

La diffraction de Kossel combinée à l'émission X induite par protons pour l'étude de multicouches nanométriques

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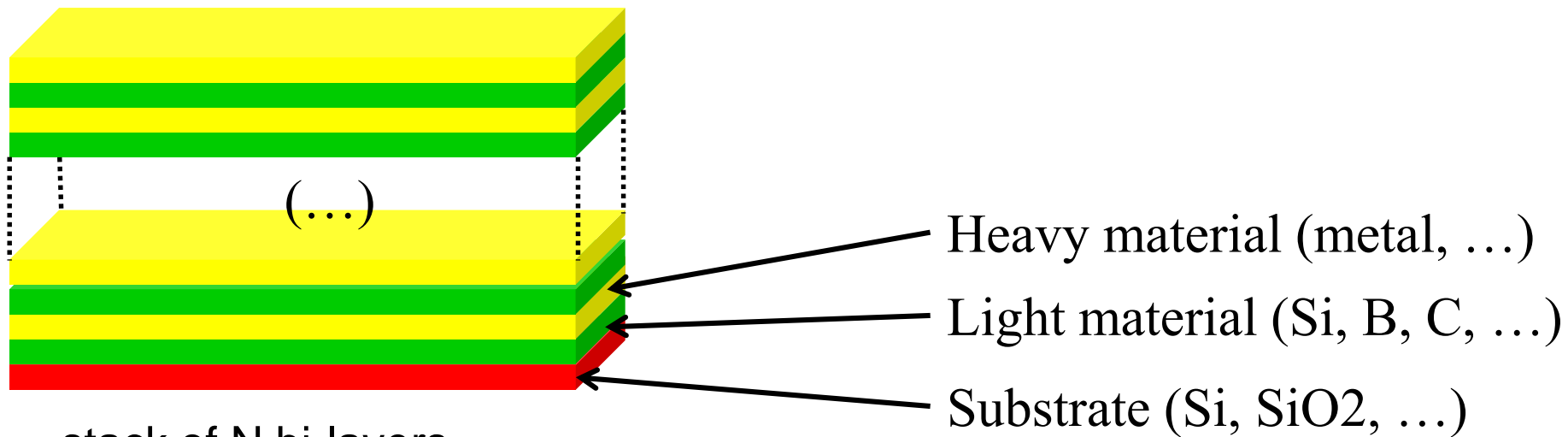
LAMS, Sorbonne Université, CNRS UMR 8220, Paris

IPOE, Tongji University, Shanghai, Chine



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



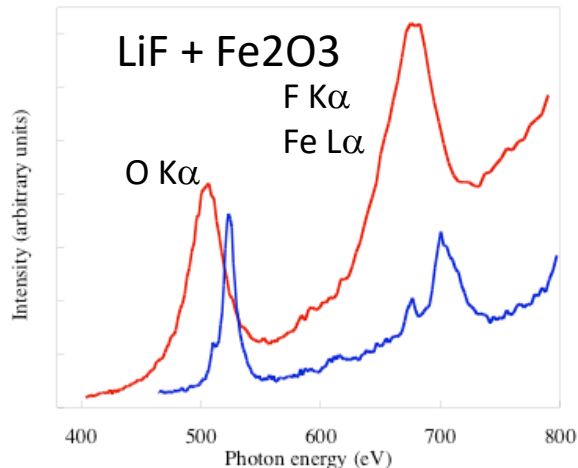
thickness_{light} + thickness_{heavy} = period d of a few nm

↳ 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

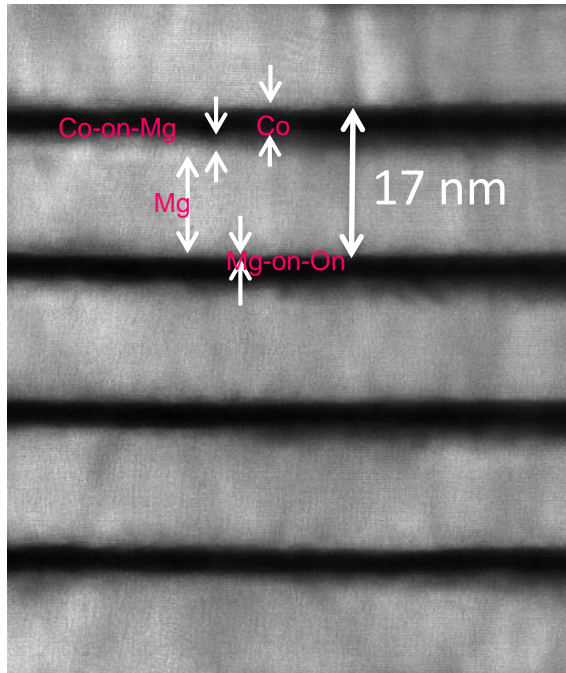


Imaging at a given wavelength

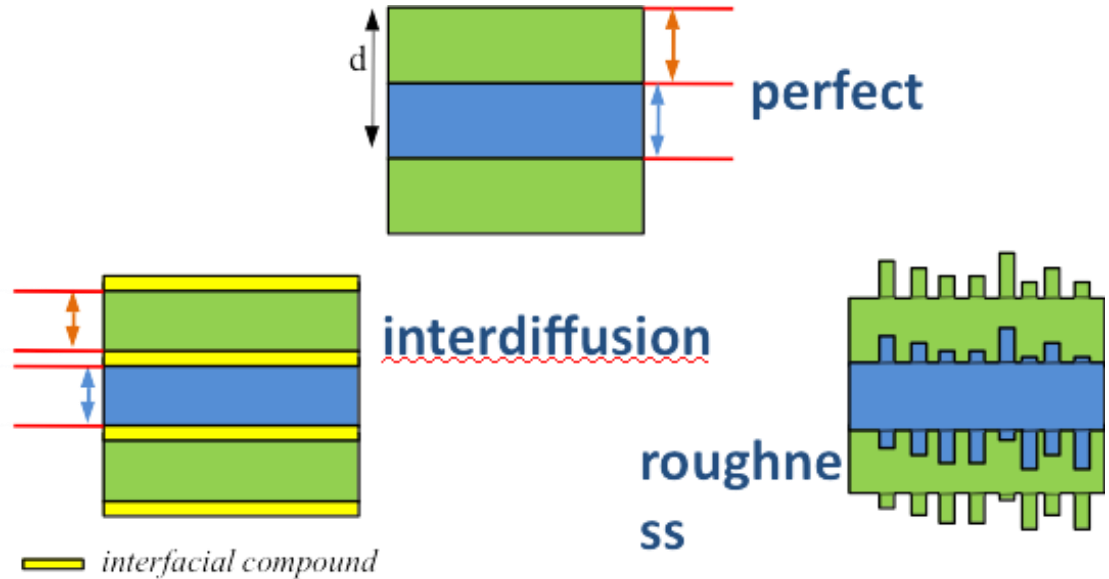


Photolithography
@ 13.5 nm, 6.x nm

Motivation and challenges



Co
Mg
Co
Mg
Co
Mg

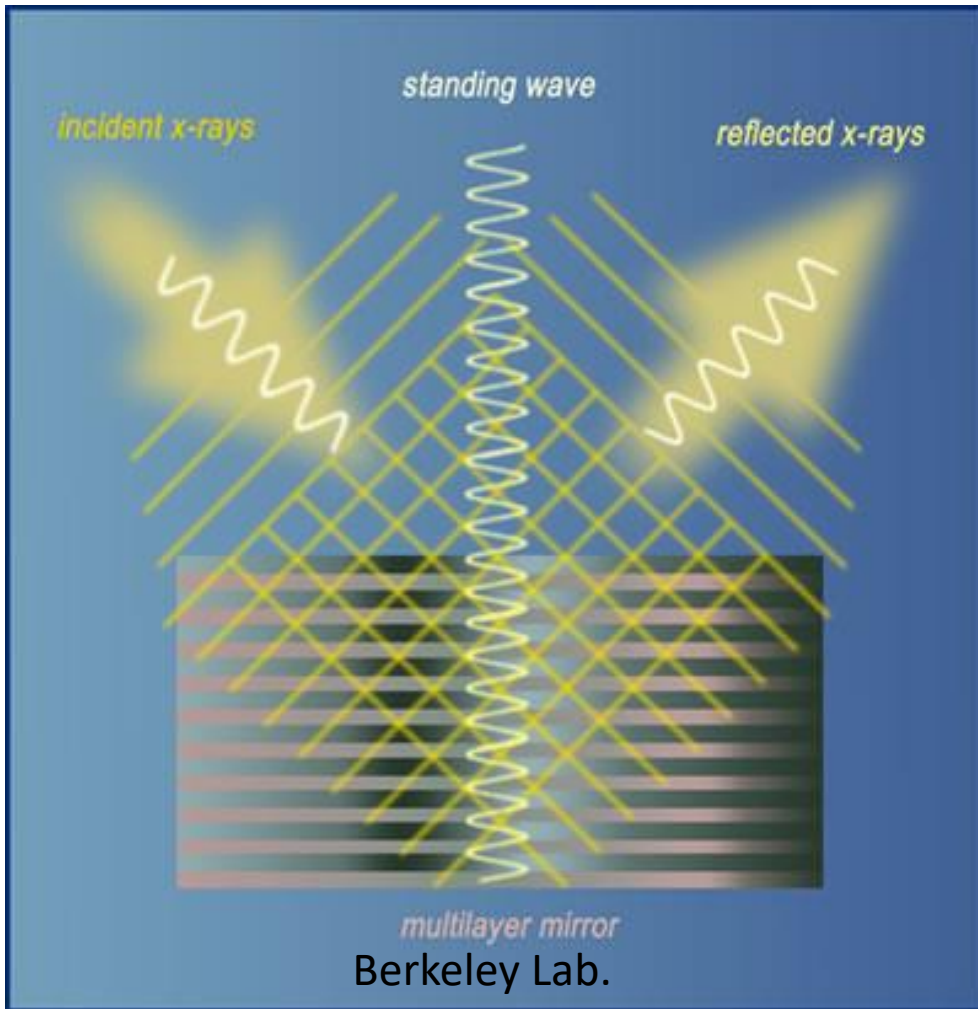


	Visible $\lambda=500\text{nm}$	EUV $\lambda=30.4\text{nm}$
d	$\sim 125\text{nm}$	Co_2.6nm/Mg_13.6nm
σ	$\sim 10\text{ nm}$	$\sim 0.5\text{-}0.8\text{nm}$

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

Interface is the largest challenge for EUV multilayer!

X-ray standing waves



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

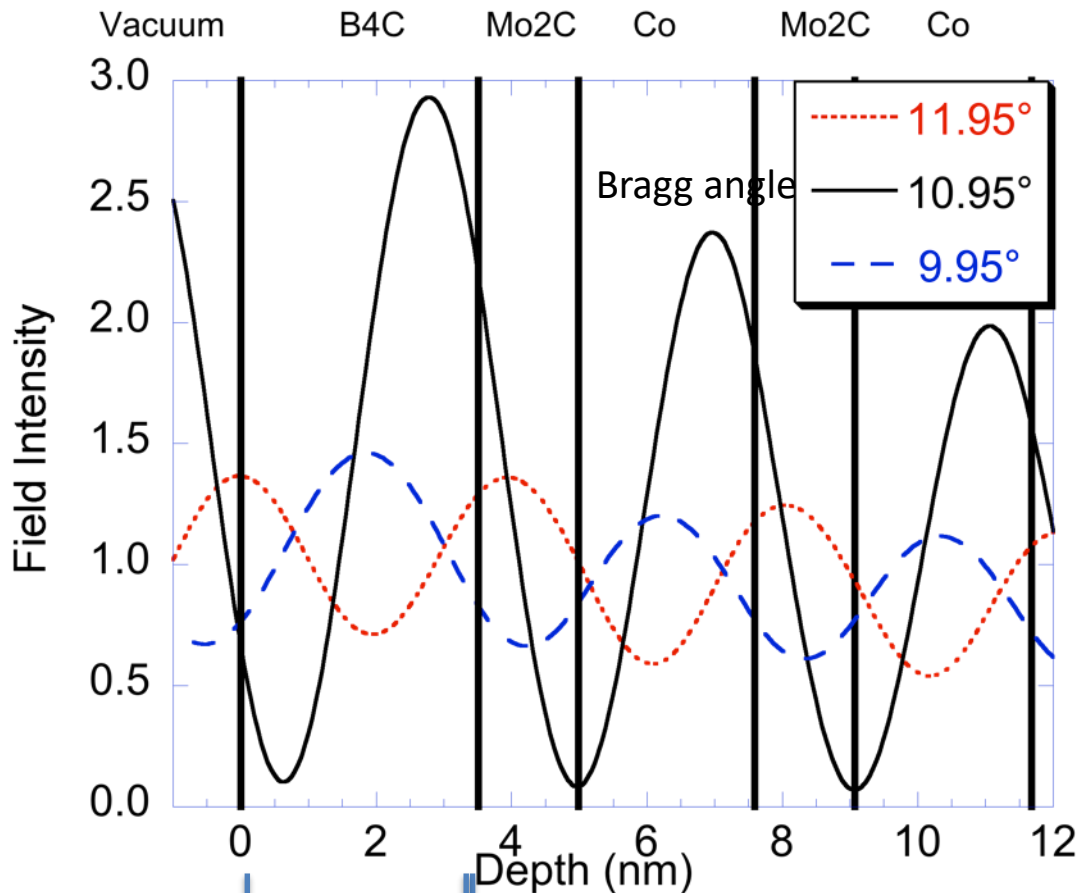
- Fluorescence or photoelectrons

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



Rotate sample
(change the wavelength)
Change incident or detection angle

↓
Shift of the maxima

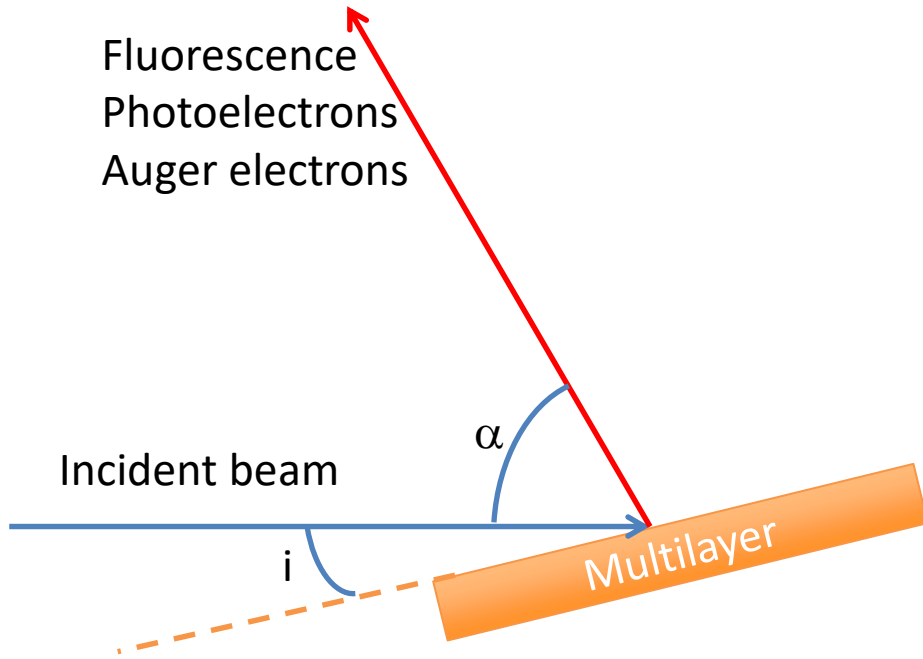
Analysis by

- XPS
- XRF
- AES

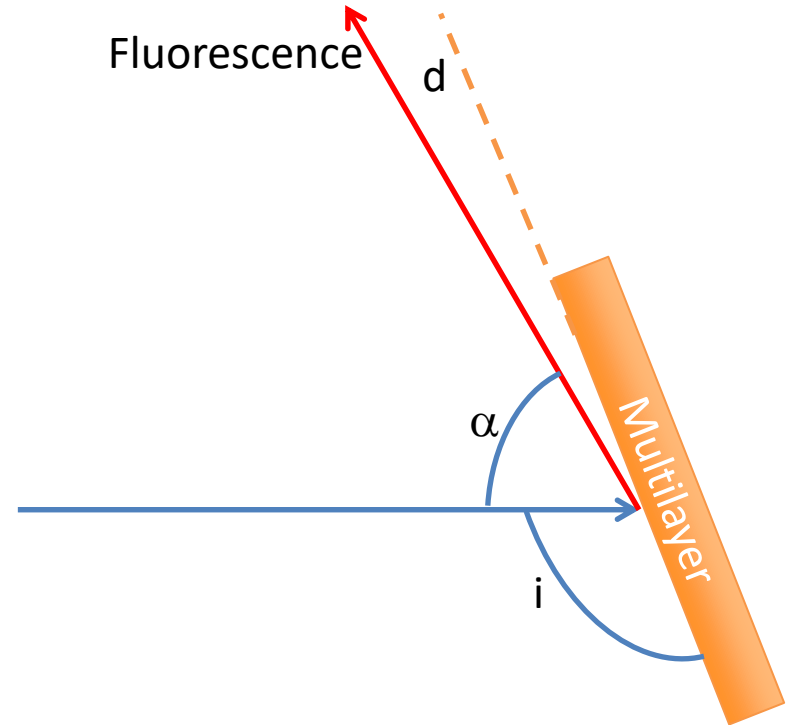
of a

- Multilayer
- Superficial material

Two XSW modes



Glancing incidence mode
“Normal” or GI



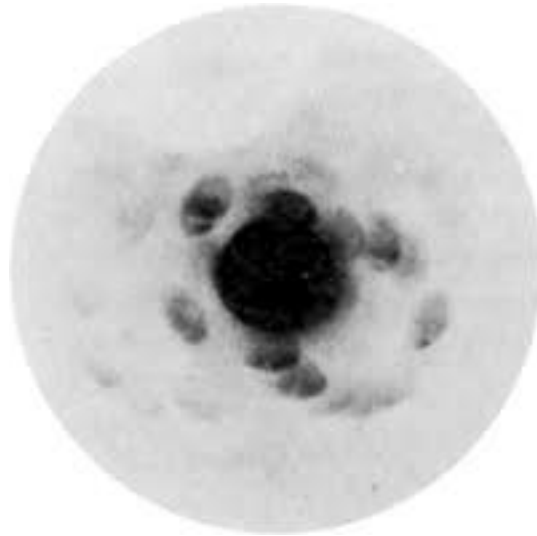
Glancing exit mode
“Kossel” or GE

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

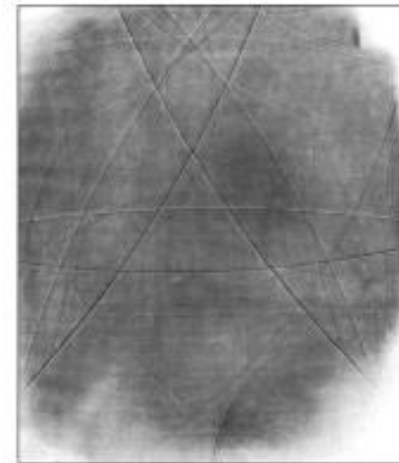
1912: von Laue, Friedrich, Knipping



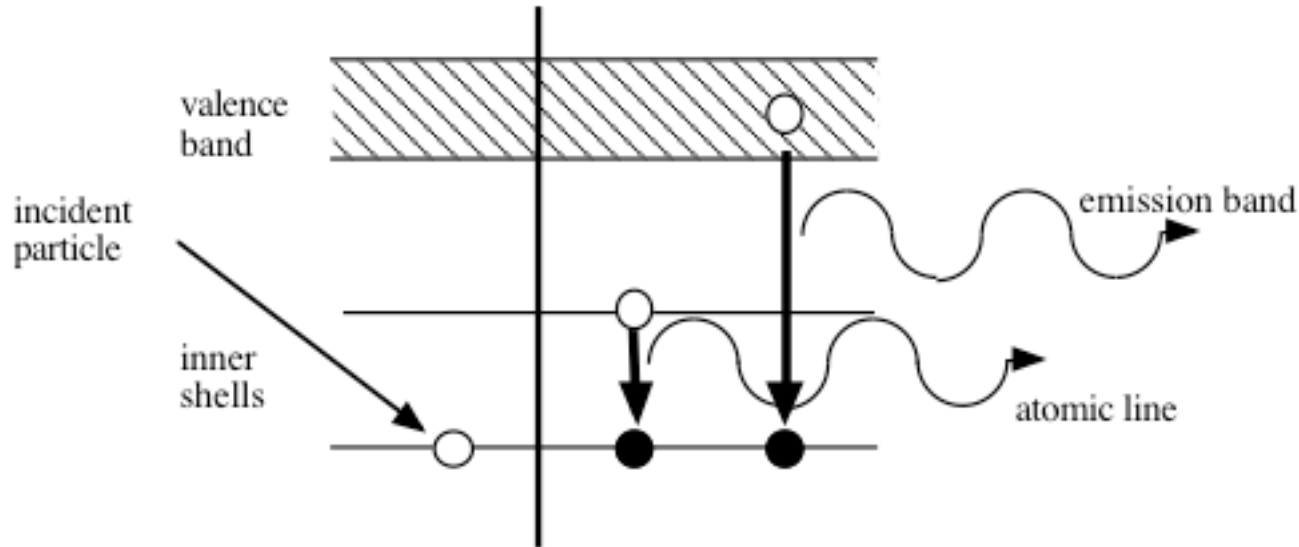
W. Kossel

1935

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



X-ray emission spectroscopy



Observation of the **intensity** and **energy** distribution of the emitted radiation

Information about the **number (concentration)** and **chemical state** of the emitting elements

Incoming beam

- Electrons (EPMA)
- **Particles (PIXE)**
- X-rays (XRF)

Detection / dispersion

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

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 shells.

- Advantages of protons

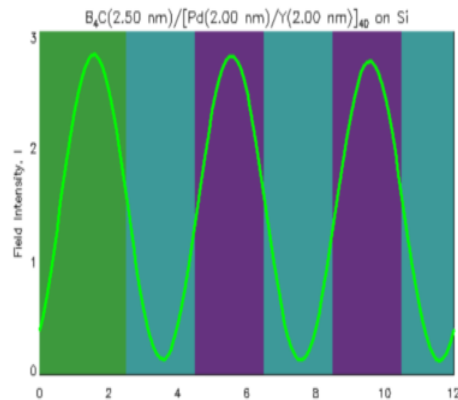
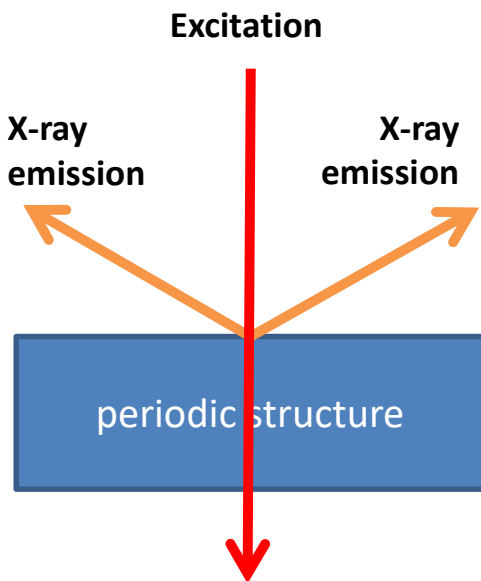
- Low scattering.
- Low Bremsstrahlung.
- Low energy loss (0.5% after penetrating the multilayer).
- Uniform ionization cross section.



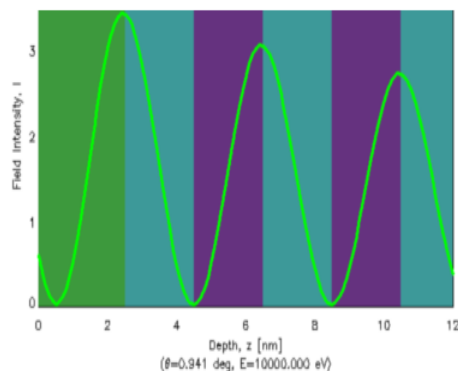
Accelerator in SAFIR

Combining PIXE with Kossel diffraction

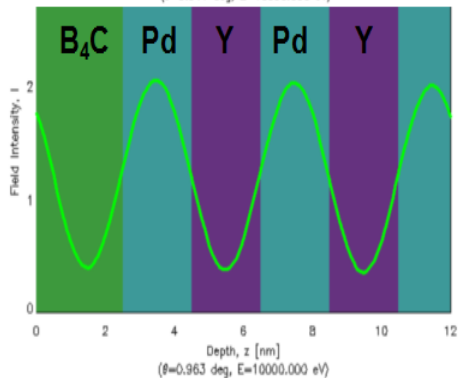
$$D = \frac{\lambda}{2 \sin \theta} = \frac{2\pi}{Q}$$



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

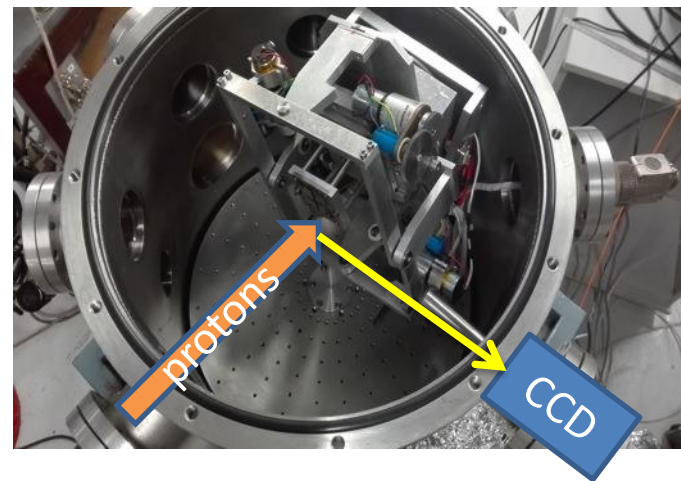
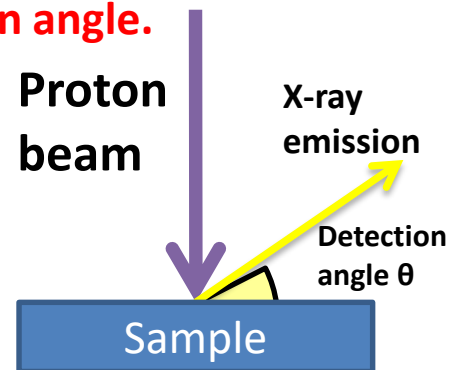


$\theta = \theta_{\text{Bragg}}$

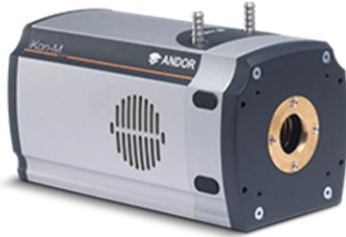


$\theta > \theta_{\text{Bragg}}$

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



Energy dispersive CCD



Andor Ikon-M CCD

~150 eV resolution @5.4 keV

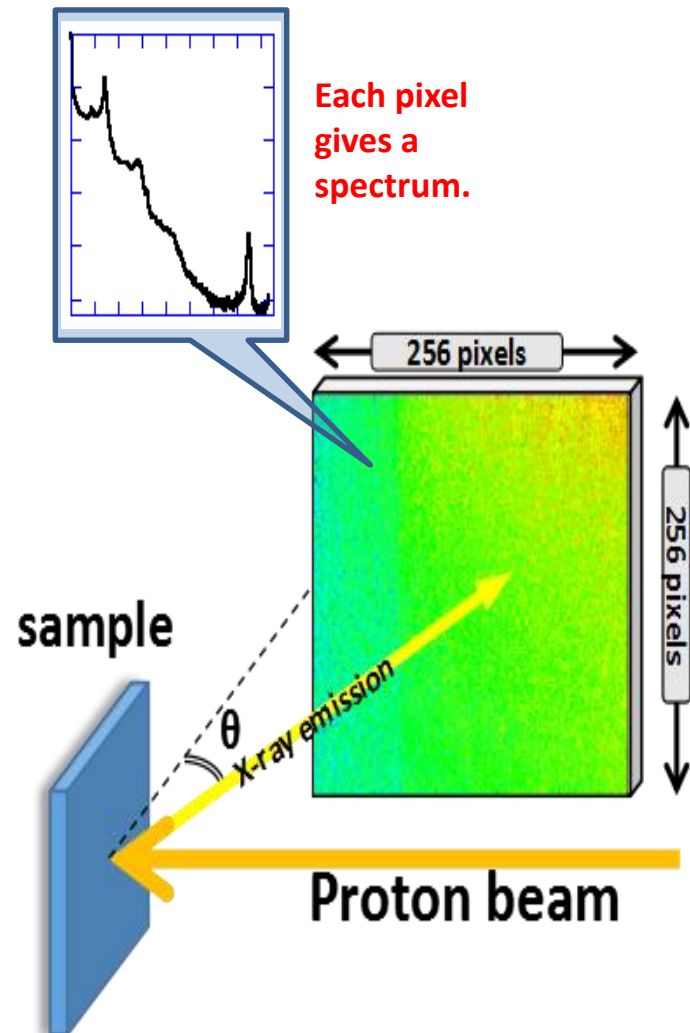
- **Advantage: spatially resolved.**

- 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 of 52 x 52 μm .

>>> **compromise of angular/energy resolution**

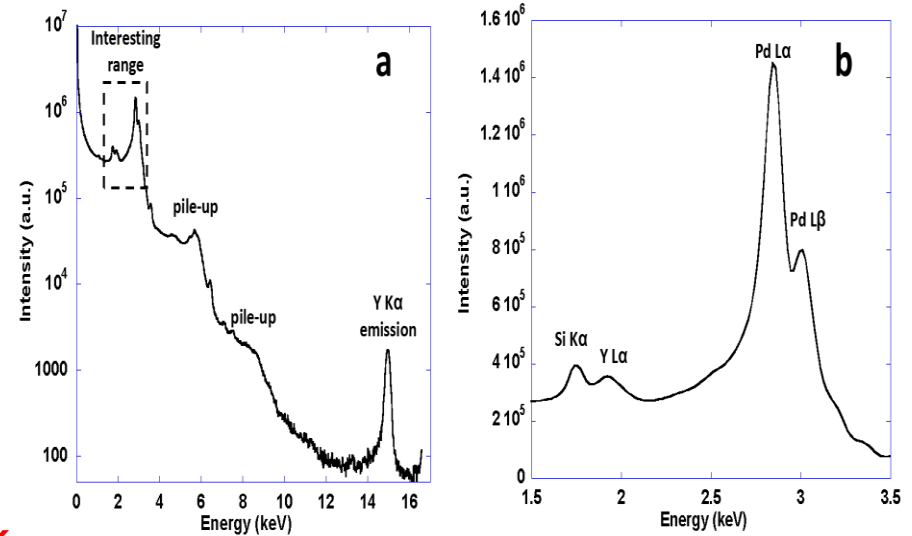
- No need to scan the angle.
- We place a 200 μm beryllium film in front of the camera to filter the scattered protons. **Protection of the camera.**
- Acquisition time significantly reduced compared to SDD.

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



X-ray emission spectrum

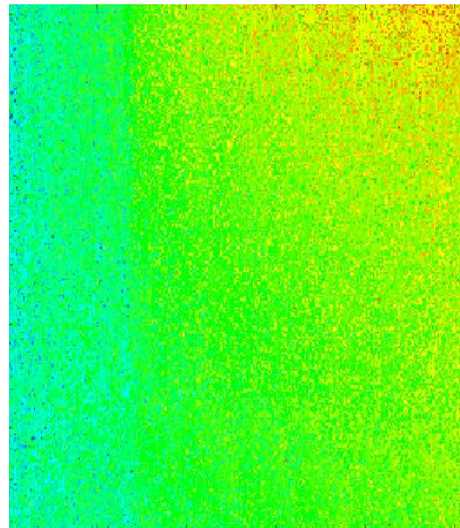
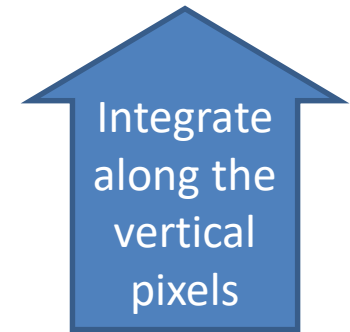
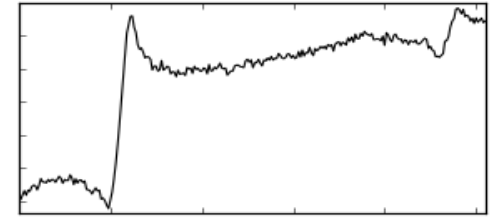
- $B_4C(2.5 \text{ nm})/[Pd(2 \text{ nm})/B_4C(2 \text{ nm})/Y(2 \text{ nm})]_{x40}/Si$
 - Energy resolution is about 150 eV at 5.9 keV (Mn $K\alpha$).
 - Pd $L\alpha$ $L\beta$, Y $L\alpha$ $K\alpha$, Si $K\alpha$ can be observed
 - Pile up effect due to multiple photons detection
 - Energy calibration 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**



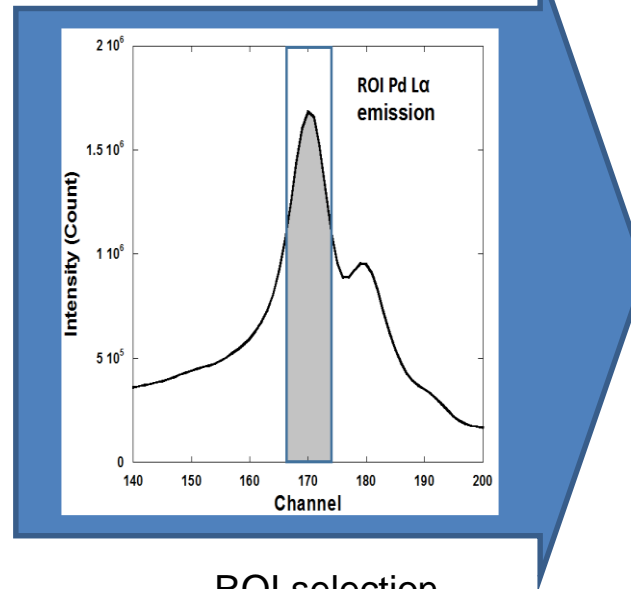
X-ray spectrum of Pd(2 nm)/ B_4C (2 nm)/Y(2 nm) multilayer:
a) overview (log scale)
b) zoomed range of interest (linear scale).

Kossel curves

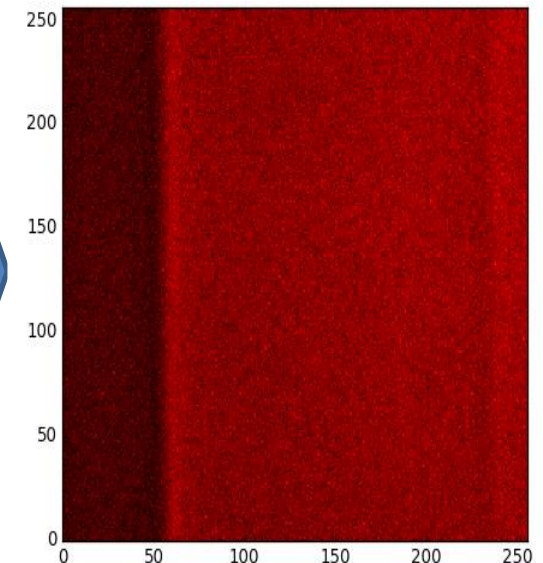
- The original image obtained by X-ray color camera contains the intensity of emitted photons of all energies.
- Kossel curve: the angular distribution of the intensity of a characteristic X-ray emission.
- To get the Kossel curve of Pd L α emission, we need 3 steps:
 1. Select region of interest (ROI) 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

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.

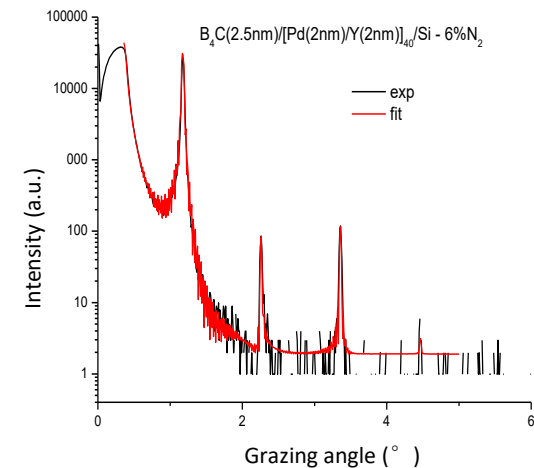
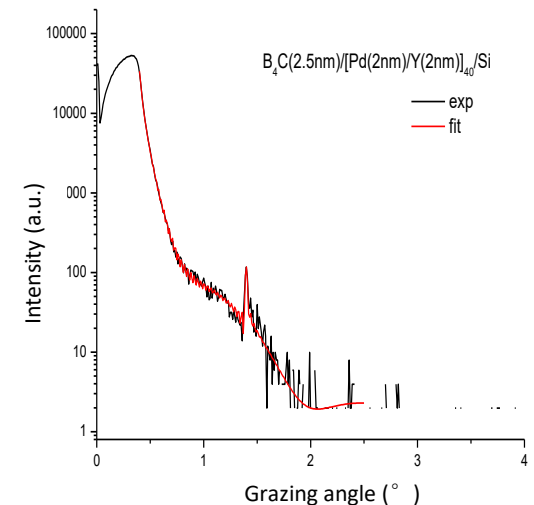
● Solution: Derivative systems

- 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).

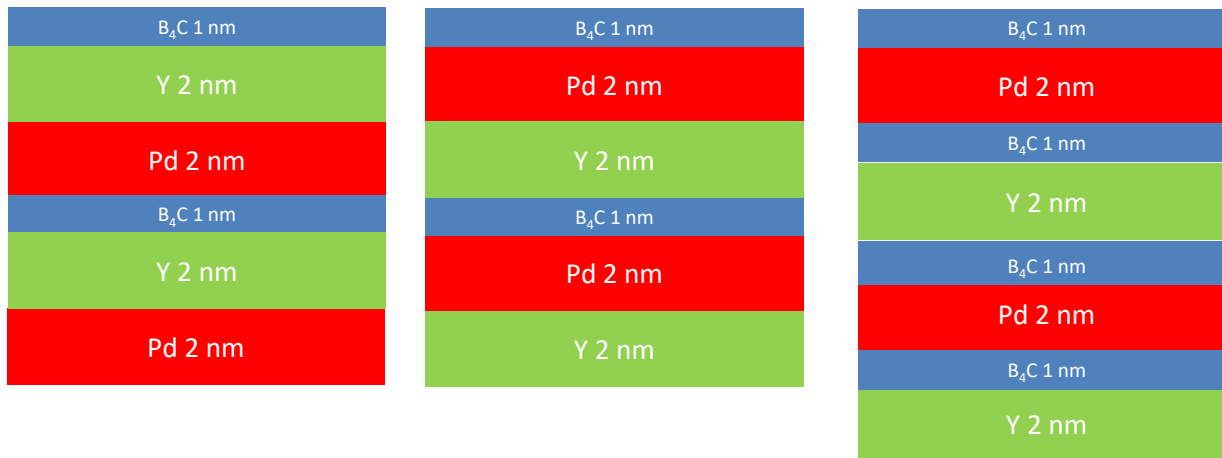
[2] Prasciolu *et al.*, "Thermal stability studies of short period Sc/Cr and Sc/B₄C/Cr multilayers," *Appl. Opt.* 53(10), 2126 (2014).

First observations of multilayer structure

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

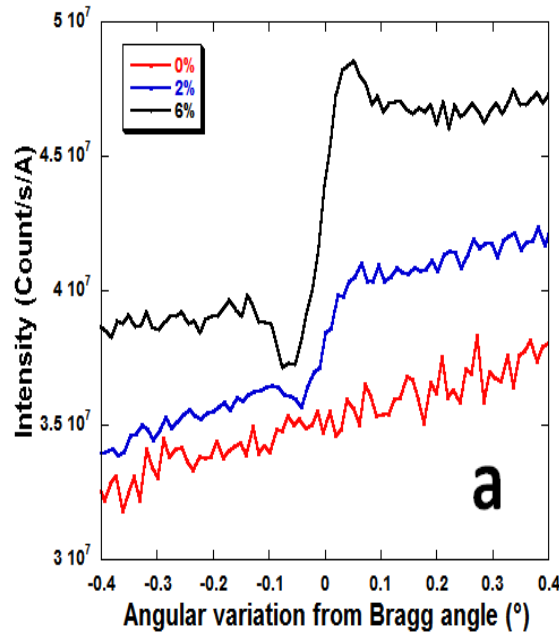
Strategies :

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

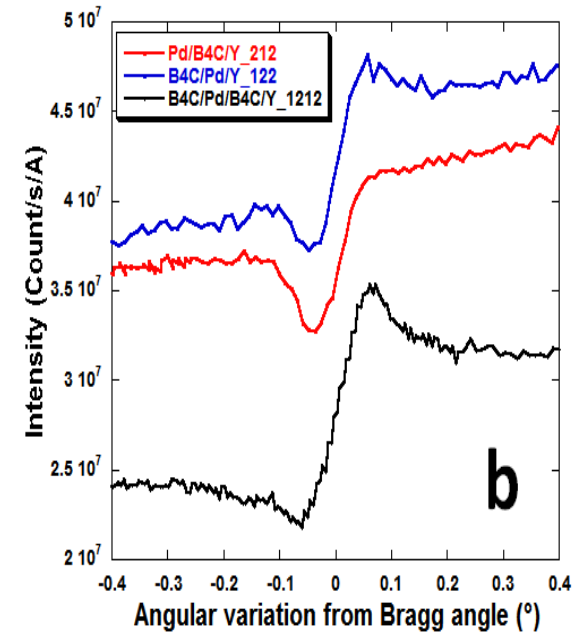


Kossel curves of Pd La emission

- 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 B₄C barrier layers. **Structural sensitivity.**



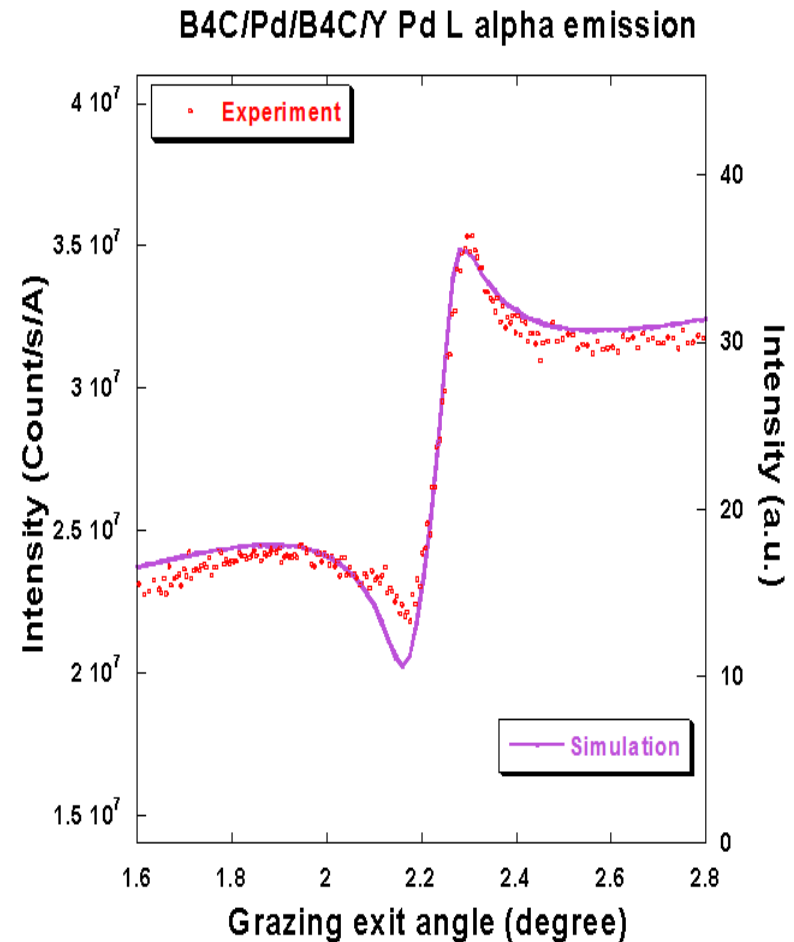
Kossel curves of the series of samples:
a) Deposited with nitrogen in the sputtering gas.



Kossel curves of the series of samples:
b) With B₄C 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

- We have observed the Kossel diffraction of proton induced Pd La emission in Pd/Y based multilayers.
- Nitridation has positive effect in preventing or reducing the interdiffusion between Pd and Y layers.
- The Pd/Y based multilayers with B₄C barrier layers located at different interfaces can be distinguished by their Kossel curves.
- Compared to our previous experiment, the data acquisition is much improved by using an energy dispersive CCD camera.
- We have developed a new method to characterize the multilayers: PIXE-Kossel.
 - Simple experimental setup.
 - Element specific diffraction patterns.
- Further work is required :
 - Improve handling of data from the CCD camera – background, frame rates etc
 - Improve theoretical simulations, including interface properties