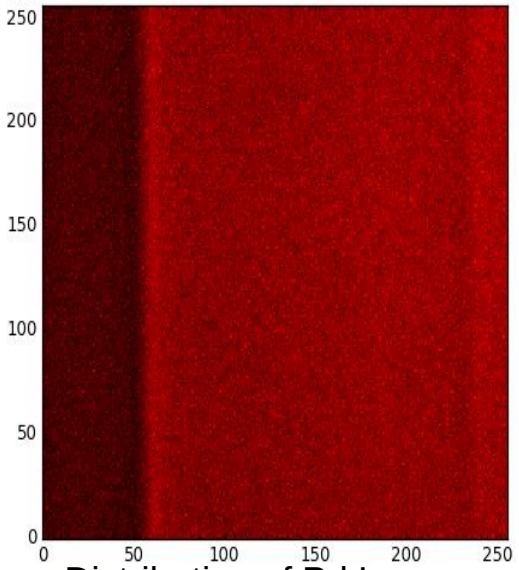
Integrate along the vertical pixels



Distribution of X-ray emission



ROI selection



Distribution of Pd Lα

Calibration of detection angle

- Pixel of the detector - grazing exit angle
- 4-layer sample:

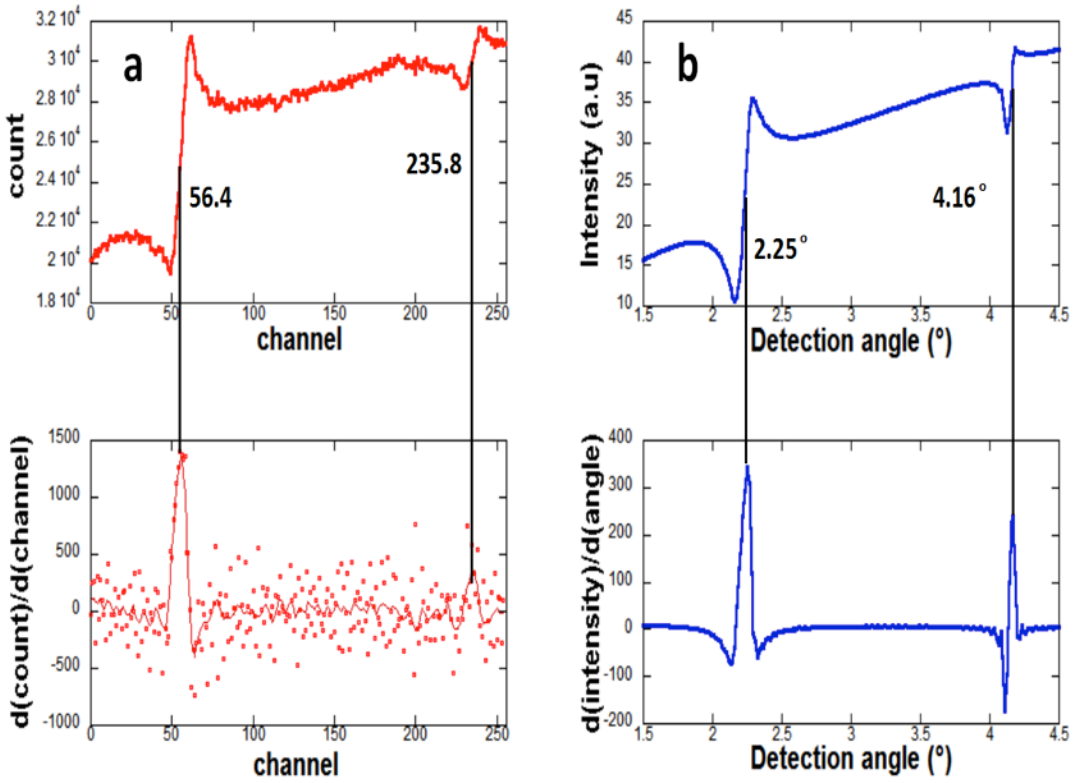
B_4C(2.5 nm)/[B_4C(1 nm)/Pd(2 nm)/B_4C(1 nm)/Y(2 nm)]$_{x40}$/Si

- 1st and 2nd order of Kossel ocillation

a) experimental curve in channel (pixel)

b) simulated curve in angle (degree)

- Precise values obtained from the derivatives of the curves



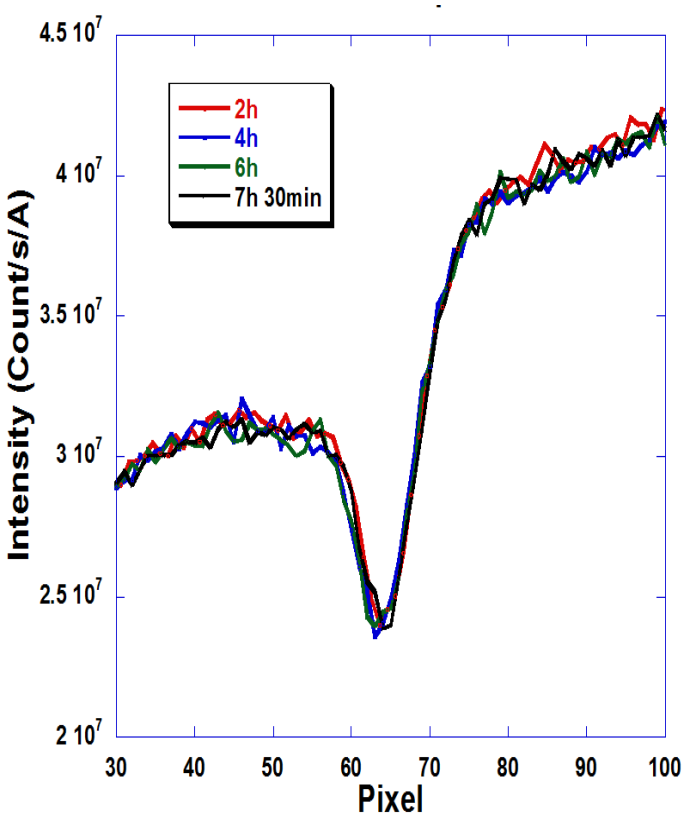
Non-destructive test

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

The structure is not changed after 7.5 h exposure

Standard measure time is 2 h

The measurement is non-destructive

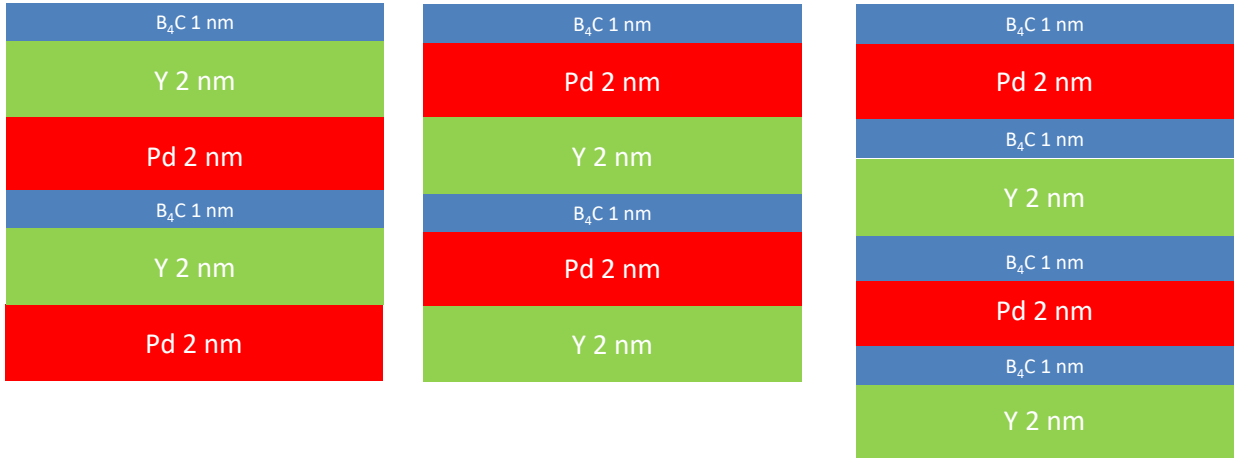


First observations of multilayer structures

It is known that Pd and Y intermix easily during magnetron sputtering, and thus need stabilising

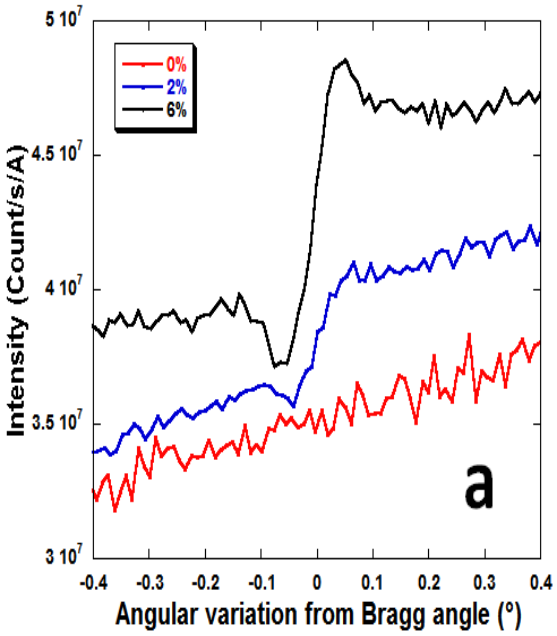
Interface engineering:

- Introduce N_2 into the plasma during growth – 0%, 2%, 6%
- Use 1 nm B_4C buffer layers

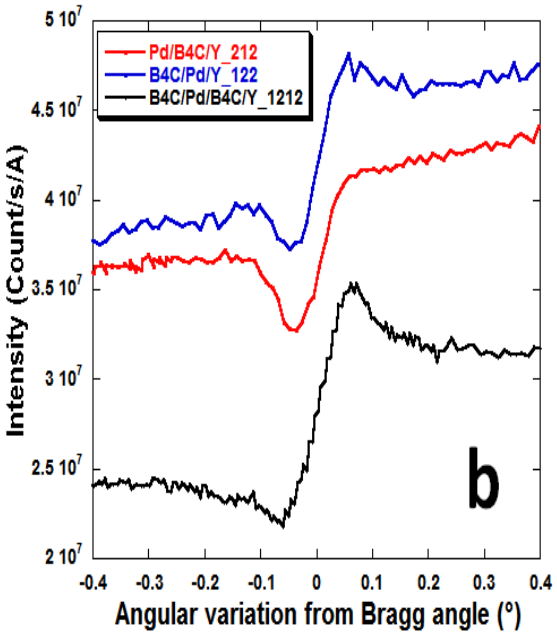


Kossel curves of Pd Lα emission

- **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.



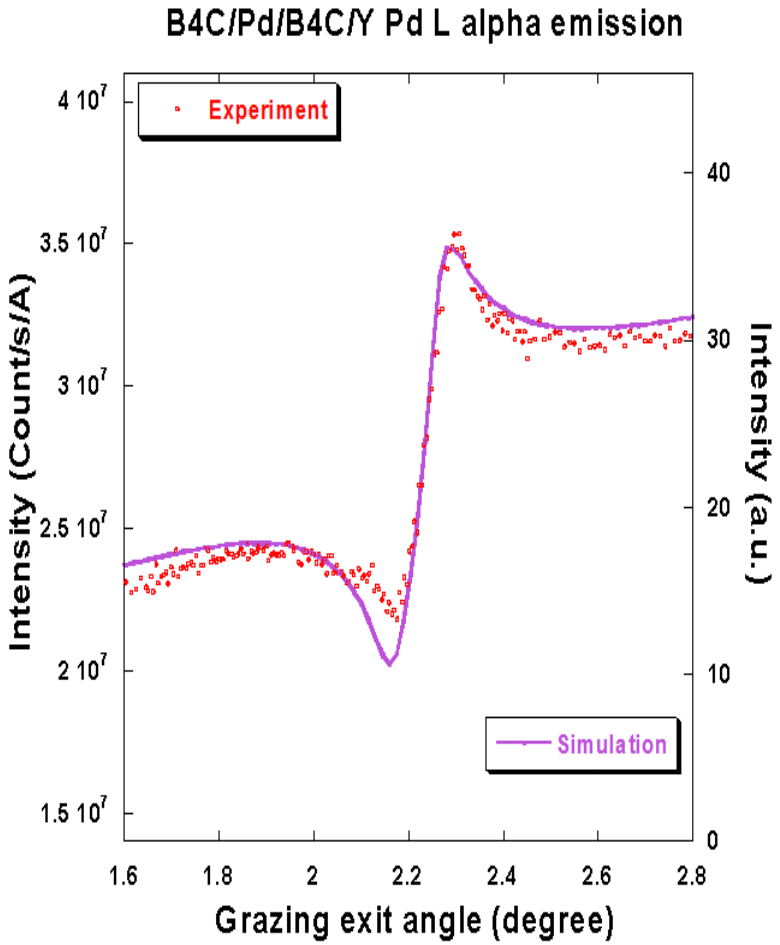
Kossel curves of the series of samples:
b) With B_4C barrier layers. The notation gives multilayer structure and layer thickness respectively.

Simulation

- Simulation of the PIXE-Kossel curve
- Code for XRF-Kossel curve

- Approach
- Uniform ionization

- Still not perfect due to background
- Improvement needed



CONCLUSION

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