Canadian Powder Diffraction Workshop 15

October 11 - 14, 2022

# Thin Film Characterization with X-Rays


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# TOPICS

1. Motivation
2. Is the film thin?
3. X-ray Attenuation

*Techniques:*

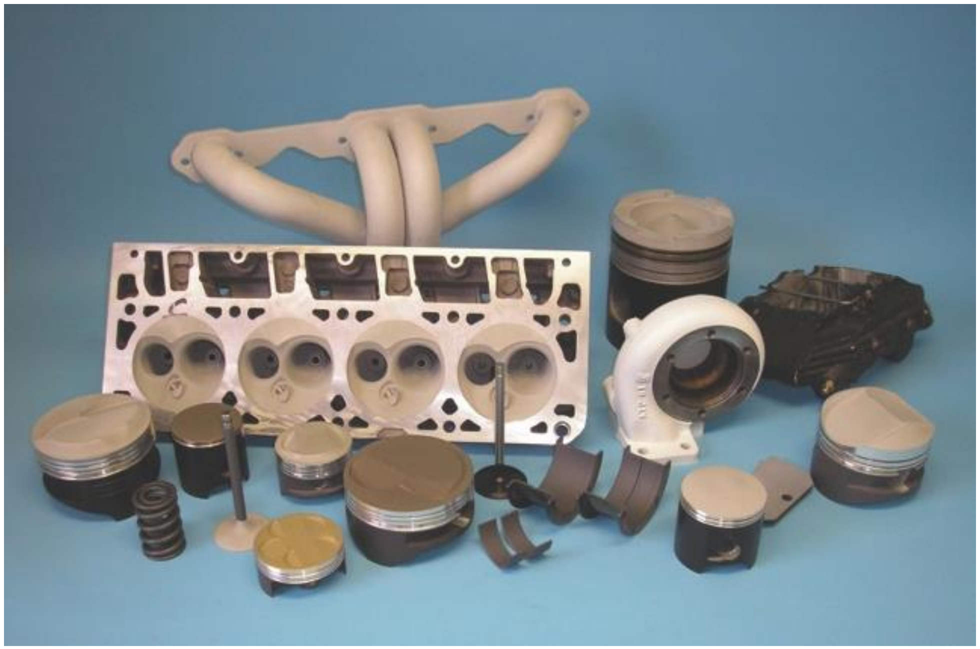
a) GI-powder XRD

b) GI-single crystal XRD

c) Reflectivity

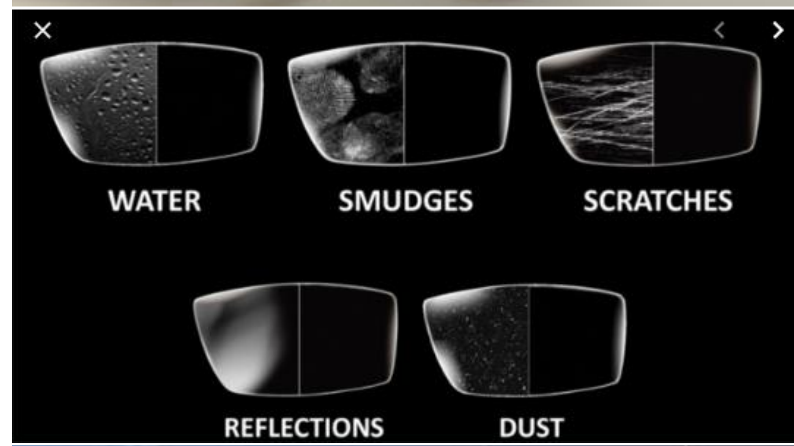
d) GISAXS

# Motivation

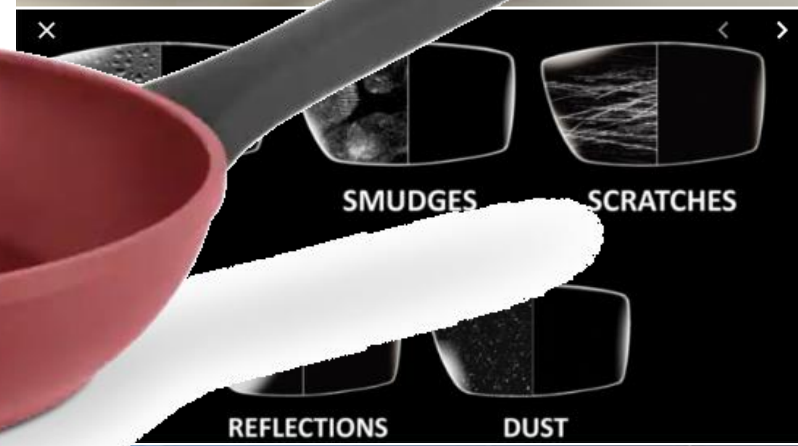


***Three Most Common Issues Coatings Address:***

***1. Friction***
***2. Heat***
***3. Corrosion***



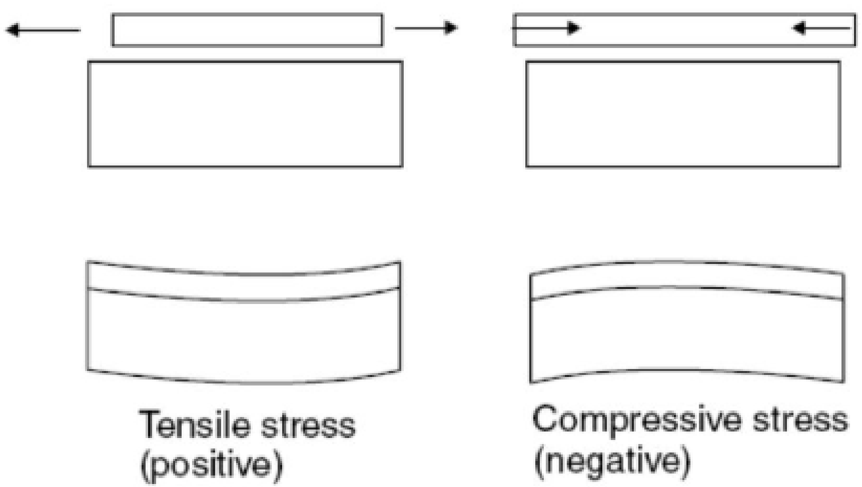

# Motivation

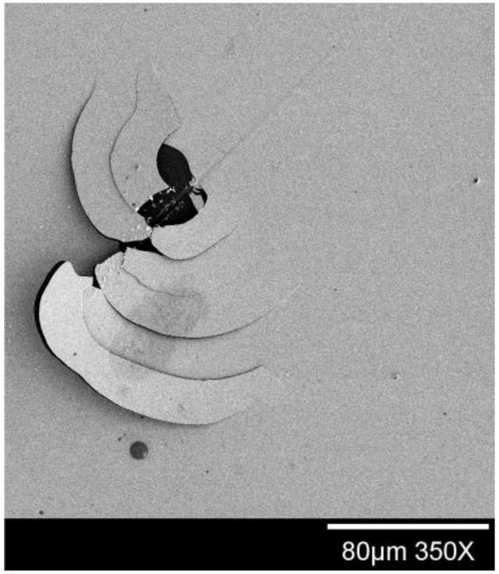



***Three Most Comm***
***Issues Coatings Address:***

***1. Friction***
***2. Heat***
***3. Corrosion***

# Structure ↔ Performance




Stress fracture patterns in ALD W/Si

# What can we measure?

Small angle x-ray reflectivity

GI-SAXS

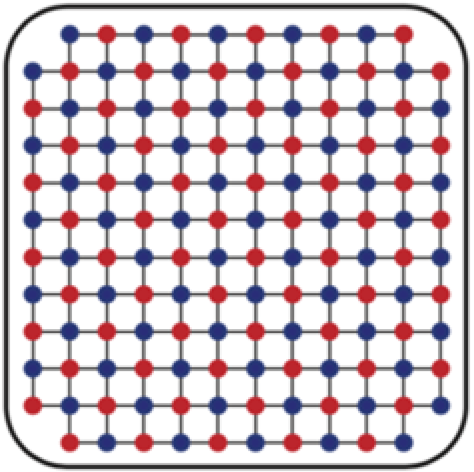
GI-WAXS -- GI – PXRD
-- GI -- RSM

Reflectivity
XRD
Pole figures

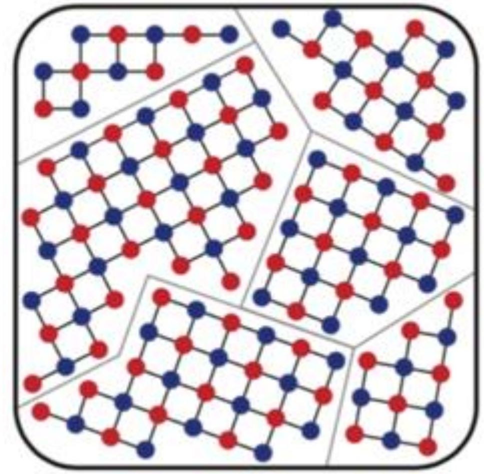
They yield information about:
✓Film thickness, roughness, porosity
✓Structure, stress, texture, defects
✓Composition, interdiffusion, gradients
✓Buried nanostructures, size, shape, ordering

# What kind of films can we measure?

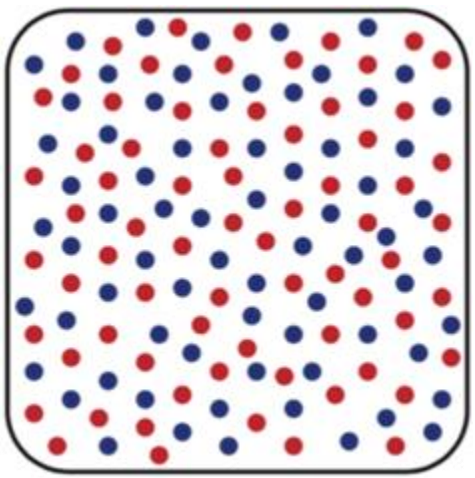
Single-crystal



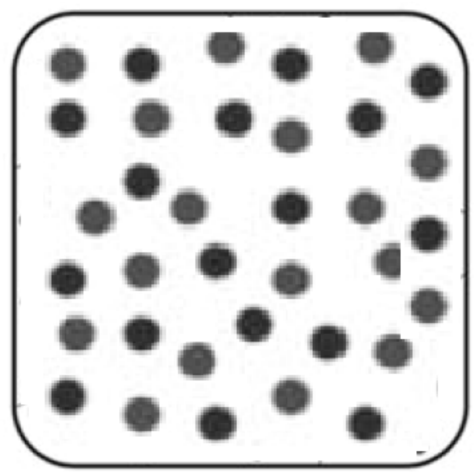
Poly-crystalline



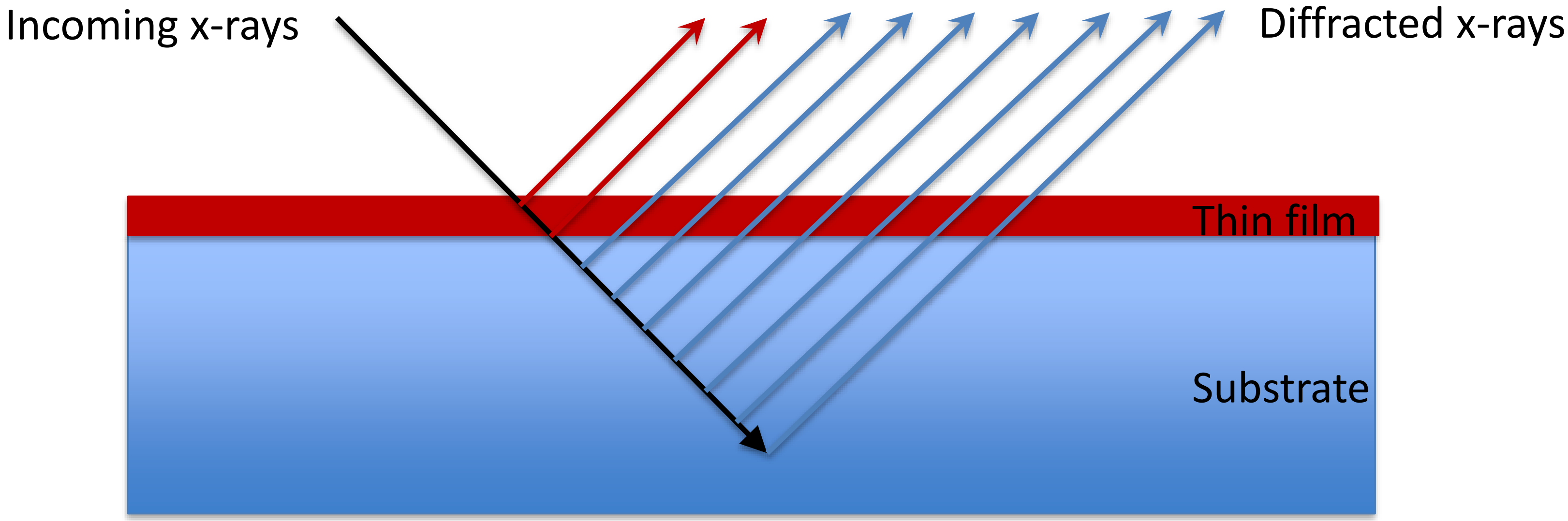
Amorphous

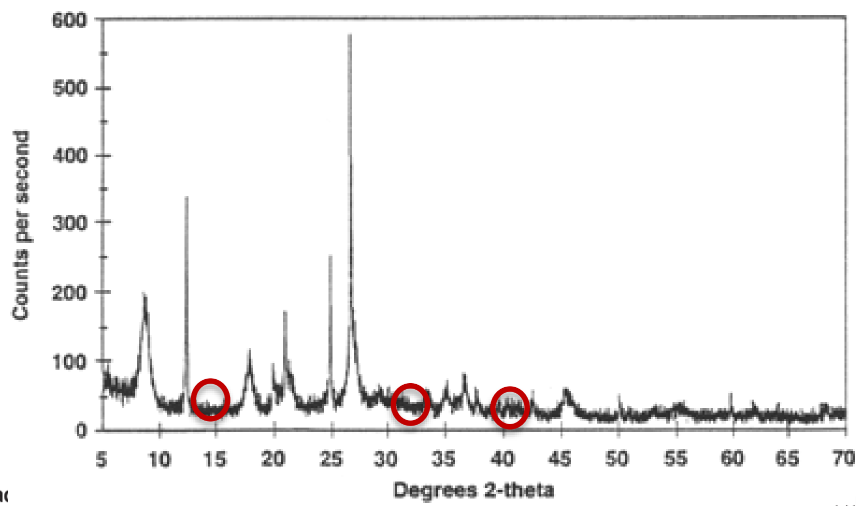


Nanostructures

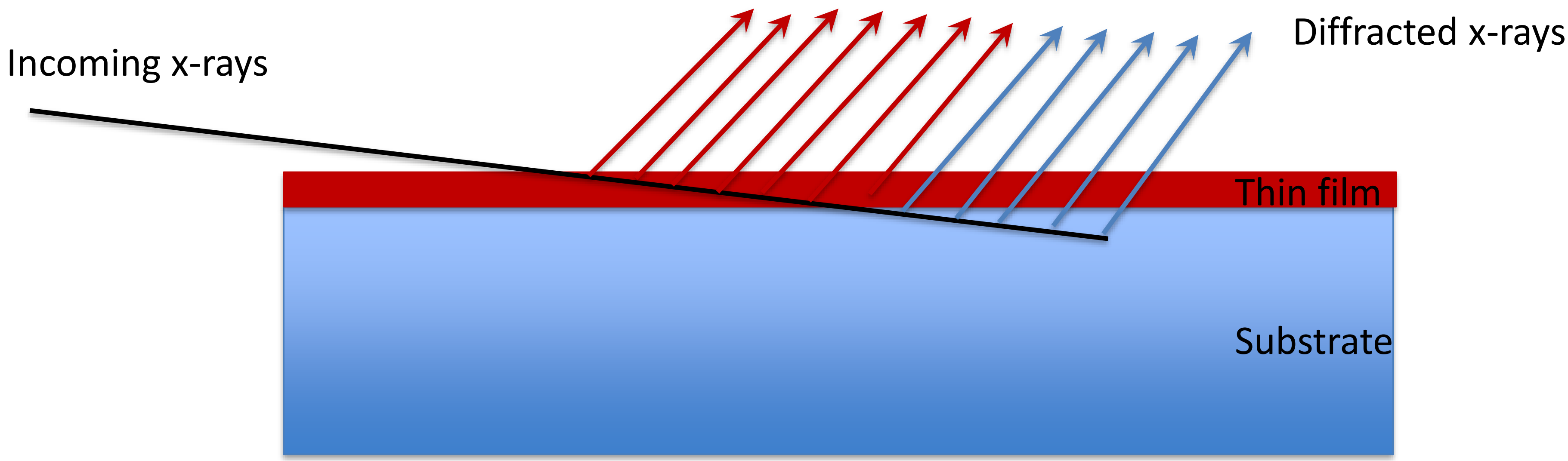


# Using X-Rays to investigate thin films



# The grazing incidence geometry enhances the film signal relative to the substrate signal



# X-Rays attenuation length

The **attenuation length** $\varepsilon$ is the distance over which the x-ray beam intensity has dropped to 1/*e* of its incident intensity.

e = 2.718281828459045
1/e = 0.367879441171

Denser materials will have shorter attenuation lengths.

Higher energies will have longer attenuation lengths

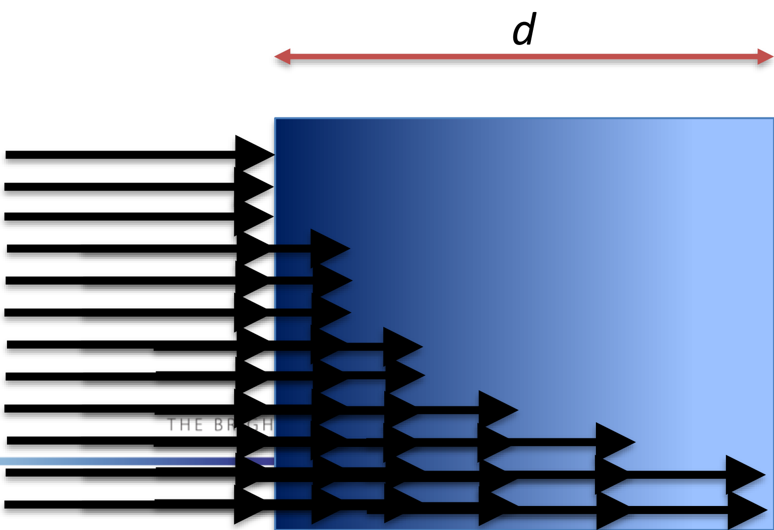
$$I = I_o \, e^{-\frac{d}{\varepsilon}}$$

The **attenuation coefficient** $\mu$ is simply the inverse of the attenuation length

$$I = I_o \, e^{-\mu . d}$$

Where to find attenuation lengths of materials:

- CXRO
- XOP/XPOWER
- …

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# X-Ray attenuation length

www.cxro.lbl.gov

THE CENTER FOR X-RAY OPTICS

- X-Ray Database
- Nanomagnetism
- X-Ray Microscopy
- EUV Lithography
- EUV Mask Imaging
- Reflectometry
- Zoneplate Lenses
- Coherent Optics
- Nanofabrication
- Optical Coatings
- Engineering
- Education
- Publications
- Contact

BERKELEY LAB

The Center for X-Ray Optics is a multi-disciplined research group within Lawrence Berkeley National Laboratory's (LBNL) Materials Sciences Division (MSD). Notice to users.

## X-Ray Interactions With Matter

Introduction
Access the atomic scattering factor files.
Look up x-ray properties of the elements.
The index of refraction for a compound material.
The x-ray attenuation length of a solid.
X-ray transmission

- Of a solid.
- Of a gas.

X-ray reflectivity

- Of a thick mirror.
- Of a single layer.
- Of a bilayer.
- Of a multilayer.

The diffraction efficiency of a transmission grating.
Related calculations:

- Synchrotron bend magnet radiation.

Other x-ray web resources.
X-ray Data Booklet

# X-Ray attenuation length

## X-Ray Attenuation Length

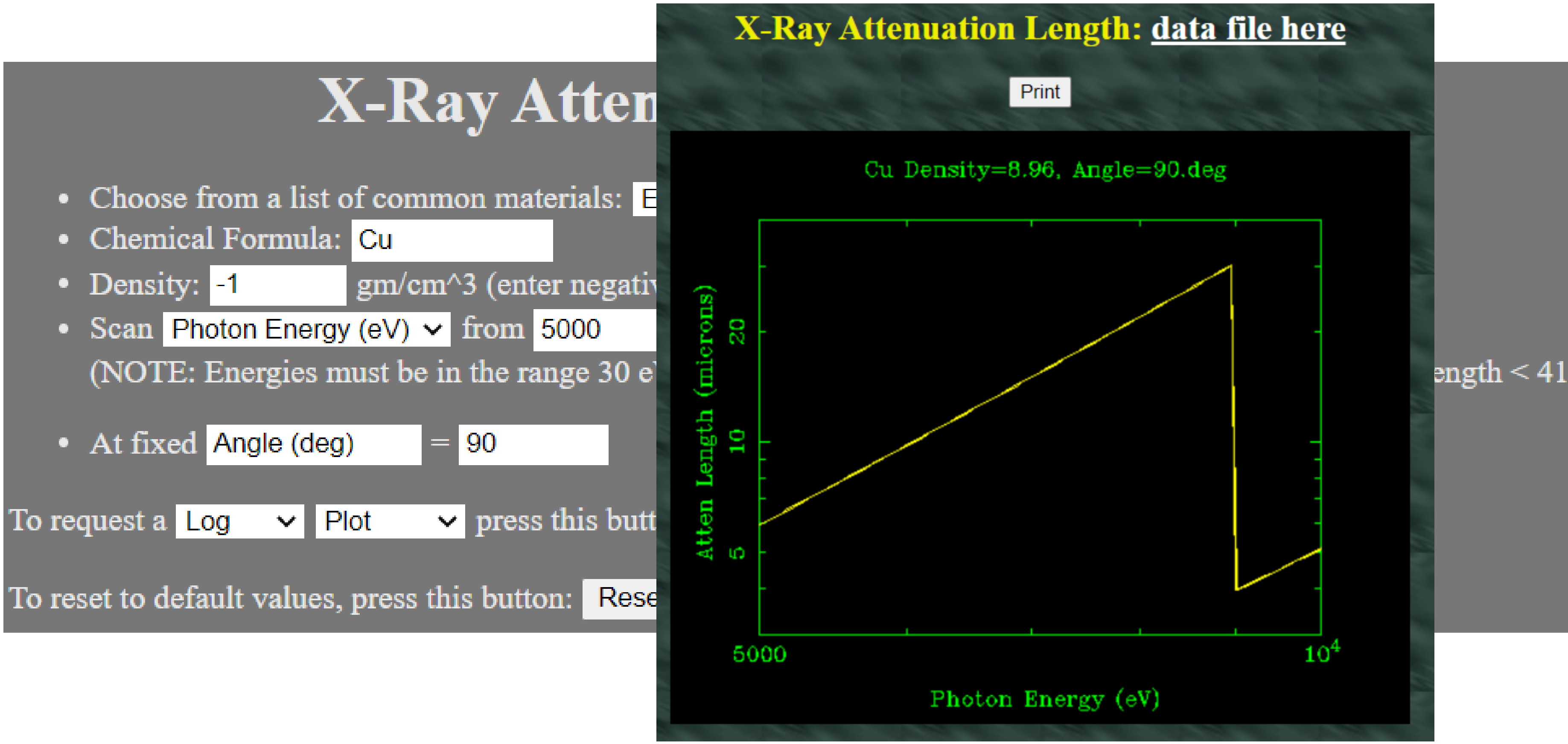
- Choose from a list of common materials: Enter Formula
- Chemical Formula: Cu
- Density: -1 gm/cm^3 (enter negative value to use tabulated values.)
- Scan Photon Energy (eV) from 5000 to 10000 in 100 steps (< 500).
  (NOTE: Energies must be in the range 30 eV < E < 30,000 eV, Wavelength between 0.041 nm < Wavelength < 41

- At fixed Angle (deg) = 90

To request a Log Plot press this button: Submit Request

To reset to default values, press this button: Reset .

# X-Ray attenuation length




```
Element 29: Cu

Edge          keV
  K         8.9789
```

www.cxro.lbl.gov

# X-Ray attenuation length

CXRO
THE CENTER FOR X-RAY OPTICS

X-Ray Database

Zone Plate Education

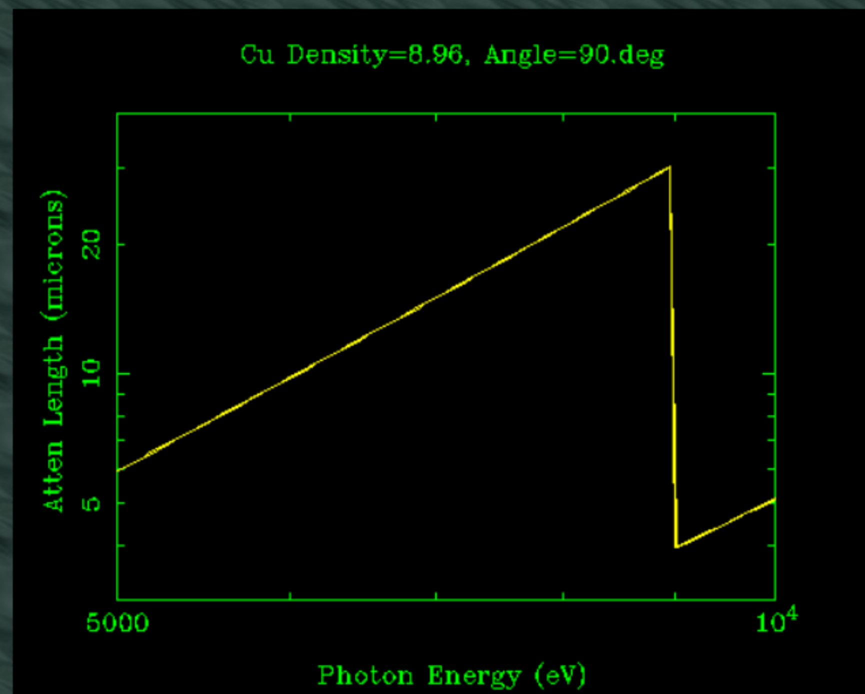
X-Ray Atten

Cu Density=8.96, Angle=90.deg
Photon Energy (eV), Atten Length (microns)

| | |
|---|---|
| 5000.00 | 5.96392 |
| 5034.78 | 6.07762 |
| 5069.80 | 6.19352 |
| 5105.06 | 6.31168 |
| 5140.57 | 6.43210 |
| 5176.32 | 6.55489 |
| 5212.33 | 6.68003 |
| 5248.58 | 6.80778 |
| 5285.09 | 6.93802 |
| 5321.85 | 7.07069 |
| 5358.87 | 7.20583 |
| 5396.14 | 7.34361 |
| 5433.67 | 7.48427 |
| 5471.47 | 7.62763 |
| 5509.53 | 7.77389 |
| 5547.85 | 7.92298 |
| 5586.44 | 8.07487 |
| 5625.29 | 8.22963 |
| 5664.42 | 8.38748 |
| 5703.82 | 8.54873 |
| 5743.49 | 8.71308 |
| 5783.44 | 8.88042 |
| 5823.67 | 9.05096 |
| 5864.17 | 9.22514 |

X-Ray Attenuation Length: data file here

Print




ength < 41

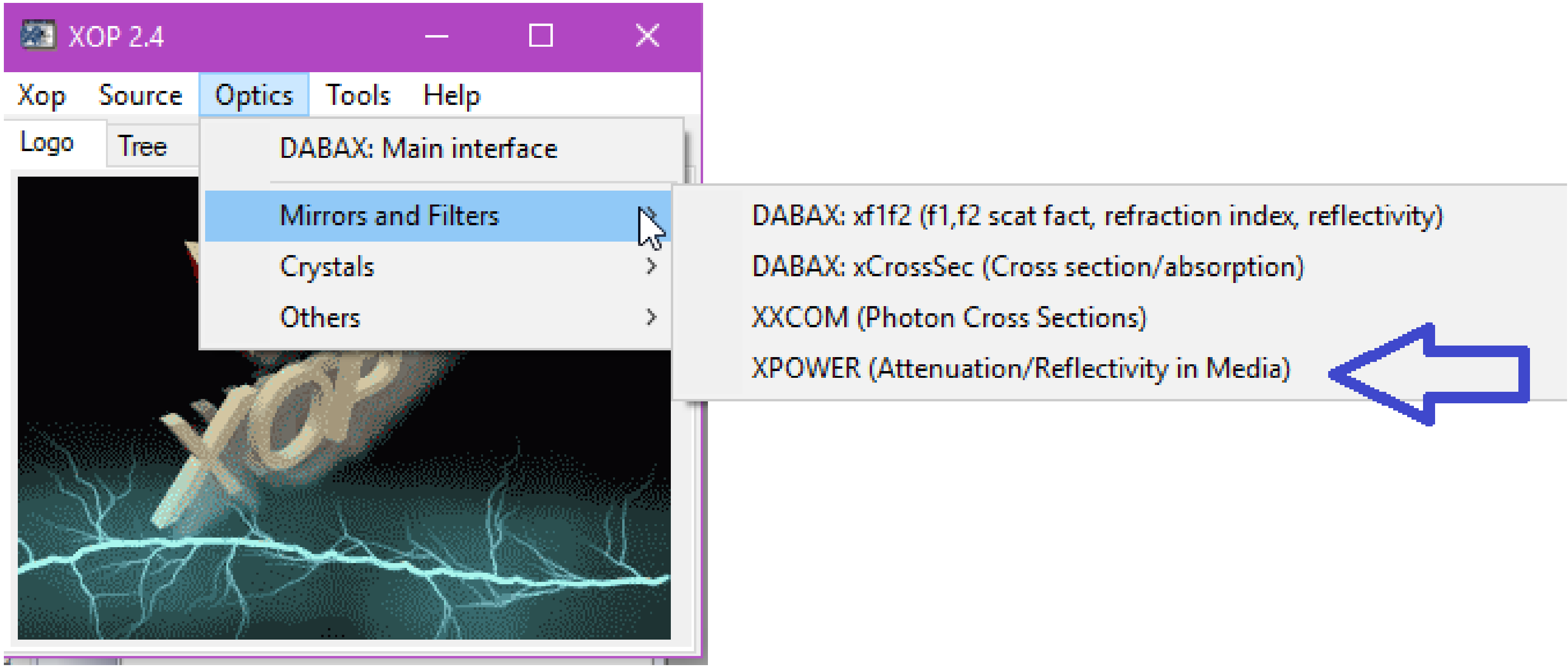
Element 29: Cu

| Edge | keV |
|---|---|
| K | 8.9789 |

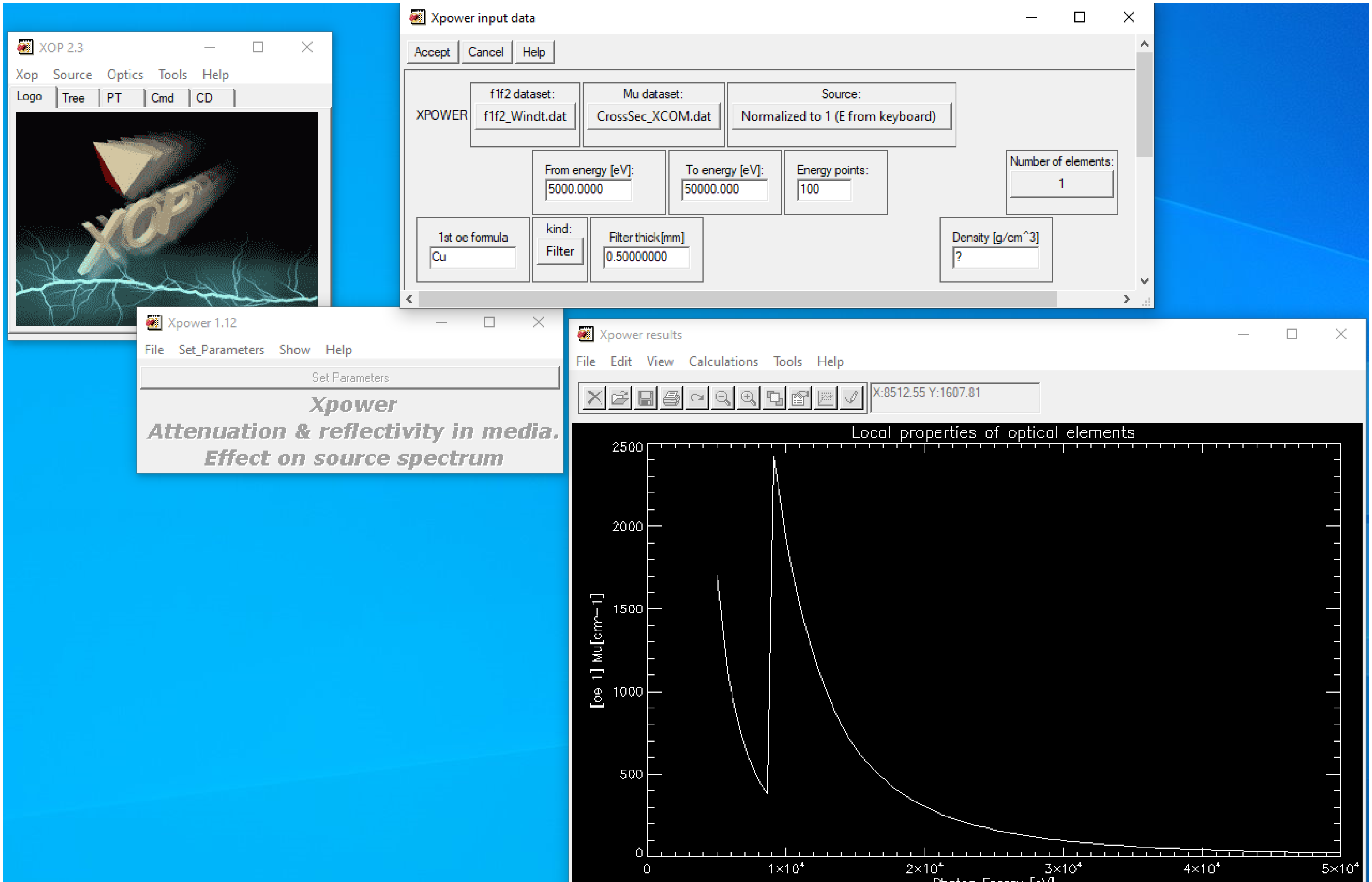
# X-Ray attenuation length

## XOP/XPOWER

https://www.aps.anl.gov/Science/Scientific-Software/XOP

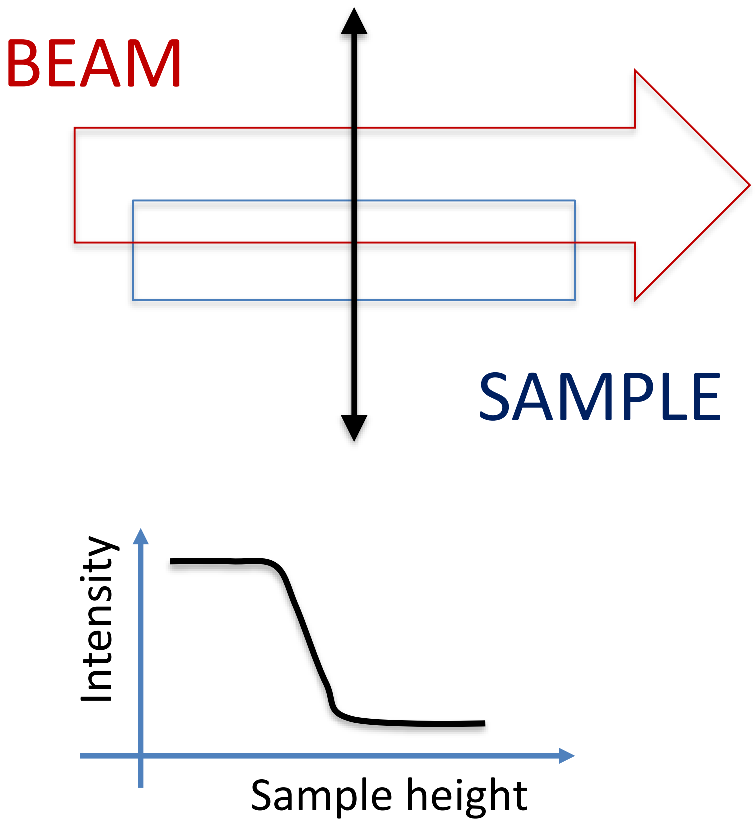


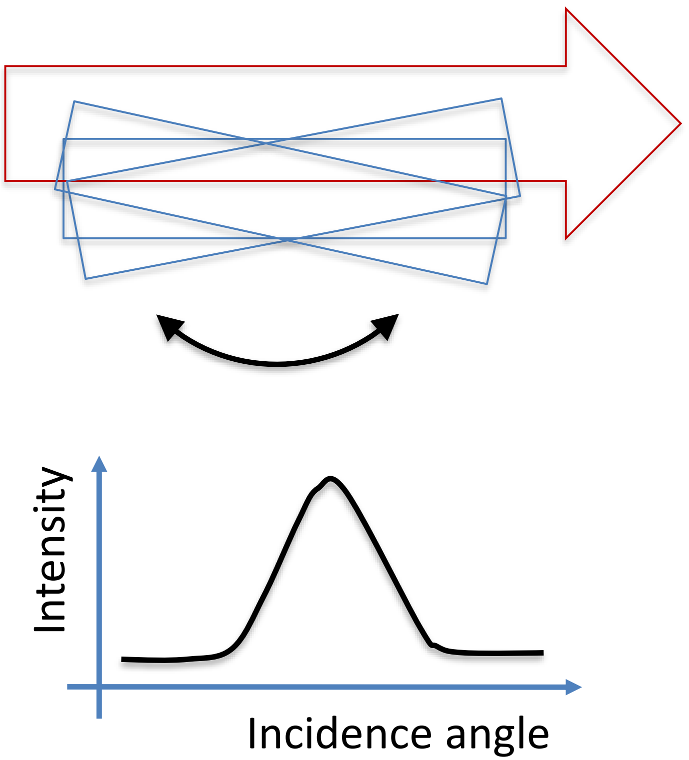
# X-Ray attenuation length



# How do we measure?

# Sample alignment




Iterate!

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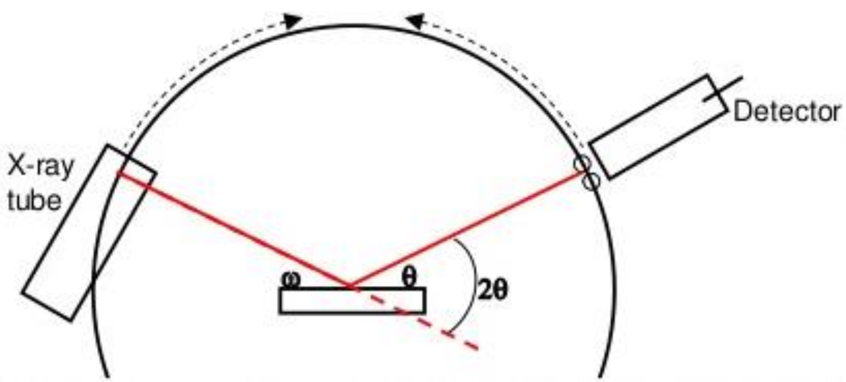
# Grazing incidence diffraction

applied to

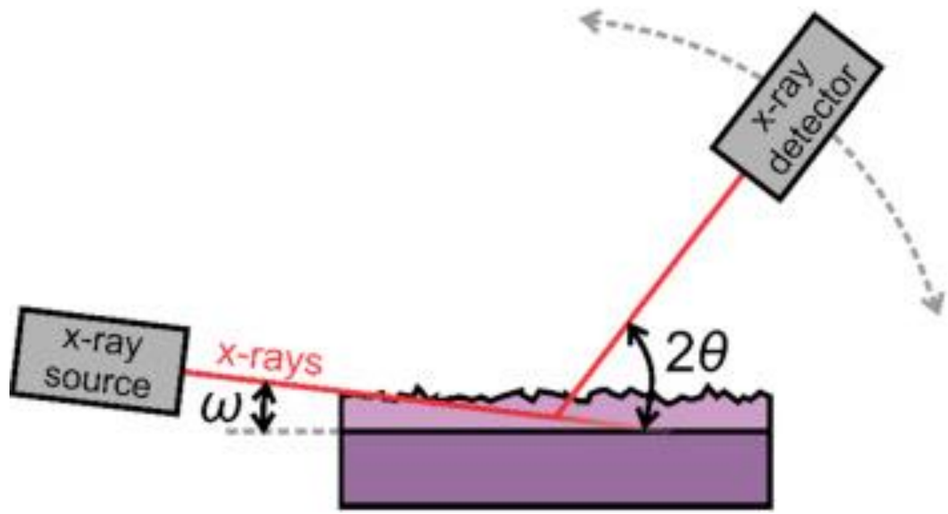
Polycrystalline films

# Grazing incidence diffraction

Regular specular geometry, $\omega = \theta$



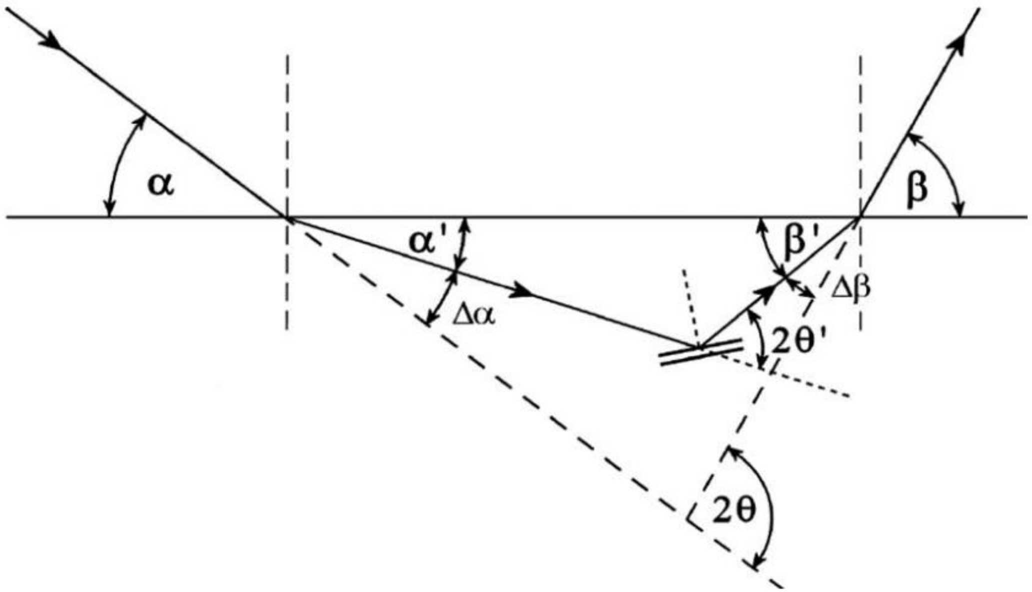

Grazing incidence geometry




https://www.sciencedirect.com/science/article/pii/S0022311517313946

# Grazing incidence diffraction

## Refraction correction

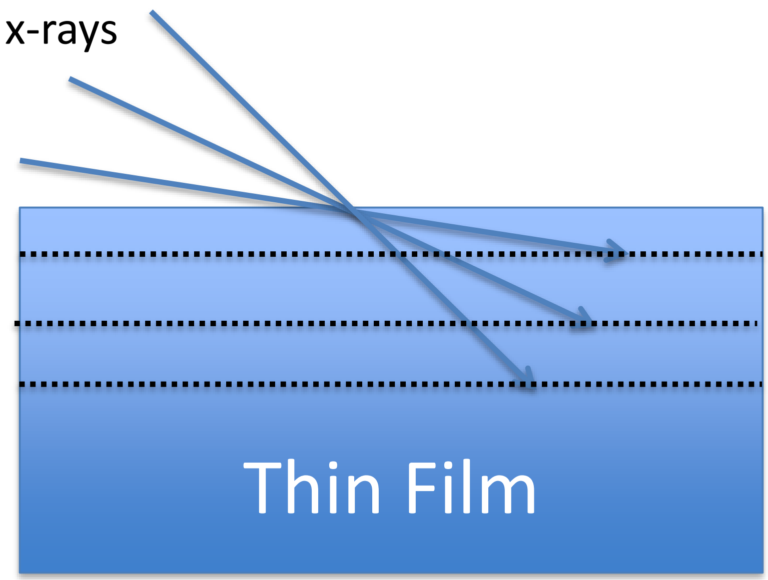


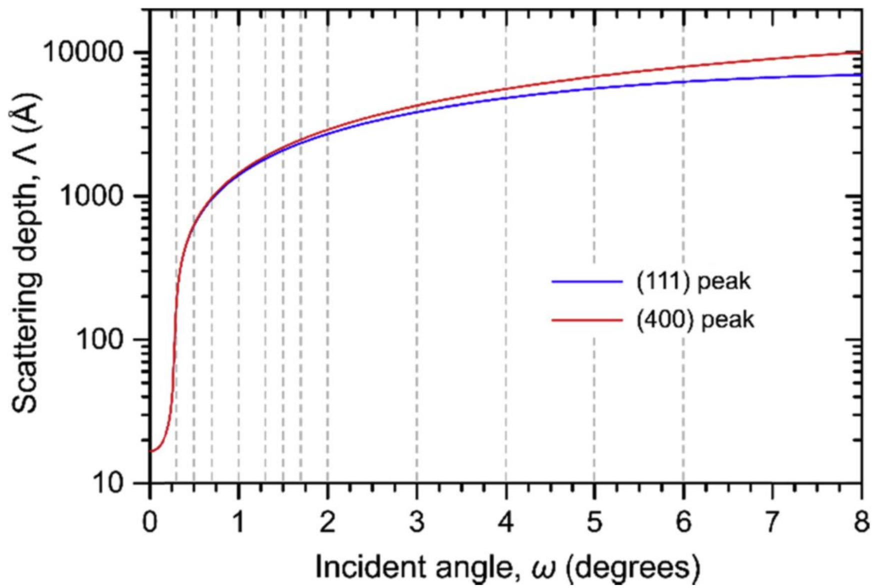

$$\Delta 2\theta = \delta[\cot \alpha + \cot(2\theta - \alpha) + 2 \tan \theta]$$

<u>Powder Diffraction **24**(S1): S11-S15, 2012</u>

# Grazing incidence diffraction

## Depth sensitivity

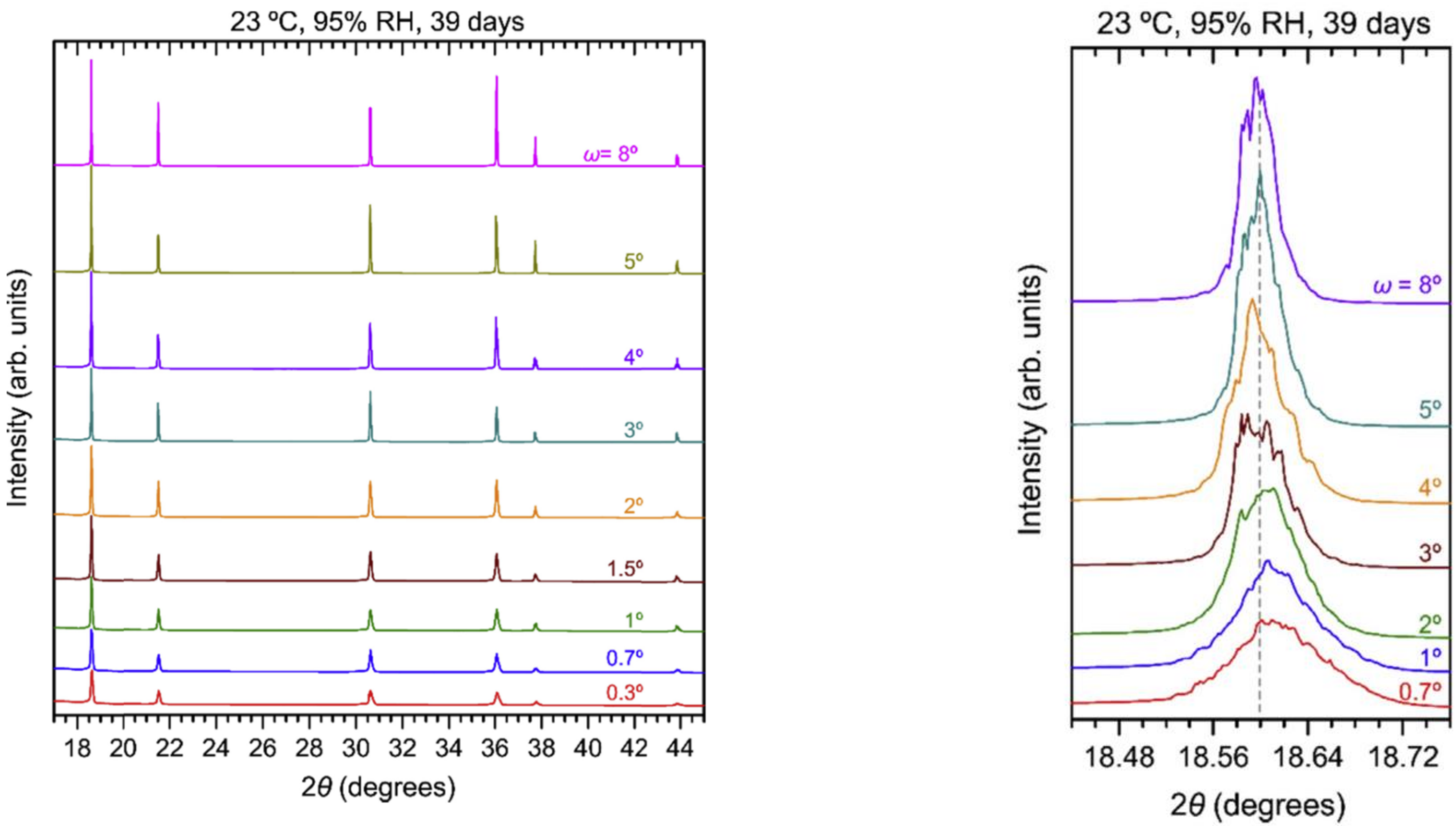



Journal of Nuclear Materials **502**: 68-75, 2018.

# Grazing incidence diffraction

Uranium Oxide ($UO_2$) exposed to air



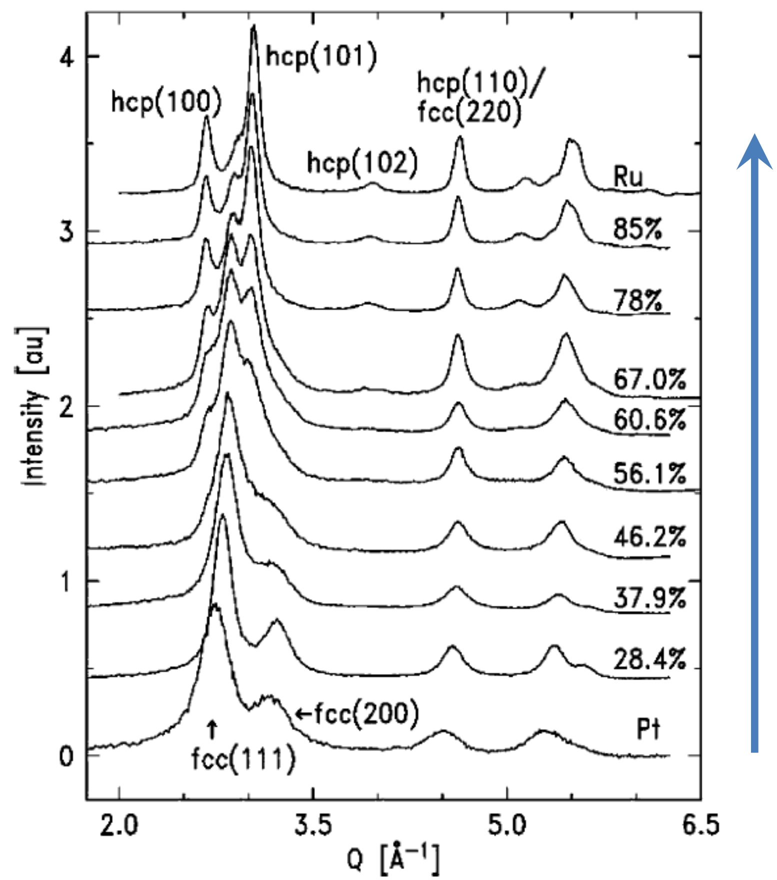

Journal of Nuclear Materials **502**: 68-75, 2018.

# Grazing incidence diffraction

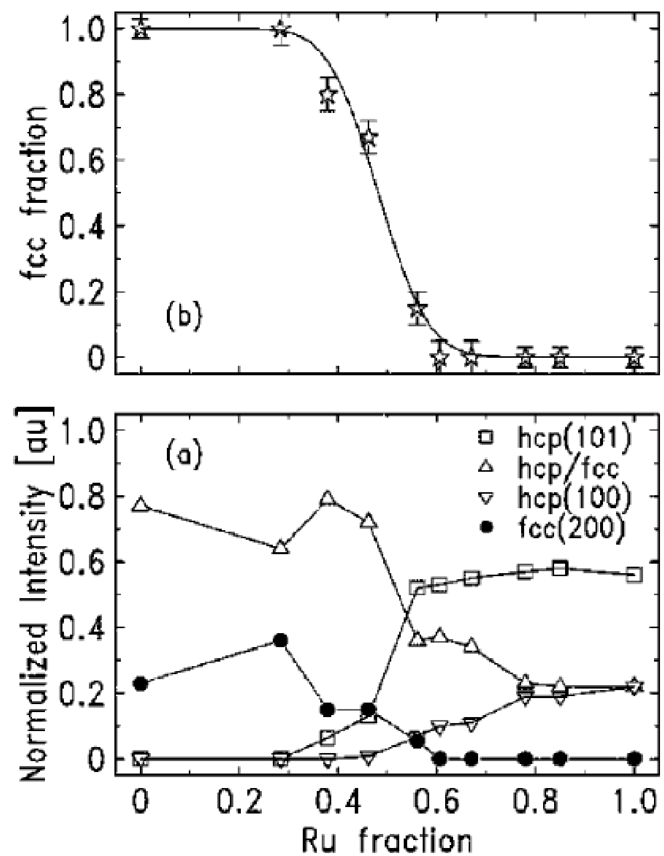
## Structure and electrocatalysis of sputtered RuPt thin-film electrodes

130 Å thick

Grazing incidence x-ray diffraction




Phase diagram determination





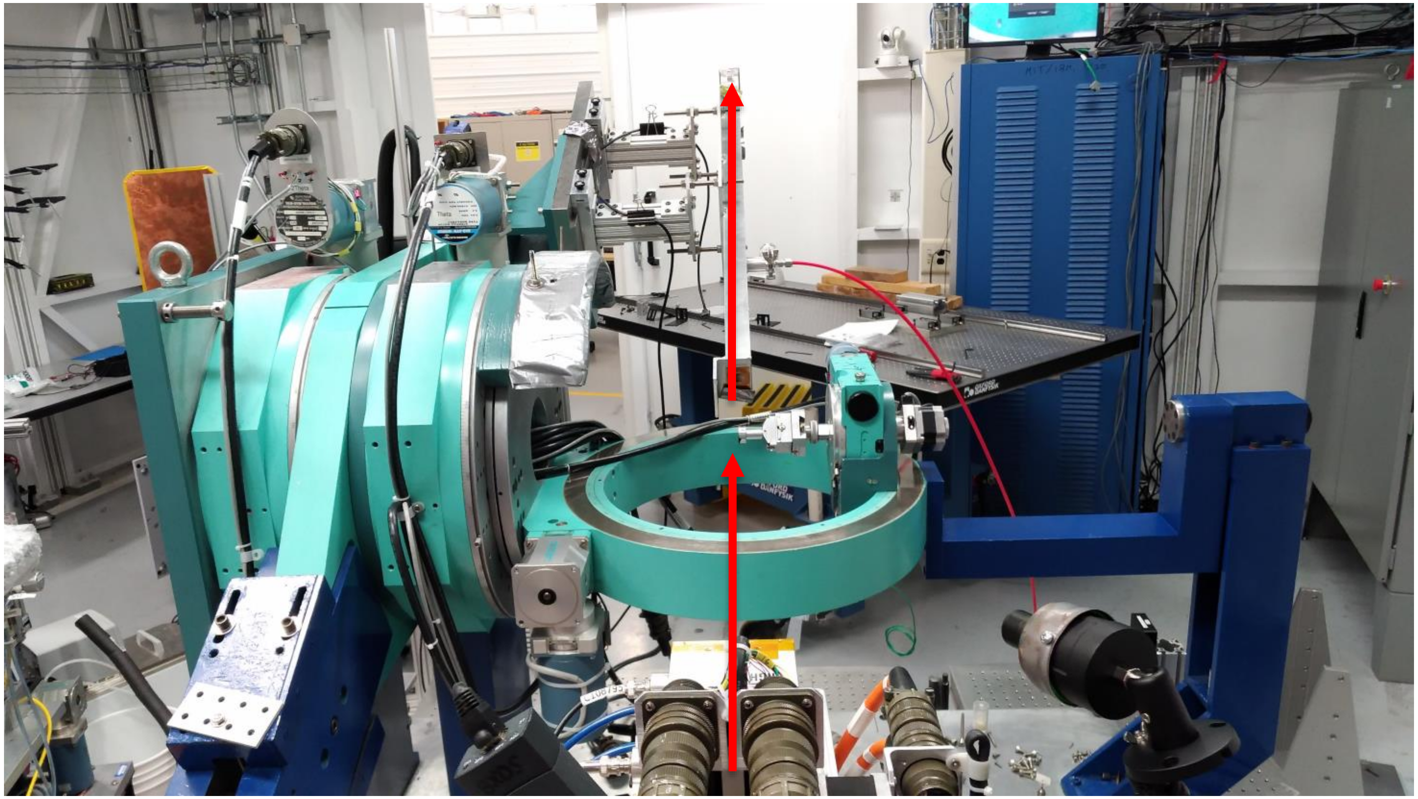

J. Phys. Chem. B **109**, 12845, 2005. Kim et al.

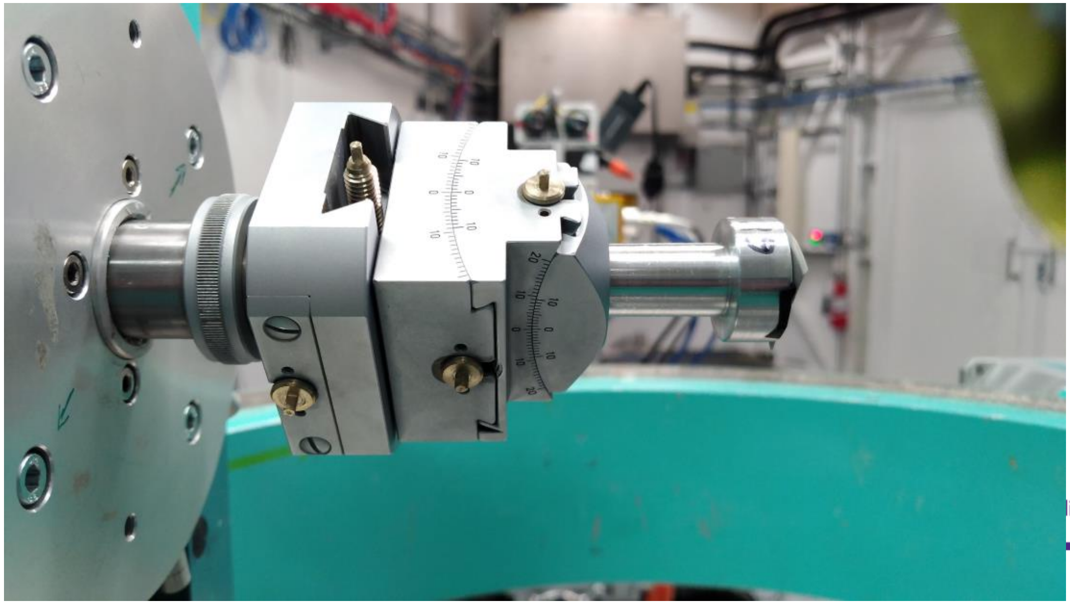
# Grazing incidence diffraction

applied to

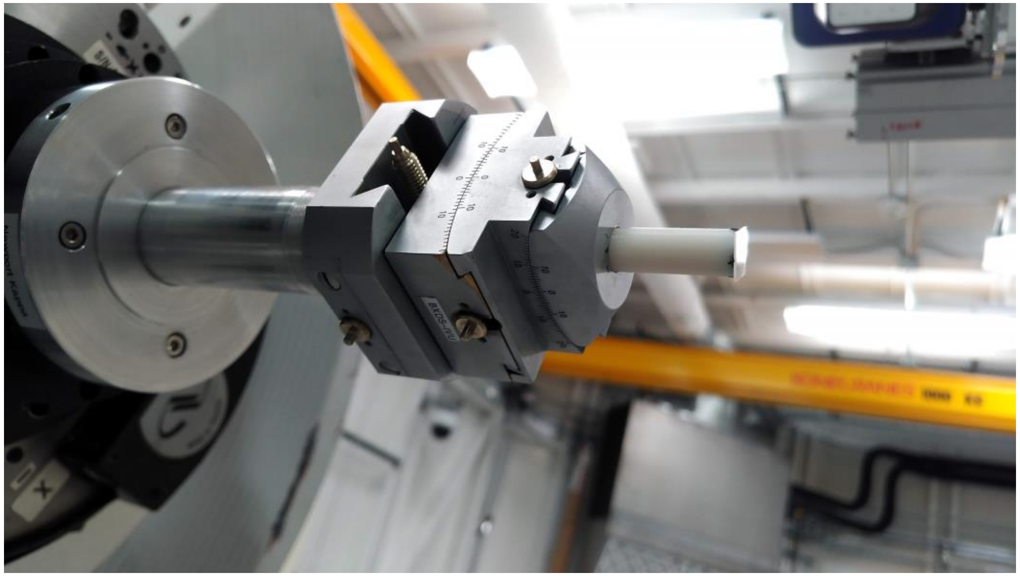
Single crystal films

# GID setup

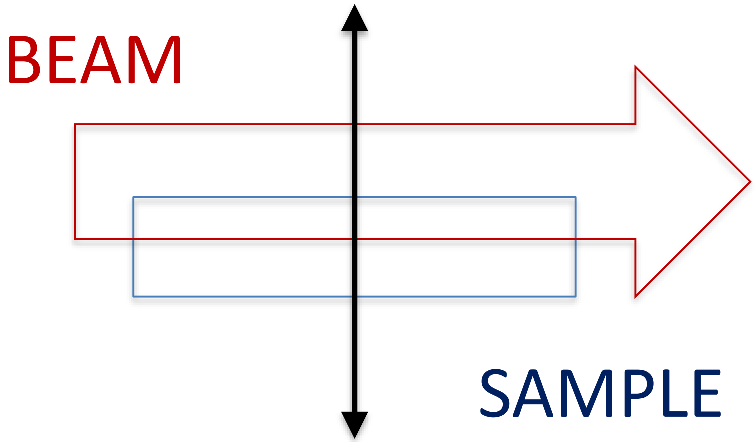


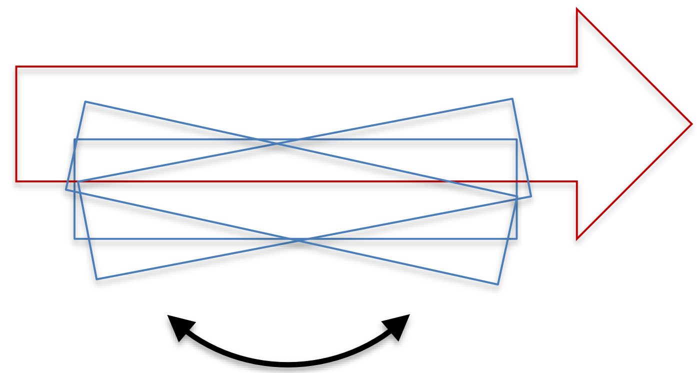


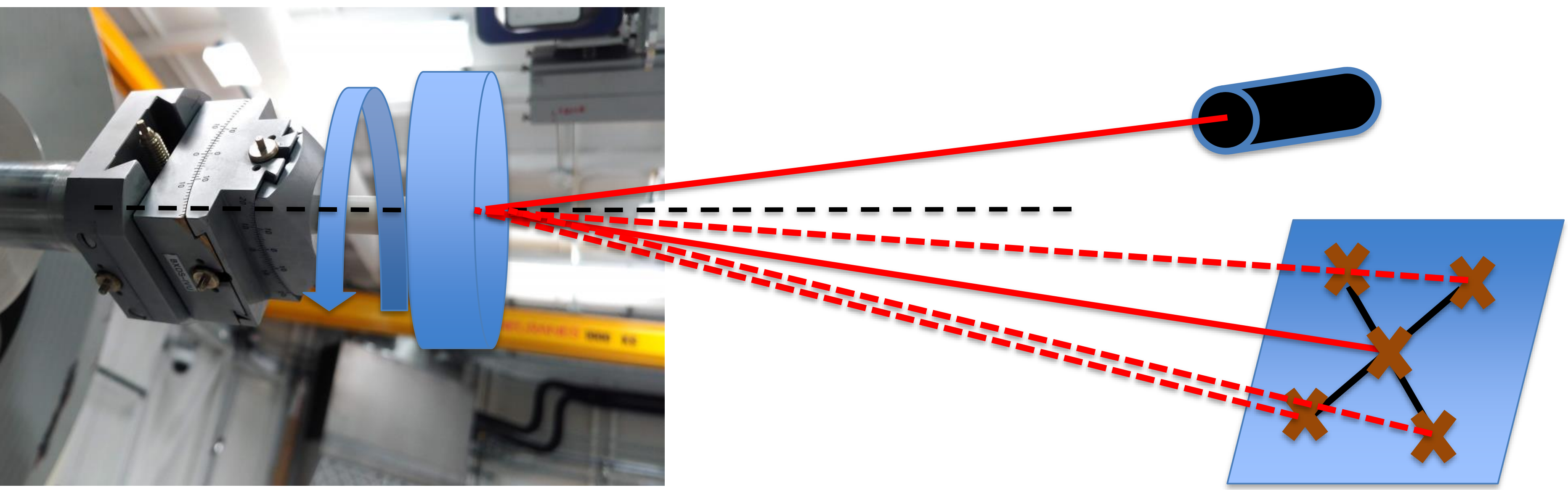
# GID setup



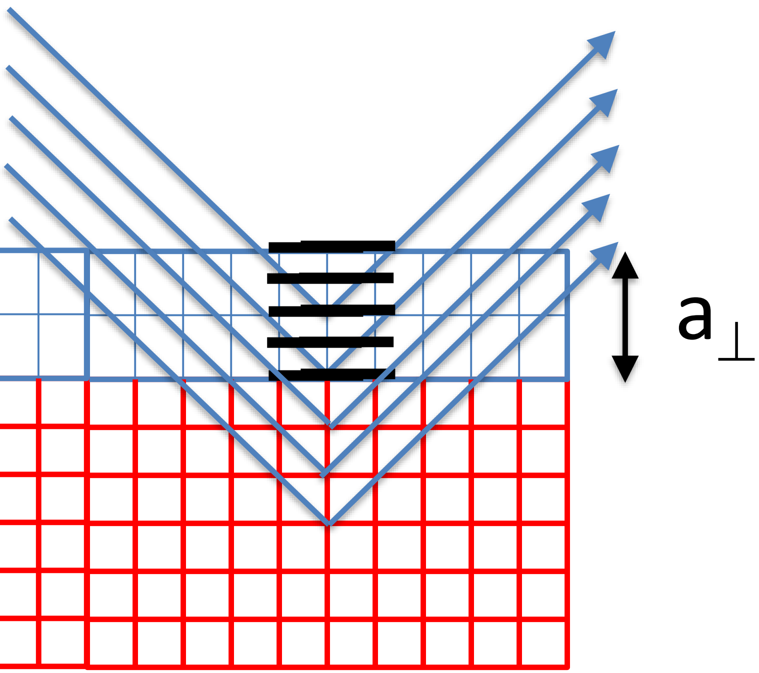
# Sample alignment

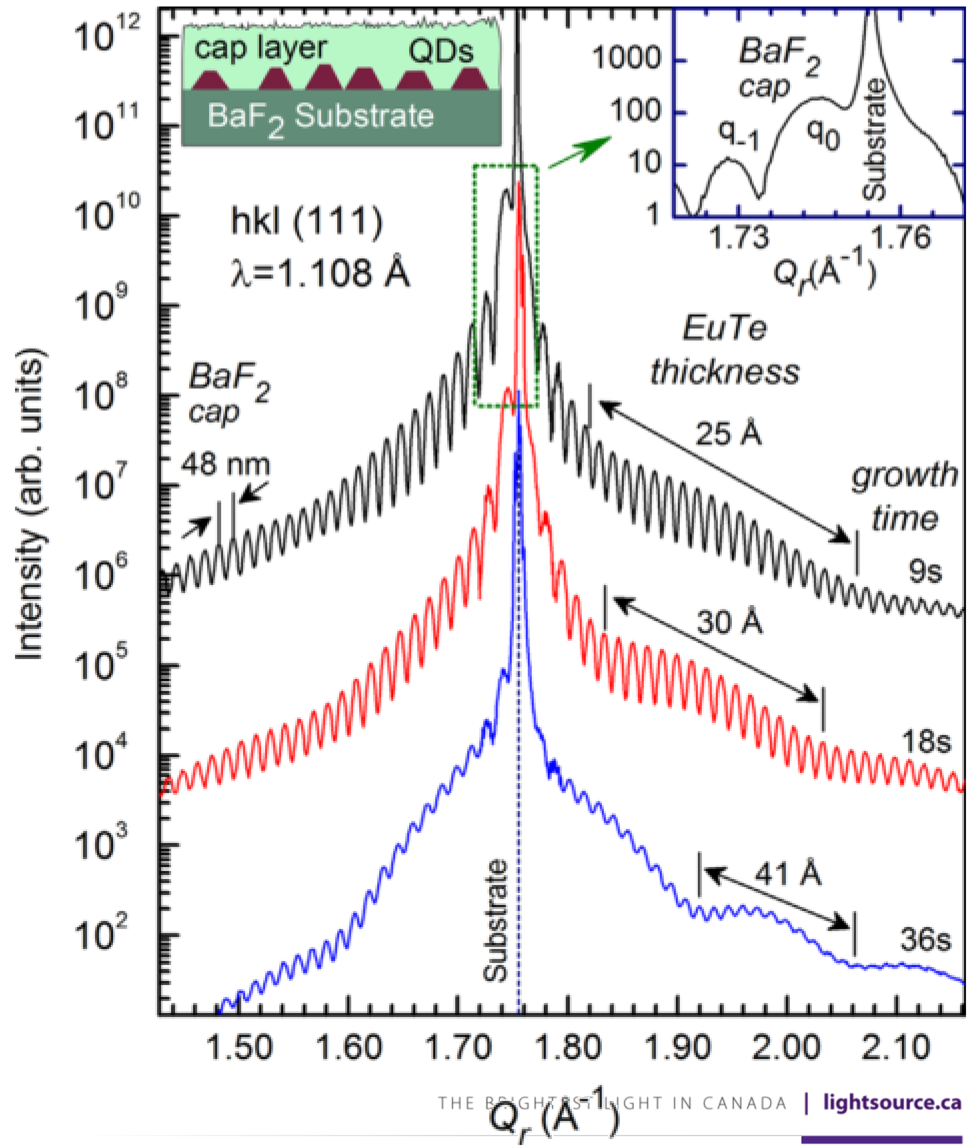




# Not-Grazing incidence diffraction

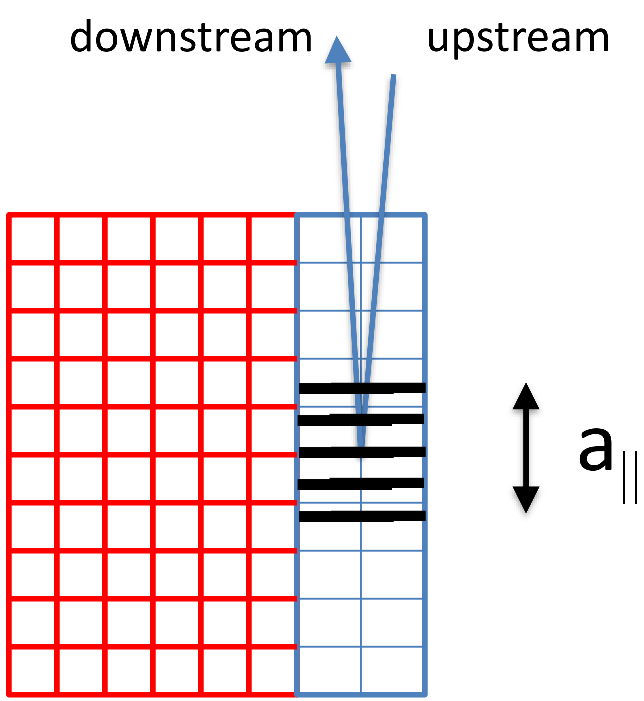


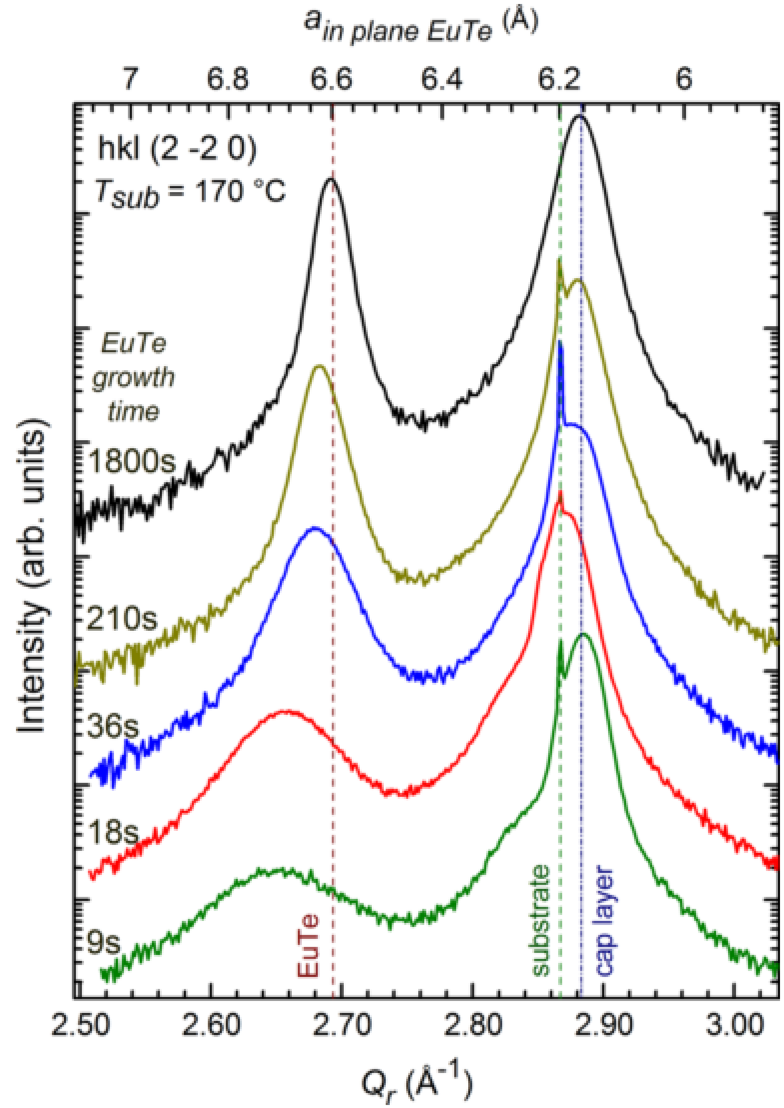






Journal of Crystal Growth **386**(0): 139-145, 2014

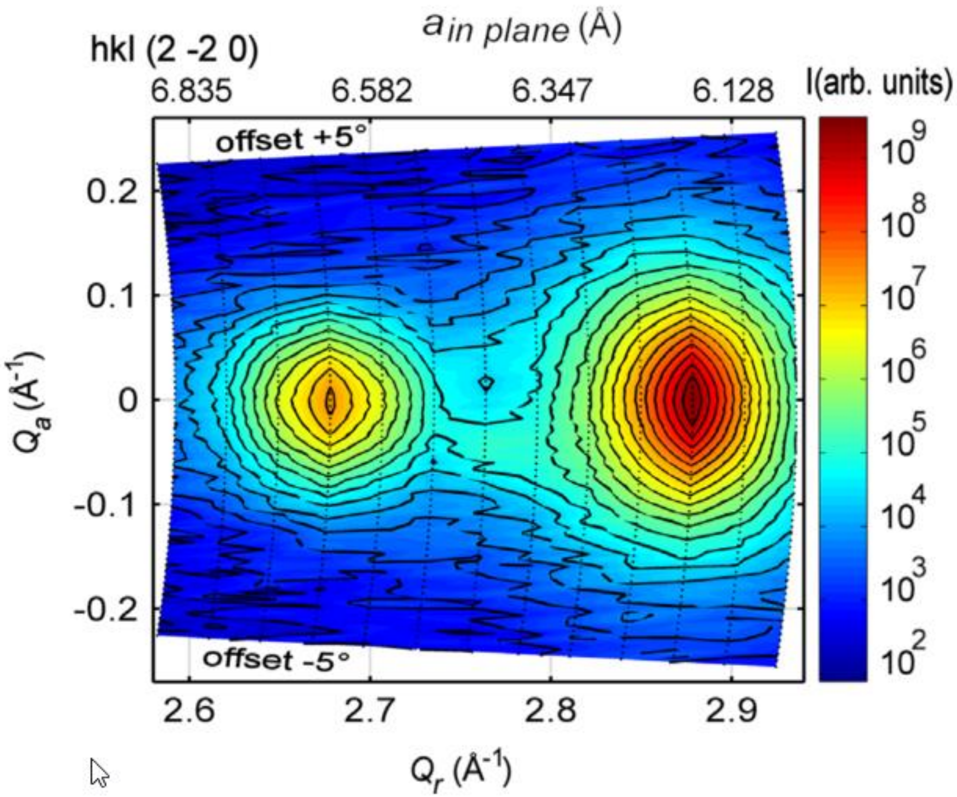
# Grazing incidence diffraction

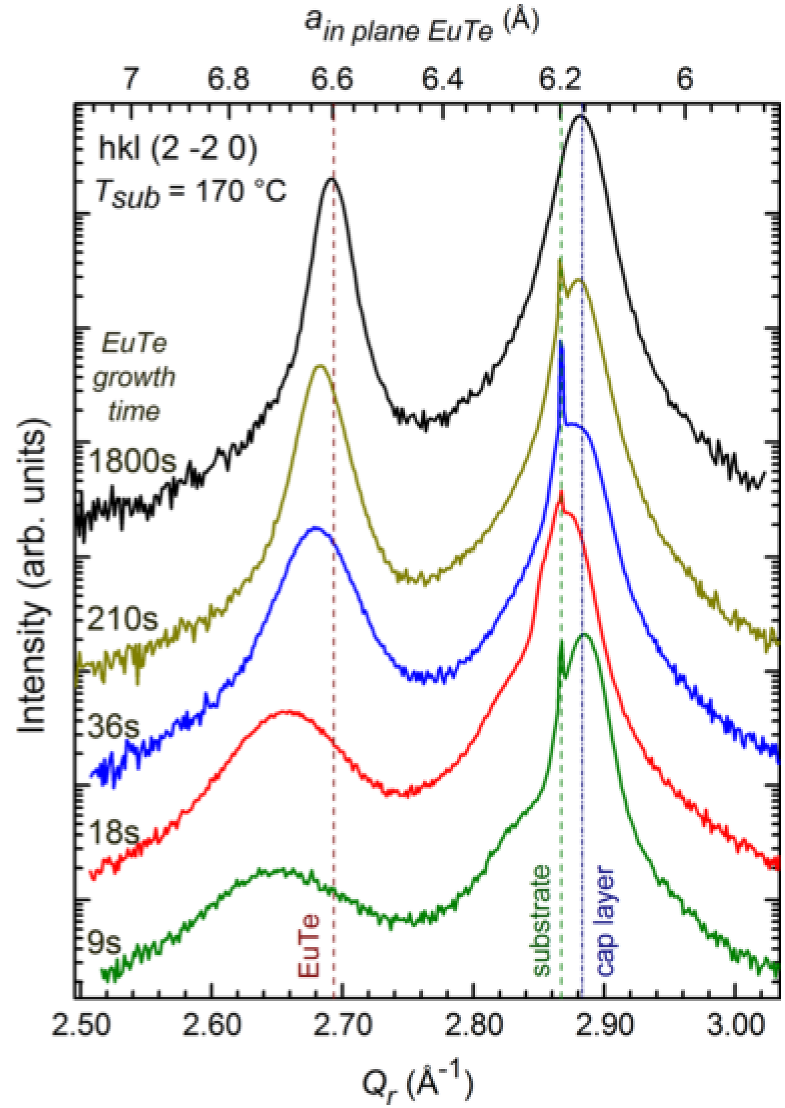



Journal of Crystal Growth **386**(0): 139-145, 2014

# Grazing incidence diffraction

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Journal of Crystal Growth **386**(0): 139-145, 2014

# Small angle x-ray reflectivity

Single crystal films

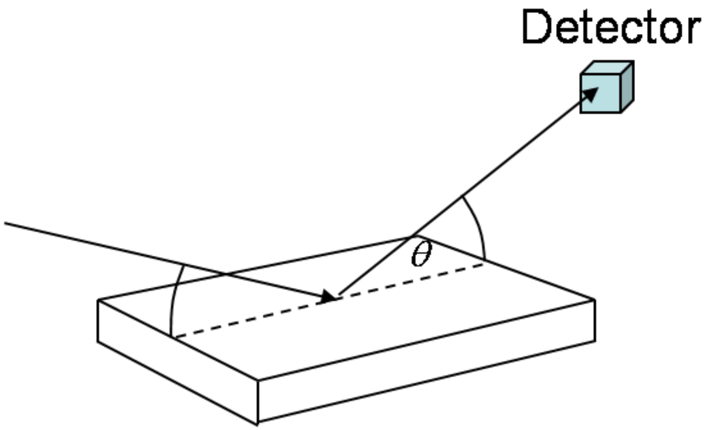
Polycrystalline films

Amorphous films

# Small angle X-Ray reflectivity

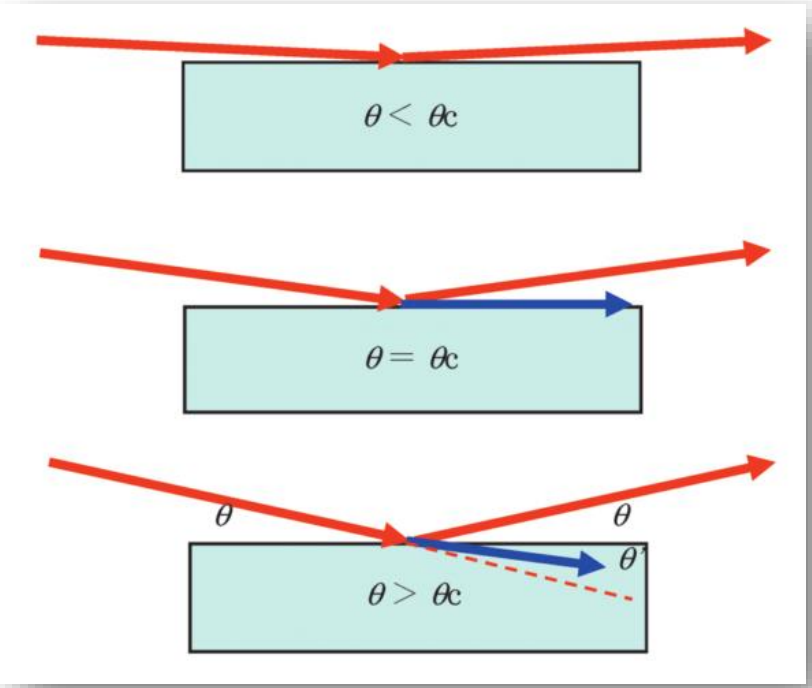
- Reflectivity yields information about the
  - Thicknesses
  - Density / porosity
  - Roughness of the interfaces

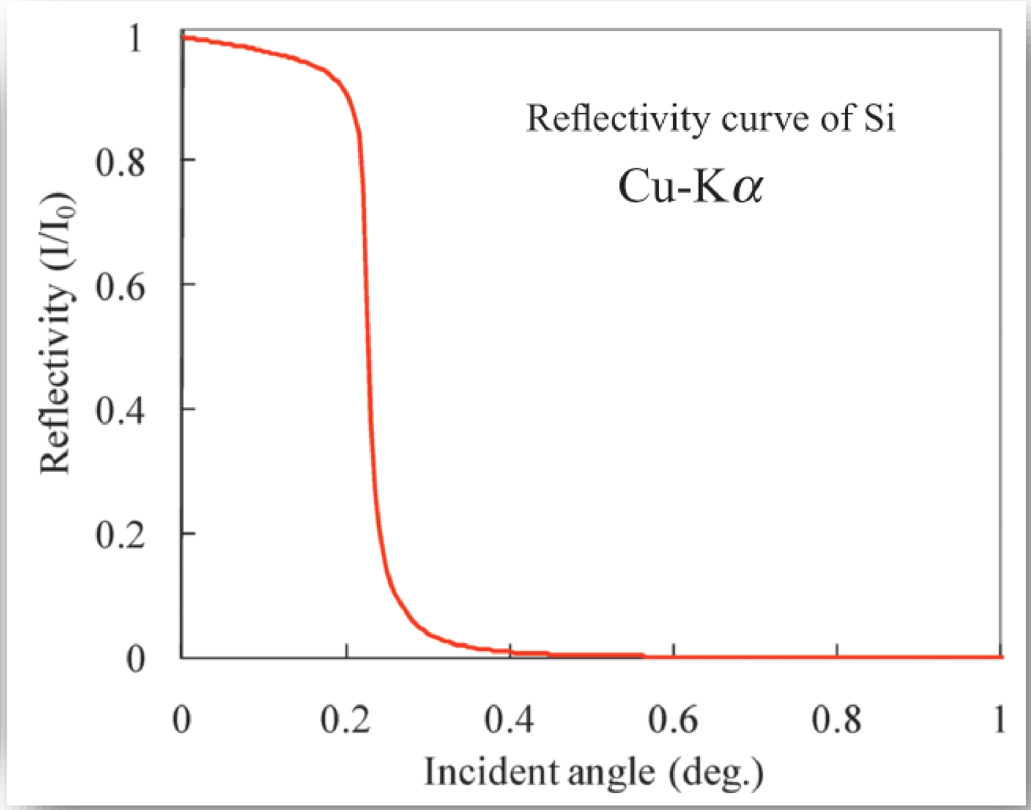
- Other names:
  - X-ray specular reflectivity
  - X-ray reflectometry
  - XRR




*No diffraction!*

# Small angle X-Ray reflectivity

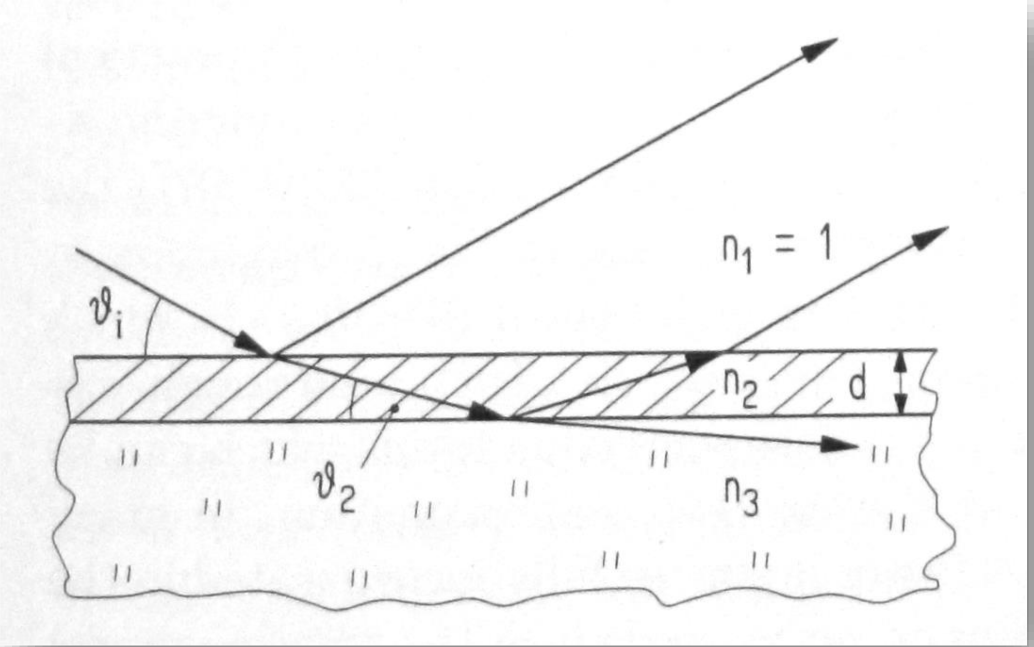



$$\theta_c \sim \lambda\sqrt{\rho}$$

*The Rigaku Journal, **26**(2), 2010*

# Small angle X-Ray reflectivity




*Snell's law*

$$n_1 \cos \vartheta_1 = n_2 \cos \vartheta_2$$

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



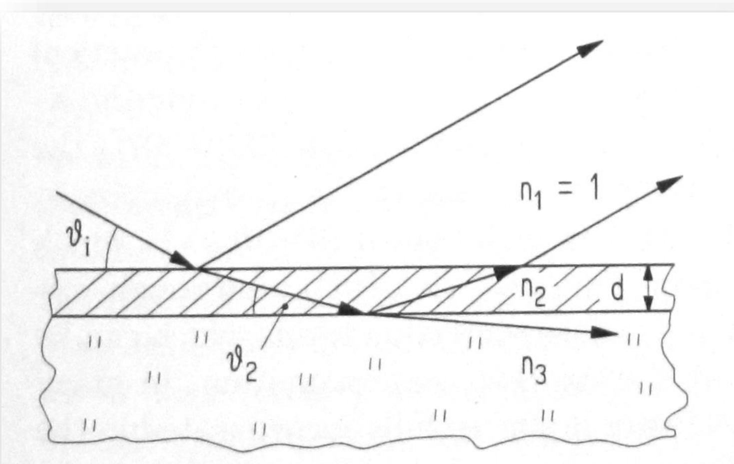
Gibaud 2013 – X-ray reflectivity chapter

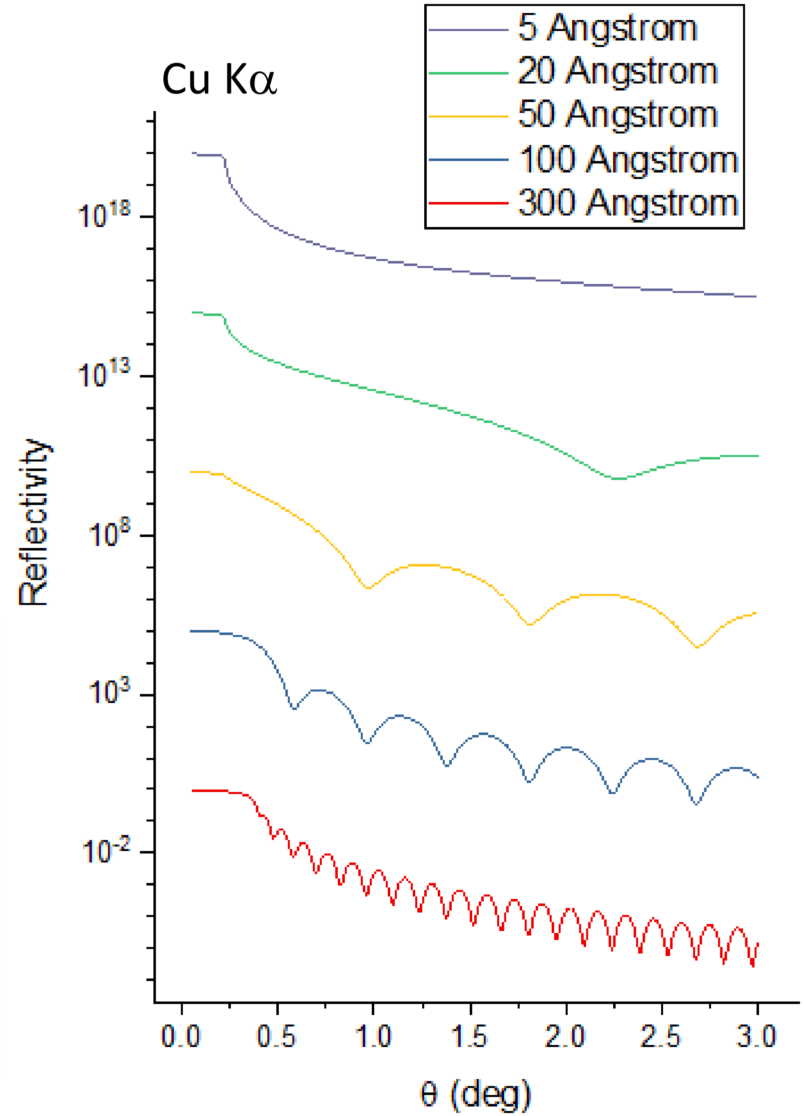
# Small angle X-Ray reflectivity

Reflectivity of a chromium film on top of silicon substrate, Cr/Si, for different thicknesses between 5 and 300 Å.

Kiessig fringes

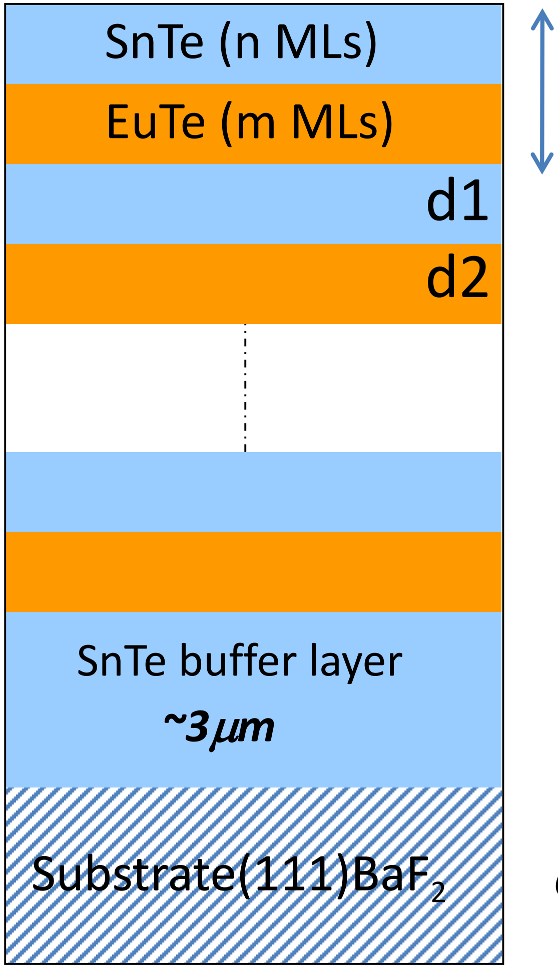
$$d = \frac{\lambda}{2\Delta\theta_r}$$



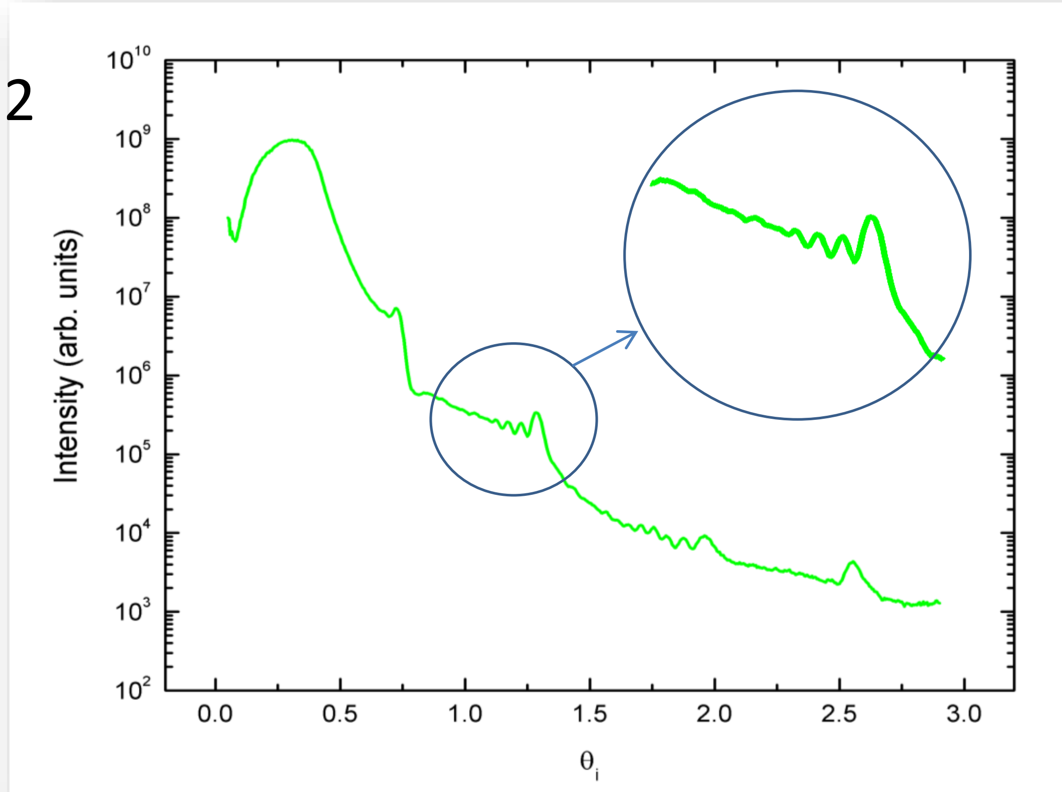




$$\frac{1.54 \cdot \text{Angstrom}}{2 \cdot 0.01 \cdot \text{deg}} = 0.4\ \mu\text{m}$$

# Small angle X-Ray reflectivity




D=d1+d2




$$d = \frac{\lambda}{2\Delta\vartheta_i}$$

<u>Kiessig fringes spacing:</u>

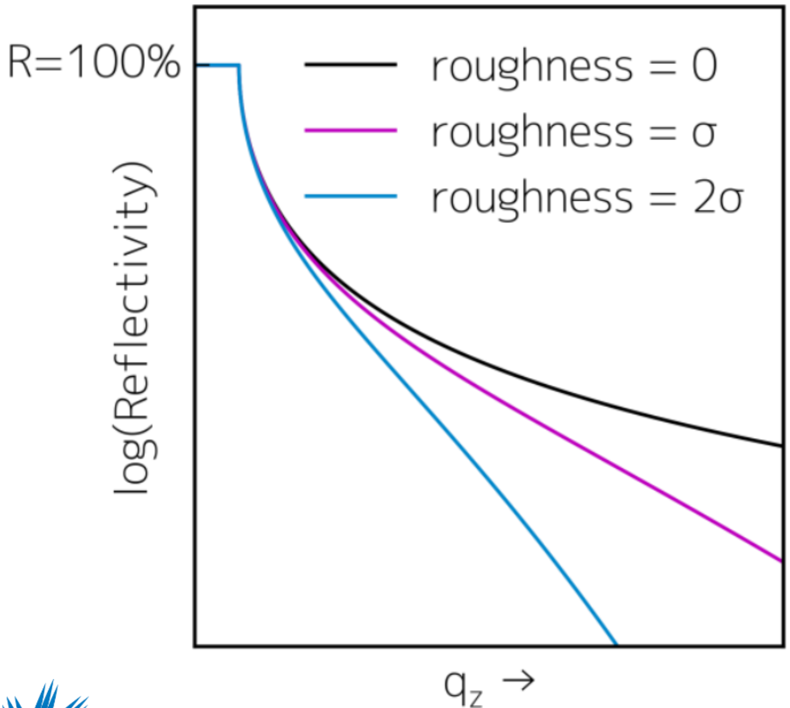
0.61 deg ~ 83 Å (SL period)

0.05 deg ~ 994.9 Å (Stack thickness)

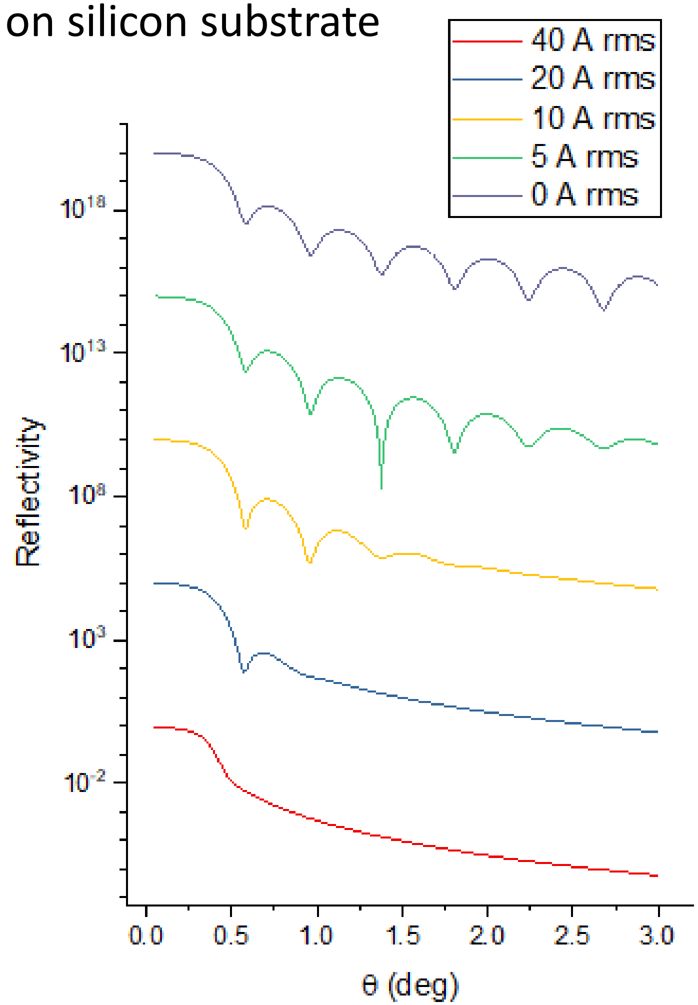
# Small angle X-Ray reflectivity

Surface roughness

$$R_{rough} = R \cdot e^{-\frac{q_z^2 \sigma^2}{2}}$$

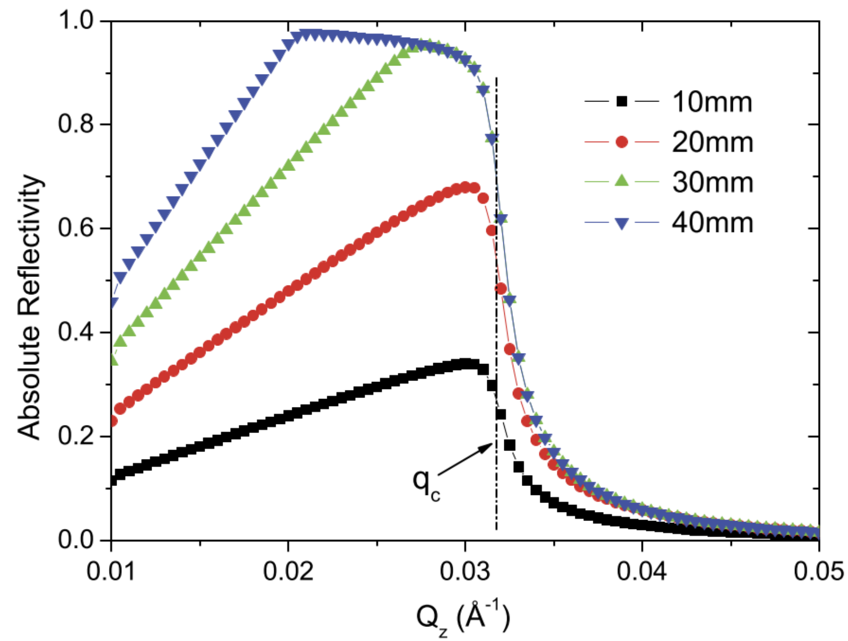



100 Angstrom chromium layer on silicon substrate



# Small angle X-Ray reflectivity

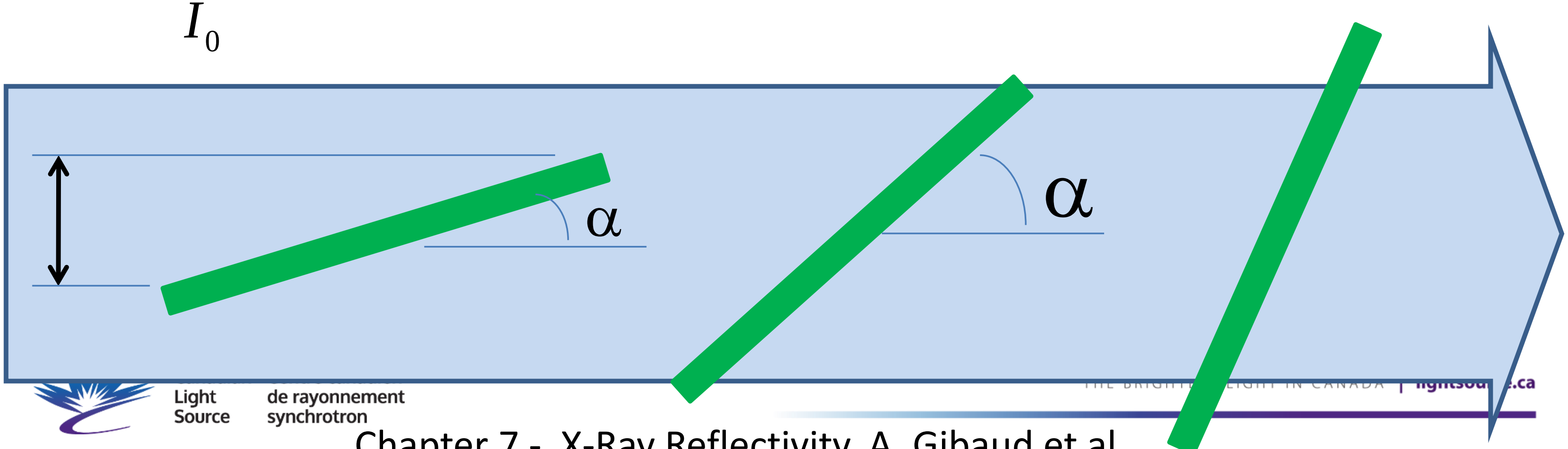
Footprint correction




Beam footprint length:

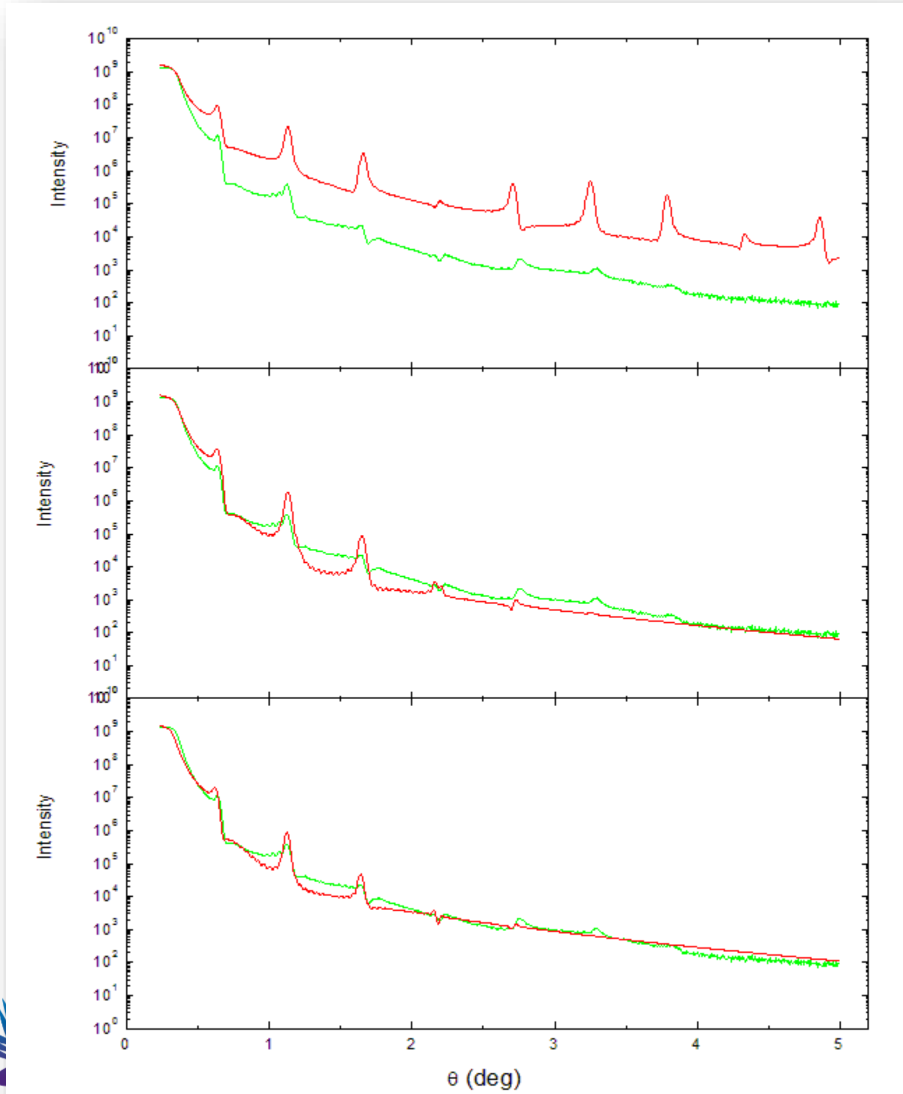
$$F = \frac{t}{\sin(\alpha)}$$

$$R = \frac{I}{I_0}$$



# Small angle X-Ray reflectivity

Fits to the measurement




Smooth interfaces

Rough interfaces

Lower densities
(porous sample?)

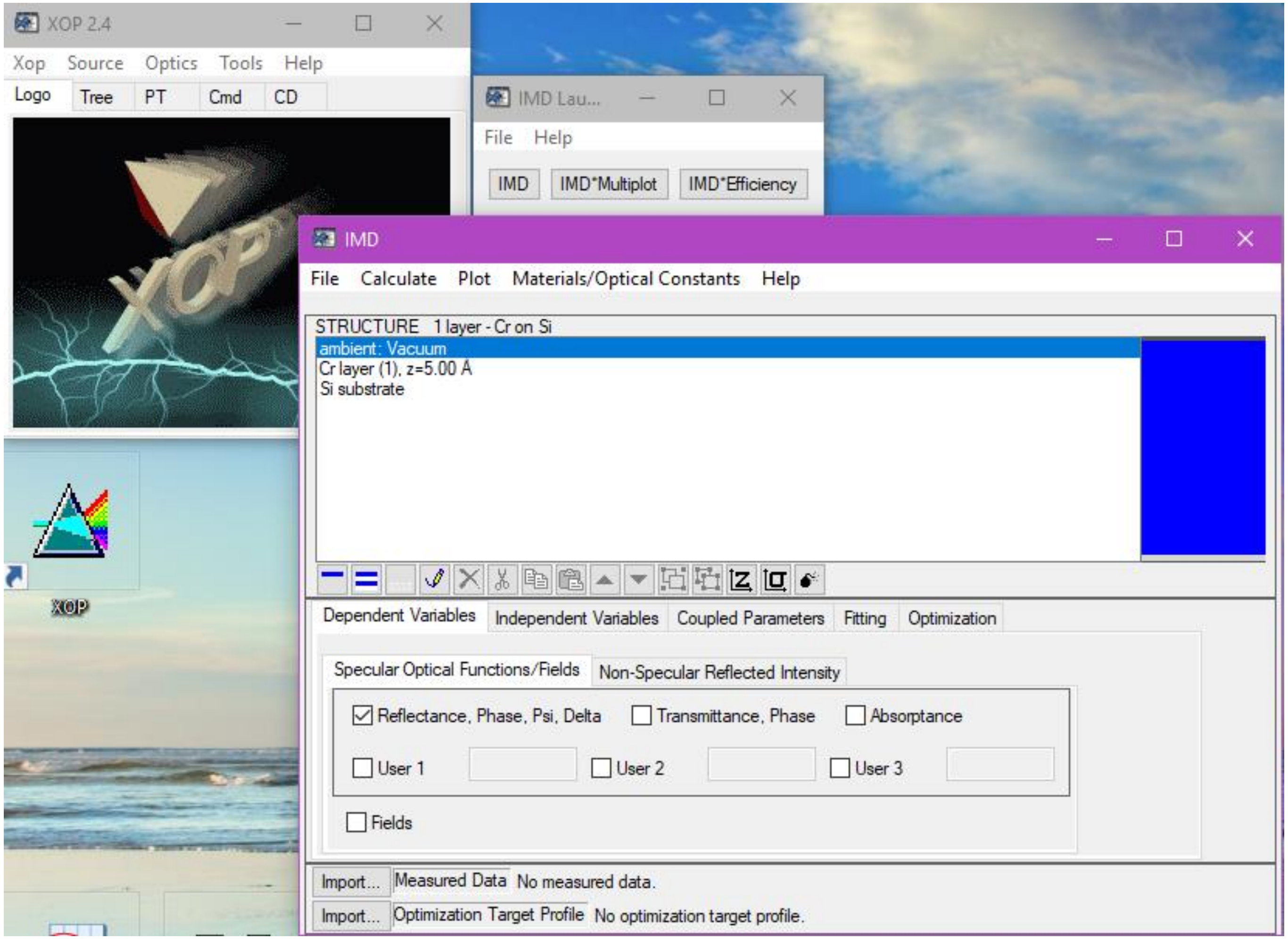
Oxide layer cap!

# Programs for simulating and fitting reflectivity

- GSAS II !
- Parratt 32
- RFit2000
- WinGixa (Panalytical)
- XOP / IMD

For more x-ray related softwares consult website:
http://gisaxs.com/index.php/Software#Crystallography

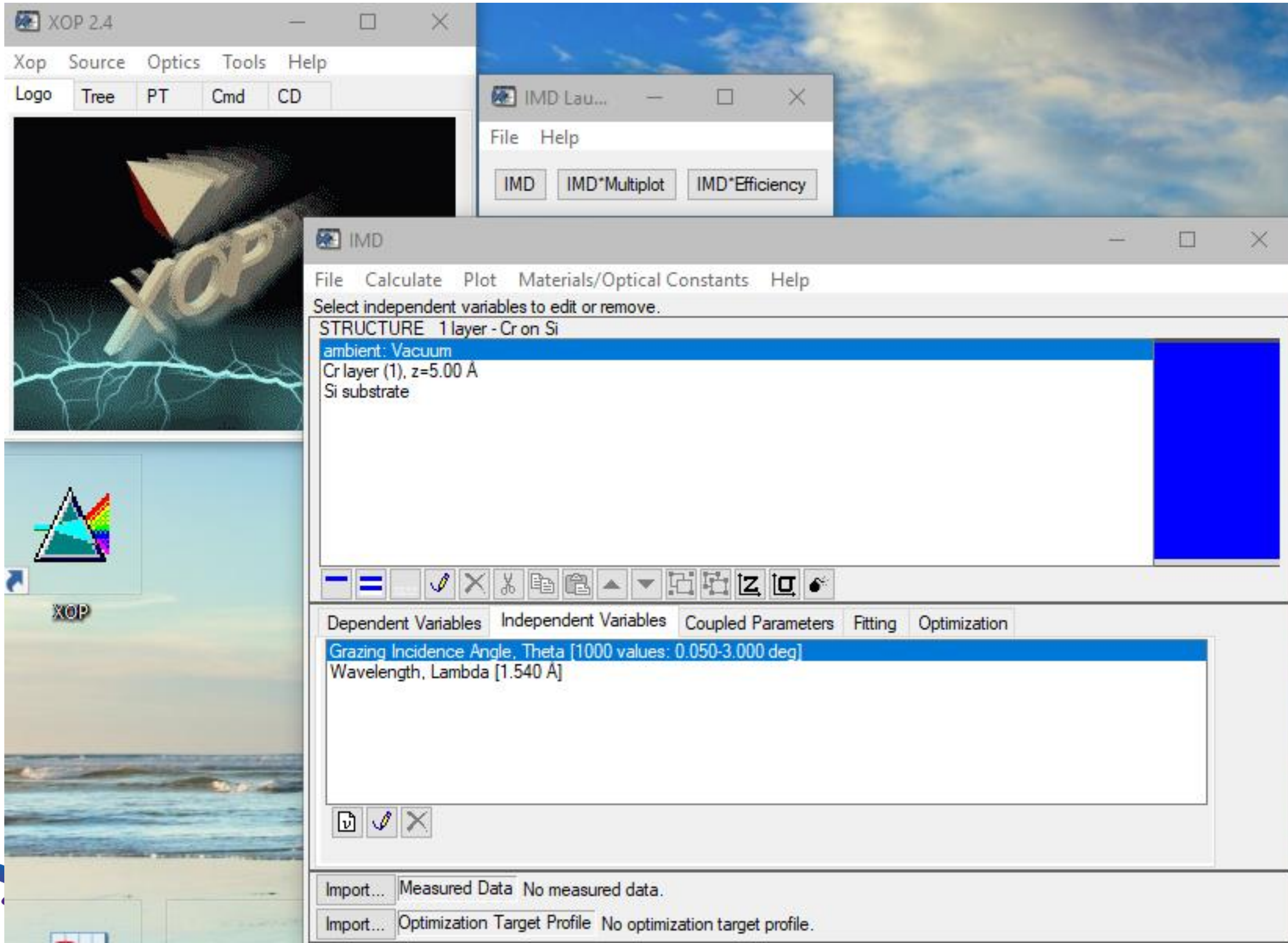
# IMD/XOP to simulate x-ray reflectivity



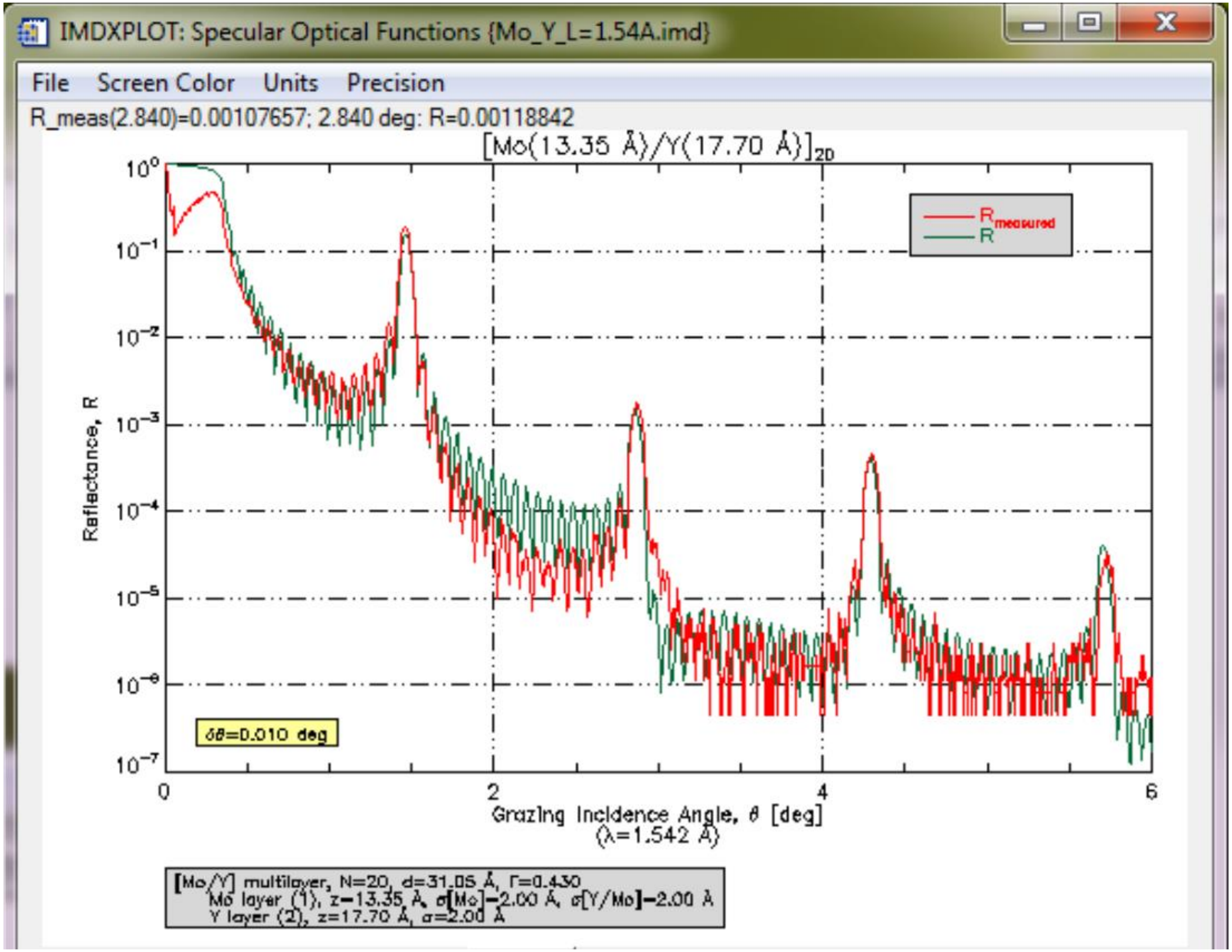

https://www.aps.anl.gov/Science/Scientific-Software/XOP

http://www.rxollc.com/idl/IMD.pdf

# IMD/XOP to simulate x-ray reflectivity



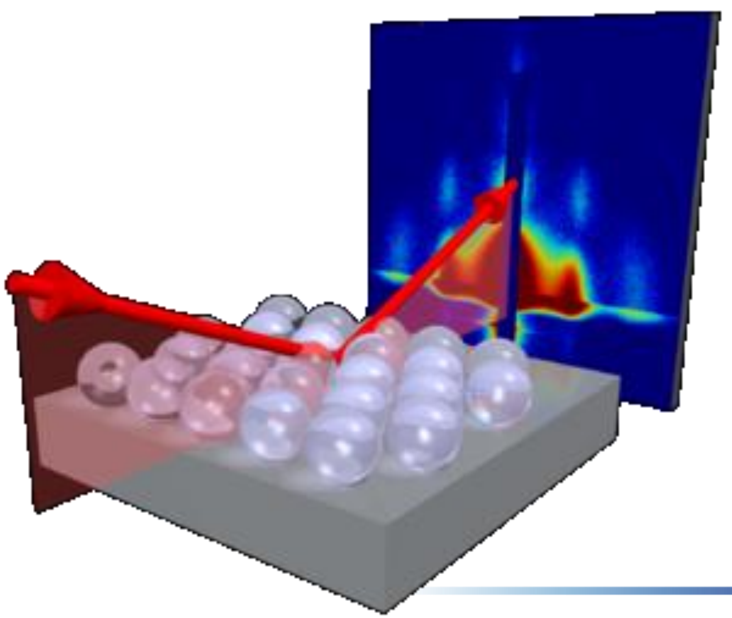
# IMD/XOP to simulate x-ray reflectivity



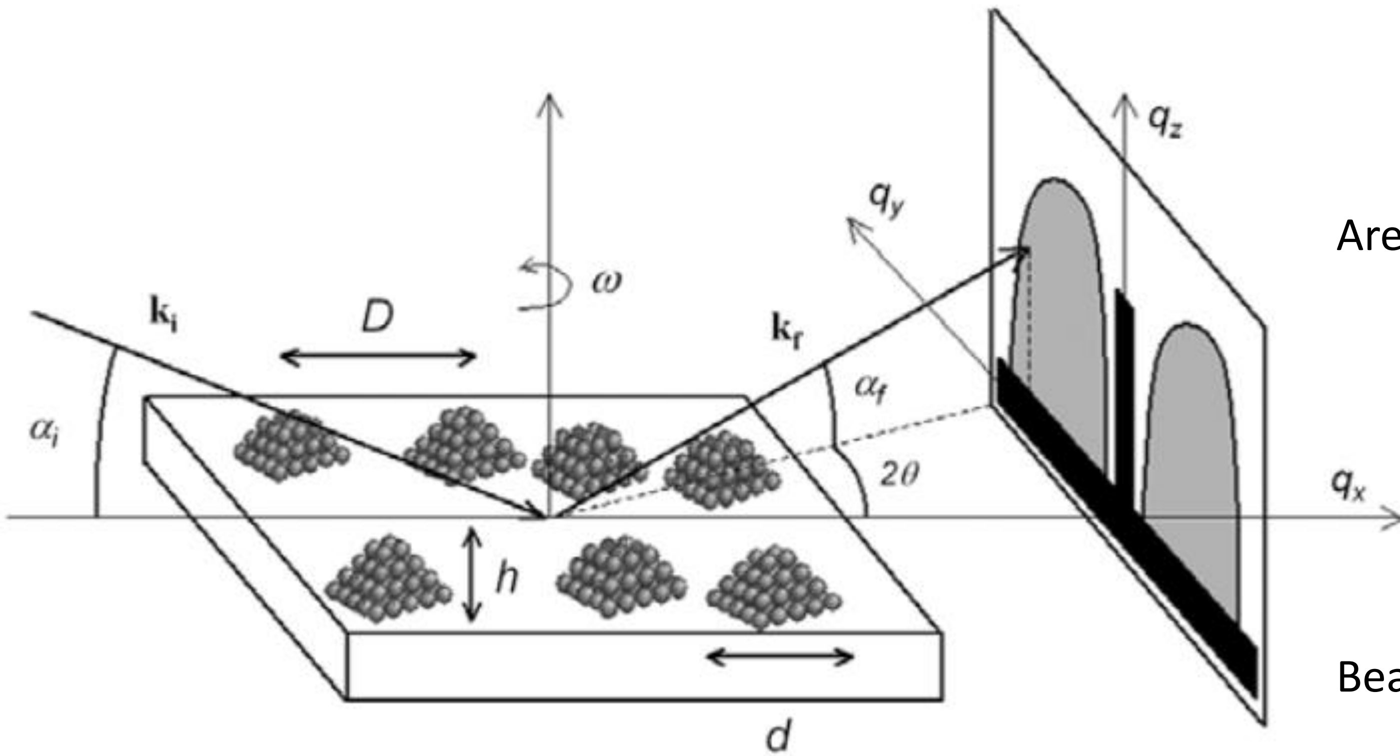
# Grazing incidence

# Small angle X-ray scattering

## GISAXS



# GISAXS measurements

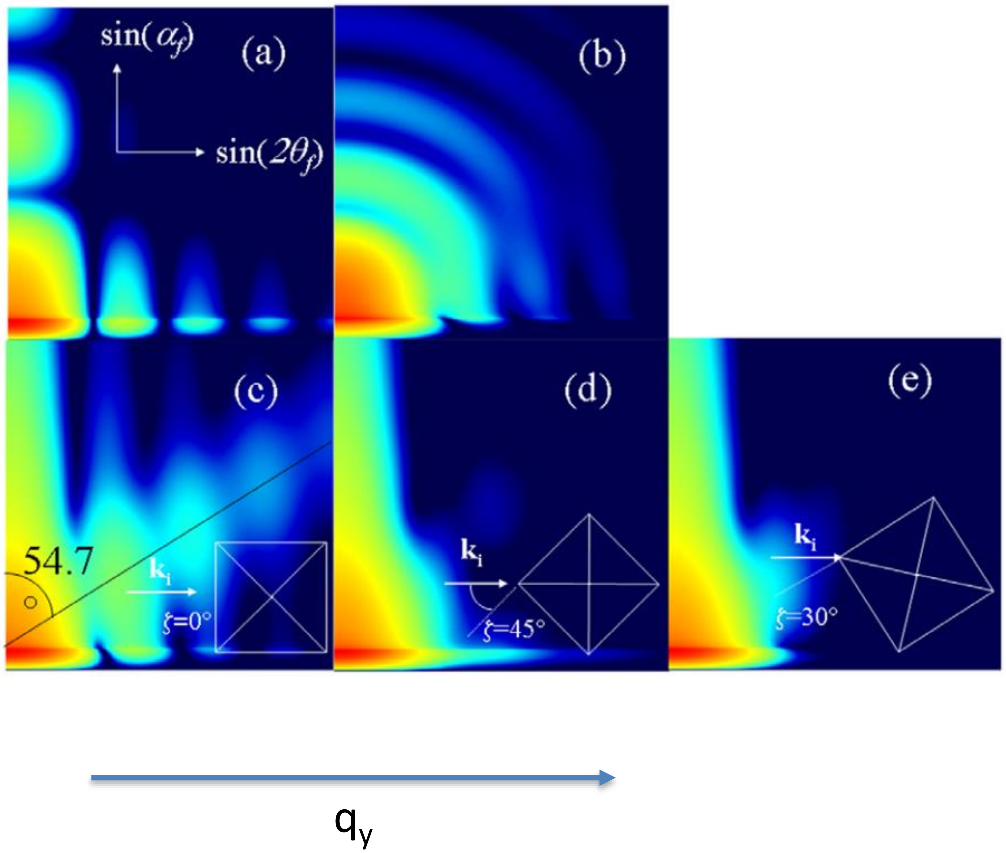


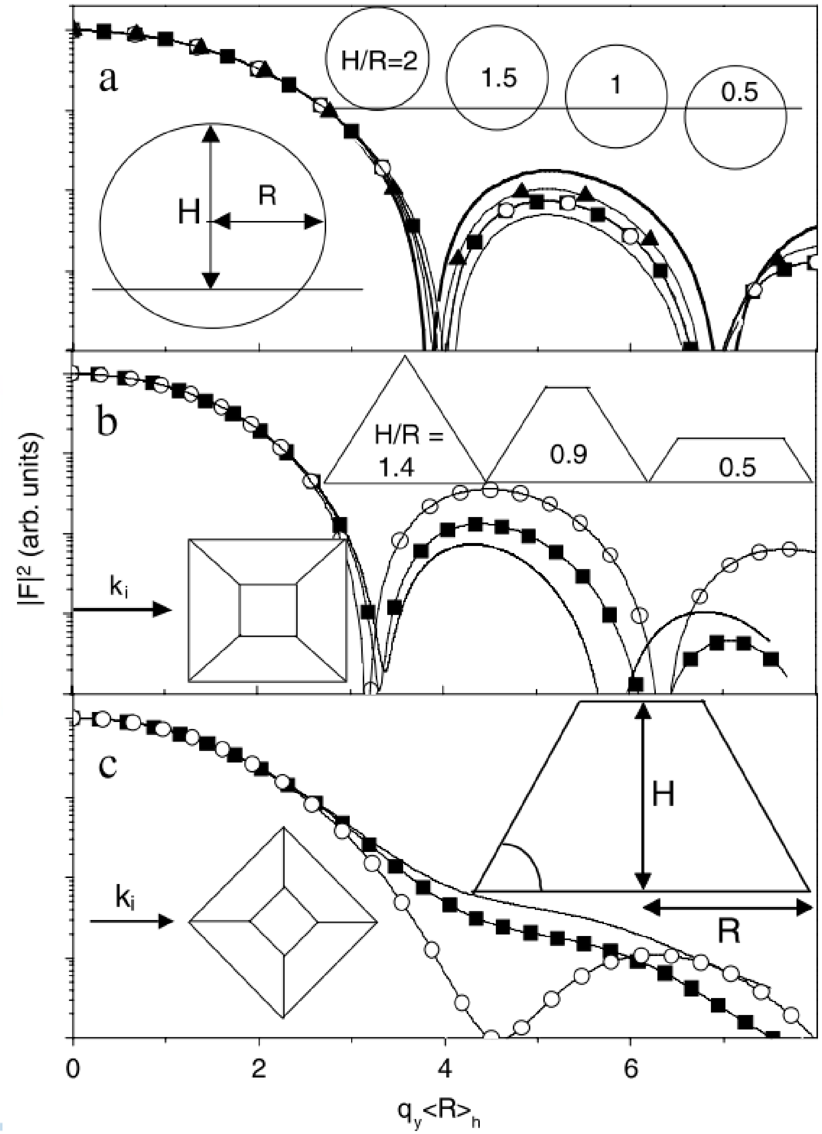

Area detector

Beam stop

Surface Science Reports **64**(8): 255-380, 2009.

# GISAXS




Canadian Light Source
Centre canadien de rayonnement synchrotron

Surface Science Reports **64**(8): 255-380.

# Modelling software

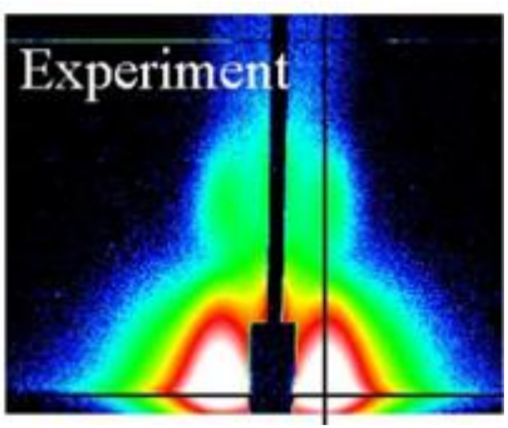
- R. Lazzari, IsGISAXS: A program for grazing-incidence small-angle X-ray scattering analysis of supported islands, J. Appl. Crystallogr. 35 (2002) 406–421.
- http://www.insp.jussieu.fr/oxydes/IsGISAXS/isgisaxs.htm

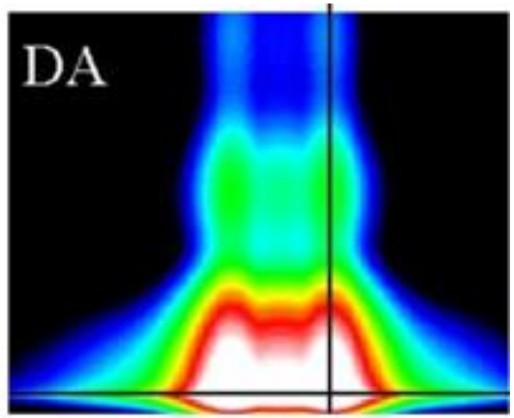
- Jiang, Z. (2015). "GIXSGUI: a MATLAB toolbox for grazing-incidence X-ray scattering data visualization and reduction, and indexing of buried three-dimensional periodic nanostructured films." Journal of Applied Crystallography **48**(3): 917-926.
- https://www.aps.anl.gov/Science/Scientific-Software/GIXSGUI

- FitGISAXS, BornAgain, HipGISAXS, NANOCELL, SimDiffraction,…

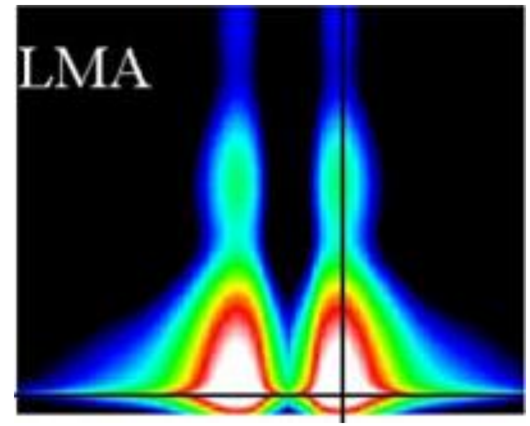
# IsGISAXS

## Pd islands on MgO(100)

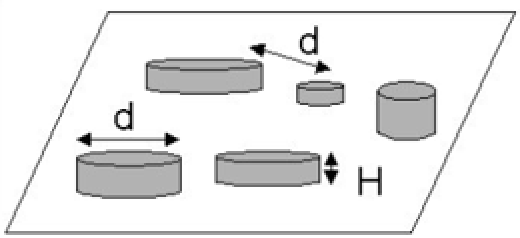



Decoupling Approximation (DA)




Local Monodisperse
Approximation (LMA)



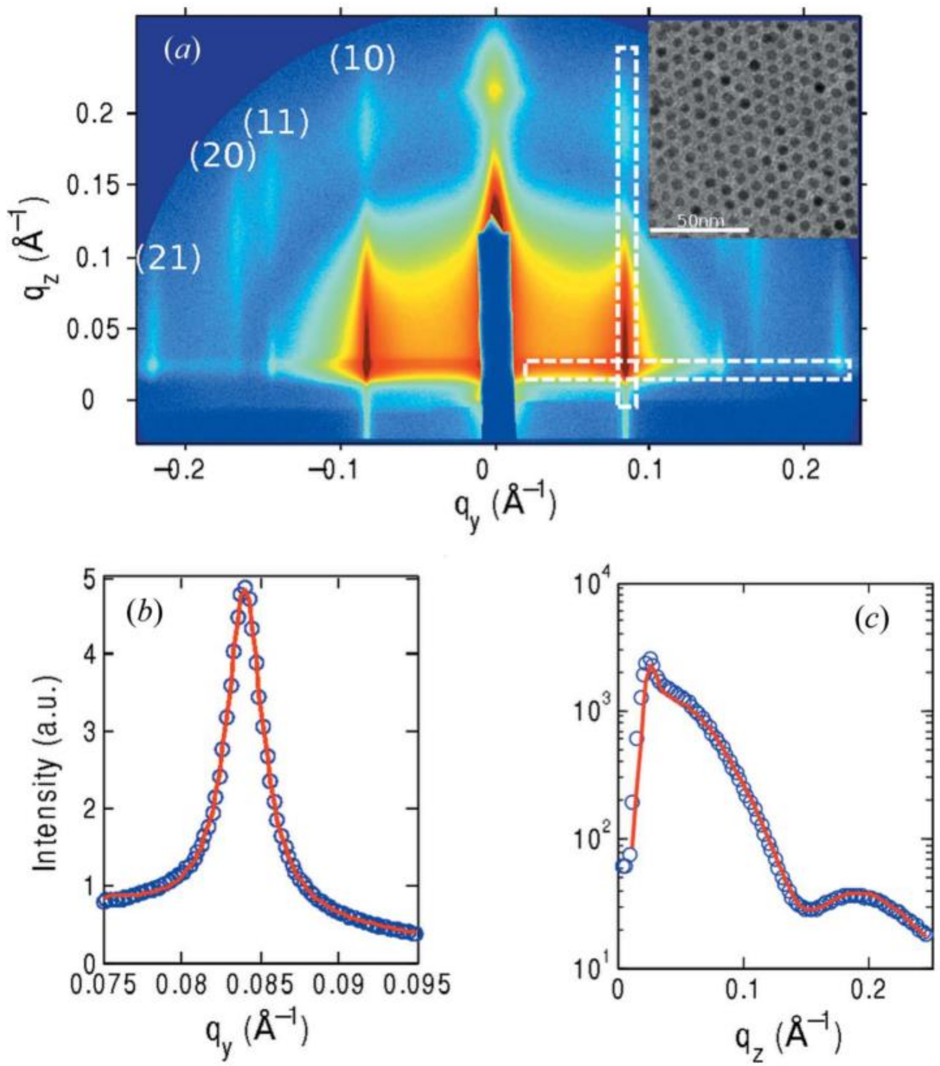

**PARAMETERS :**
**cylinder**
**D = 20.7 nm**
**d = 10.2 nm**
**H = 6.6 nm**
$\sigma_R = 1.3$
$\sigma_H = 1.1$



http://www.insp.jussieu.fr/oxydes/IsGISAXS/isgisaxs.htm#Introduction

# GISAXS

Spherical gold nanoparticles in silicon

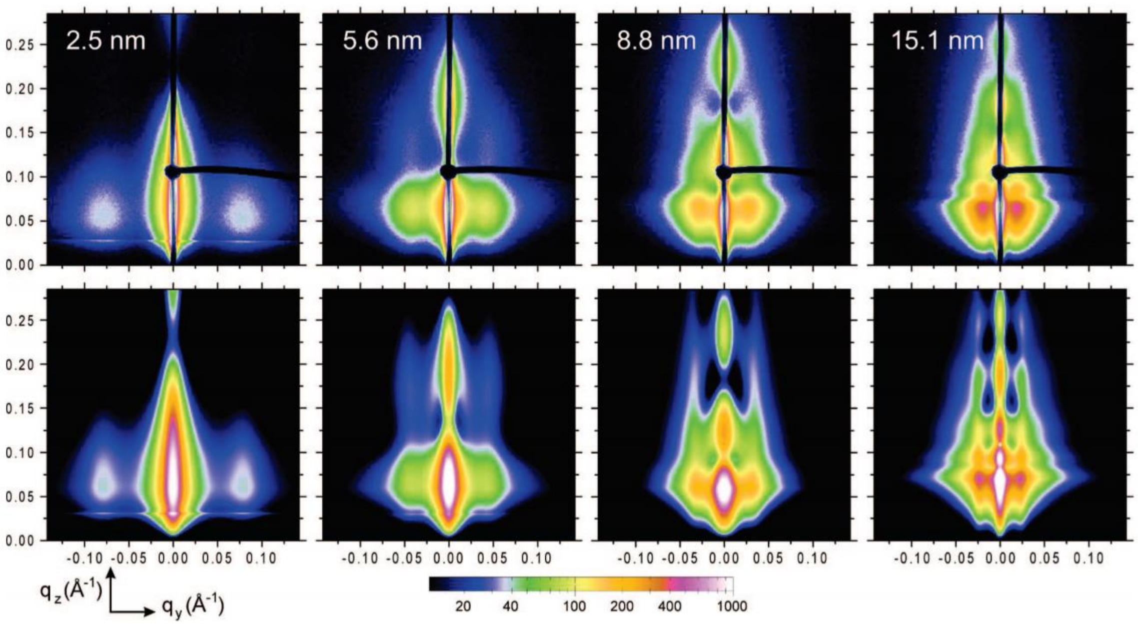


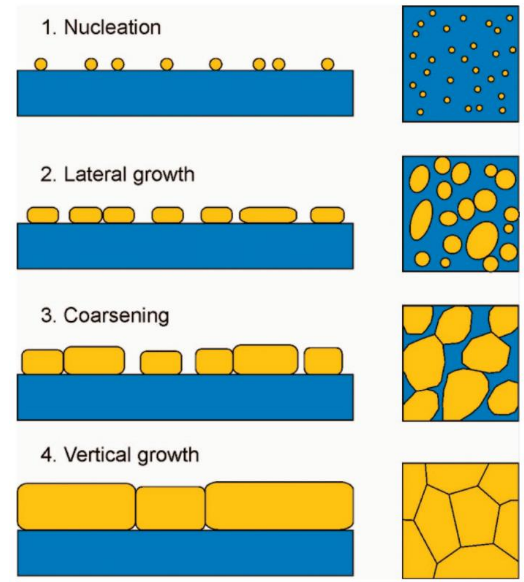



Journal of Applied Crystallography **48**(3): 917-926, 2015

# In Situ GISAXS

## Gold film growth on conducting polymer



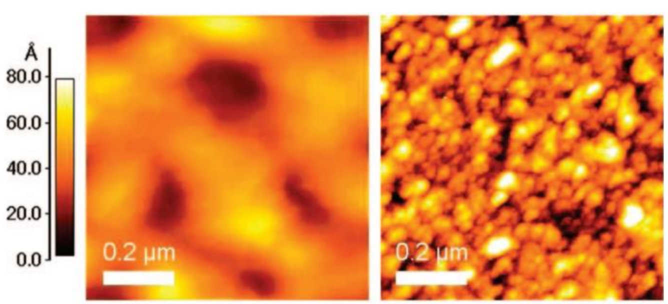



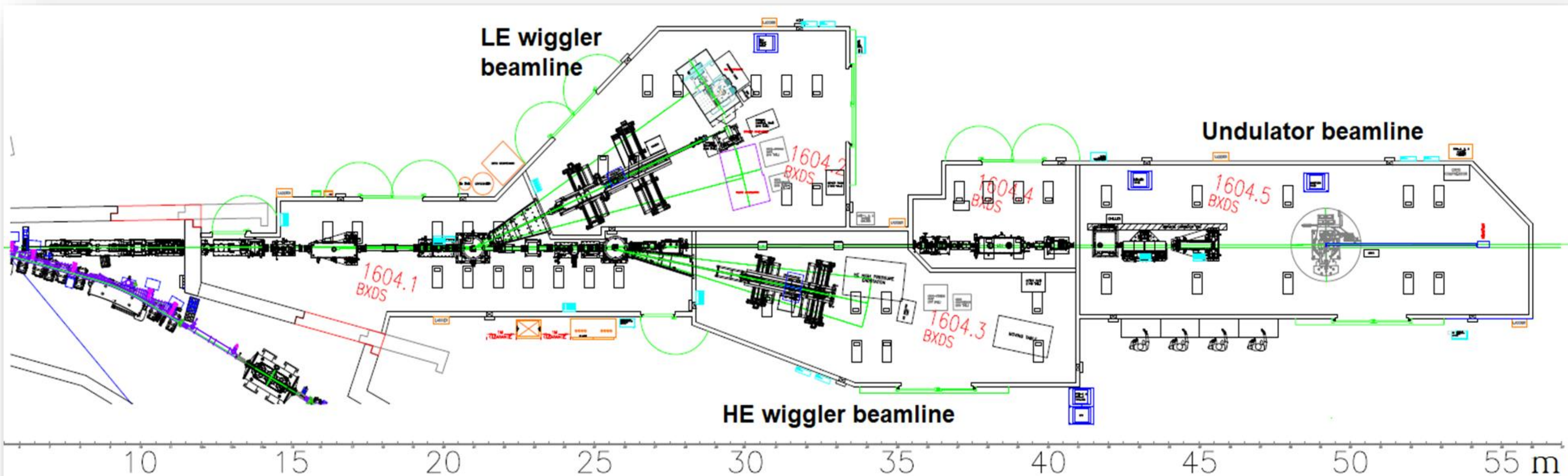

**Table 1. Morphological Parameters Extracted from Simulation of the Data by Use of a Model Consisting of Parallelepiped and Spheroid Particle Geometries To Describe the Cluster Shape[a]**

| $t$ (min) | $d_0$ (nm) | $d$ (nm) | $r_p$ (nm) | $\sigma_p$ (nm) | $h_p$ (nm) | $r_s$ (nm) | $\sigma_s$ (nm) | $h_s$ (nm) | $D$ (nm) | $\omega$ (nm) |
|---|---|---|---|---|---|---|---|---|---|---|
| 9 | 3.9 | 2.5 | 4.8 | 20.0 | 3.6 | 4.8 | 11.0 | 4.3 | 11.8 | 3.8 |
| 19 | 8.2 | 5.6 | 9.1 | 22.5 | 6.1 | 9.1 | 5.3 | 6.8 | 19.0 | 7.2 |
| 29 | 12.5 | 8.8 | 13.5 | 17.6 | 8.8 | 13.5 | 14.9 | 9.9 | 27.0 | 10.2 |
| 49 | 21.1 | 15.1 | 20.0 | 36.0 | 15.2 | 20.0 | 18.0 | 16.4 | 40.0 | 15.2 |



ACS Applied Materials & Interfaces **1**(2): 353-360, 2009

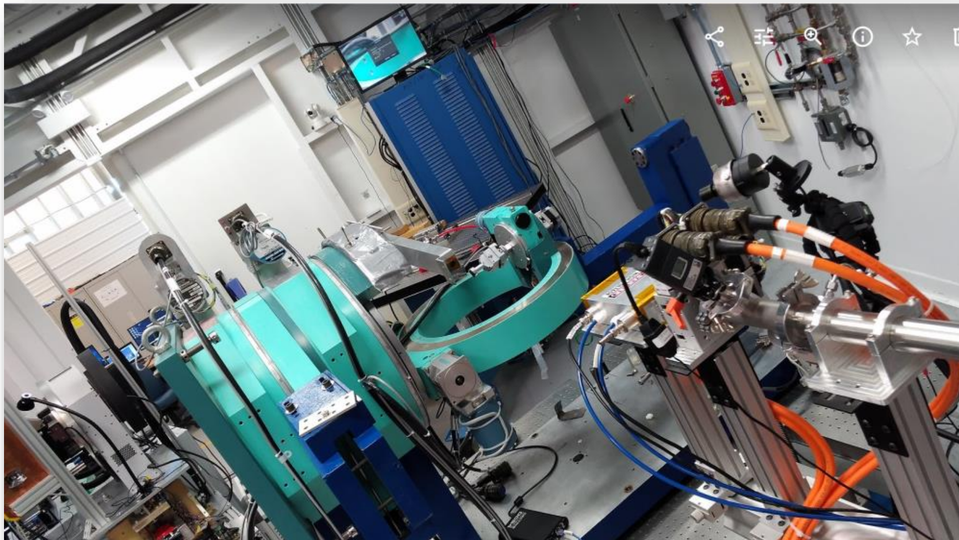
# Thin film characterization at the Brockhouse sector

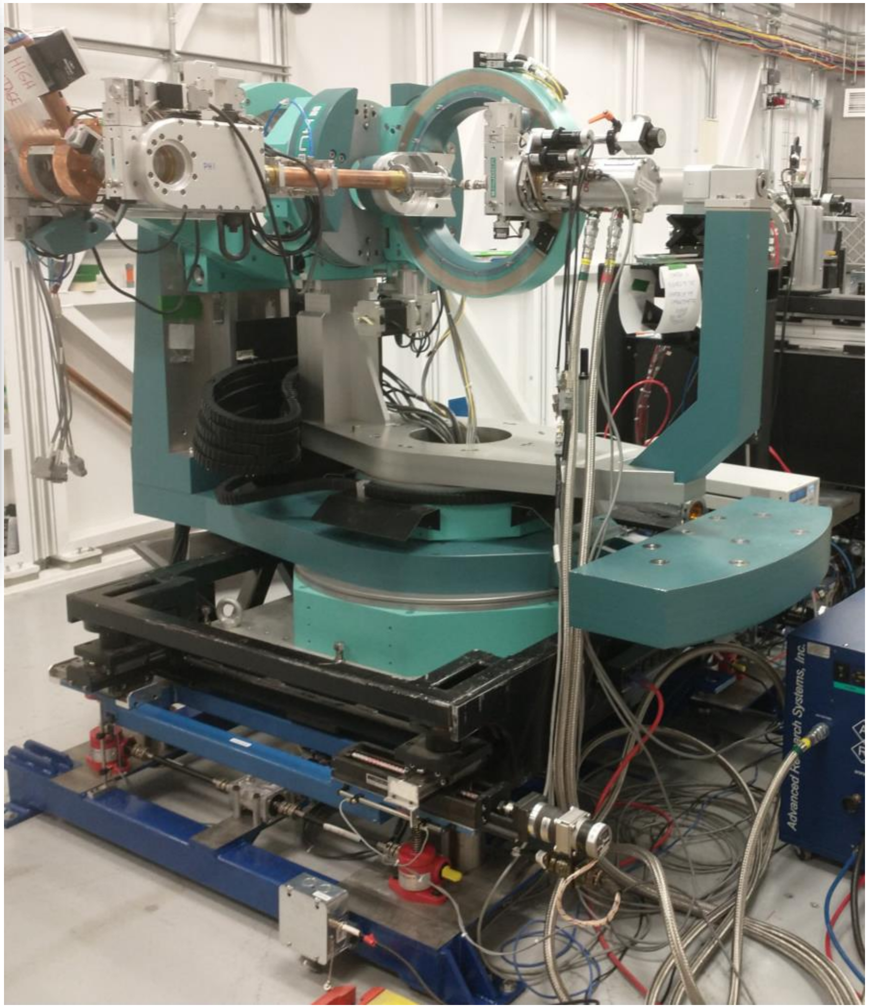



Brockhouse beamlines layout

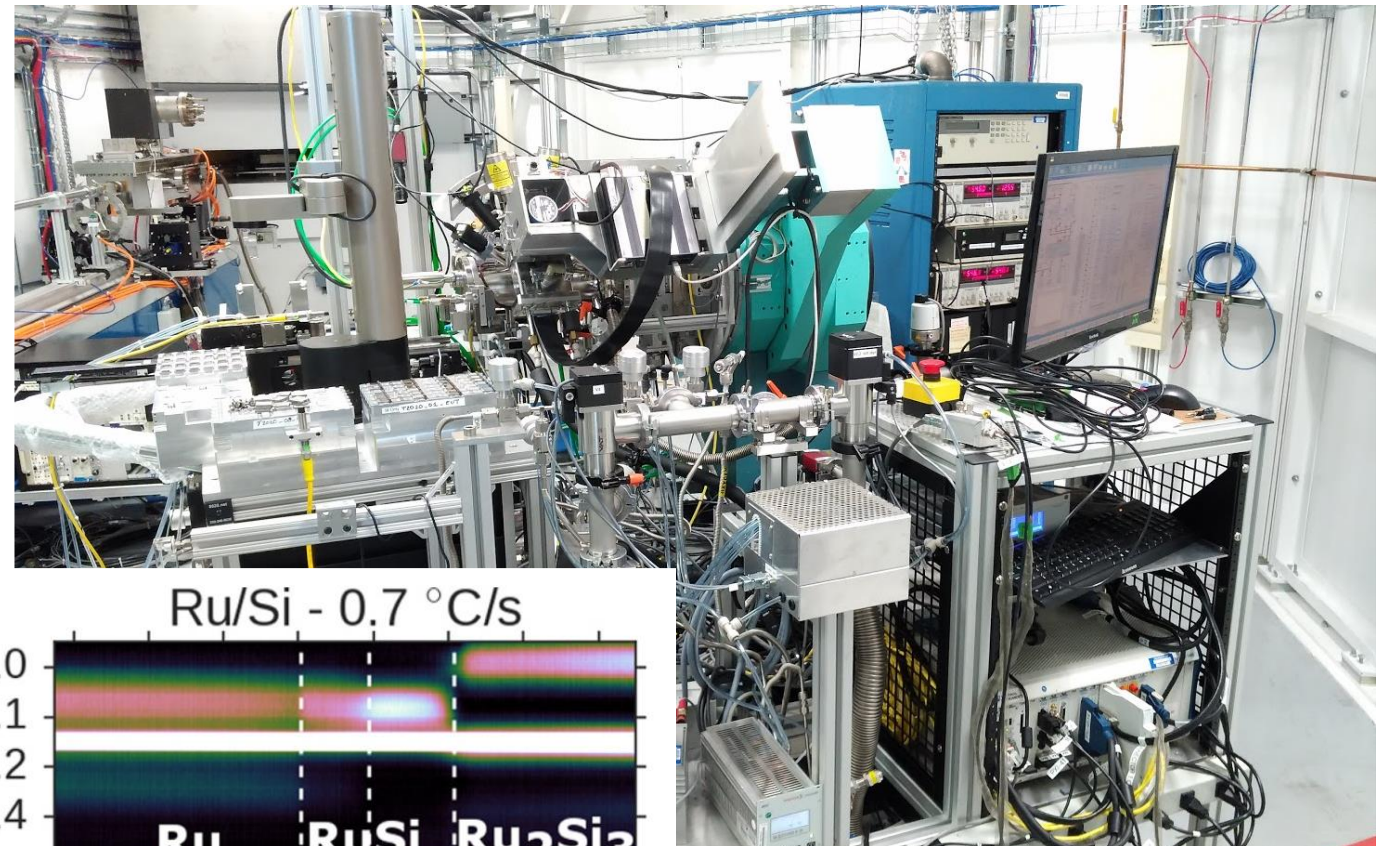
**Beamlines energy range**
Lower energy wiggler beamline: 7 – 22 keV
Undulator beamline: 5 – 24 keV
Higher Energy wiggler beamline: 20 – 95 keV

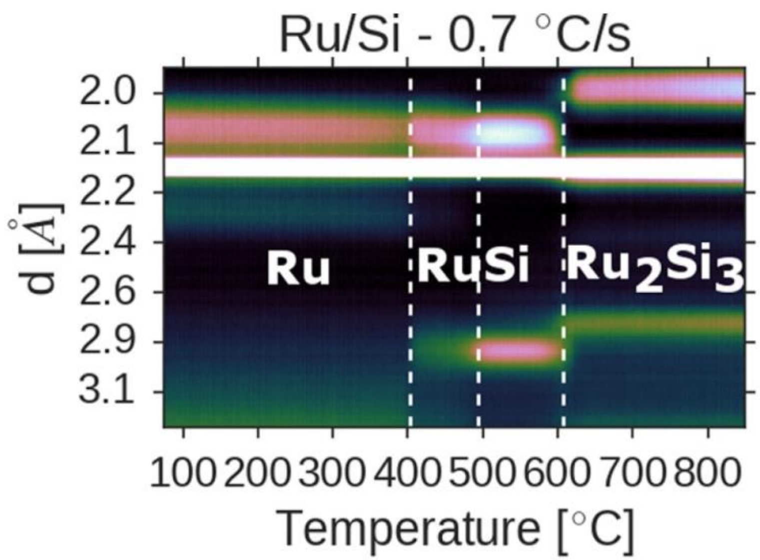
# Thin film characterization at the Brockhouse sector





# Thin film characterization at the Brockhouse sector






**IBM in-situ station**

XRD

RTA up to 1000 °C

$H_2$ or $N_2$ ultrahigh purity atmosphere

Resistance probe

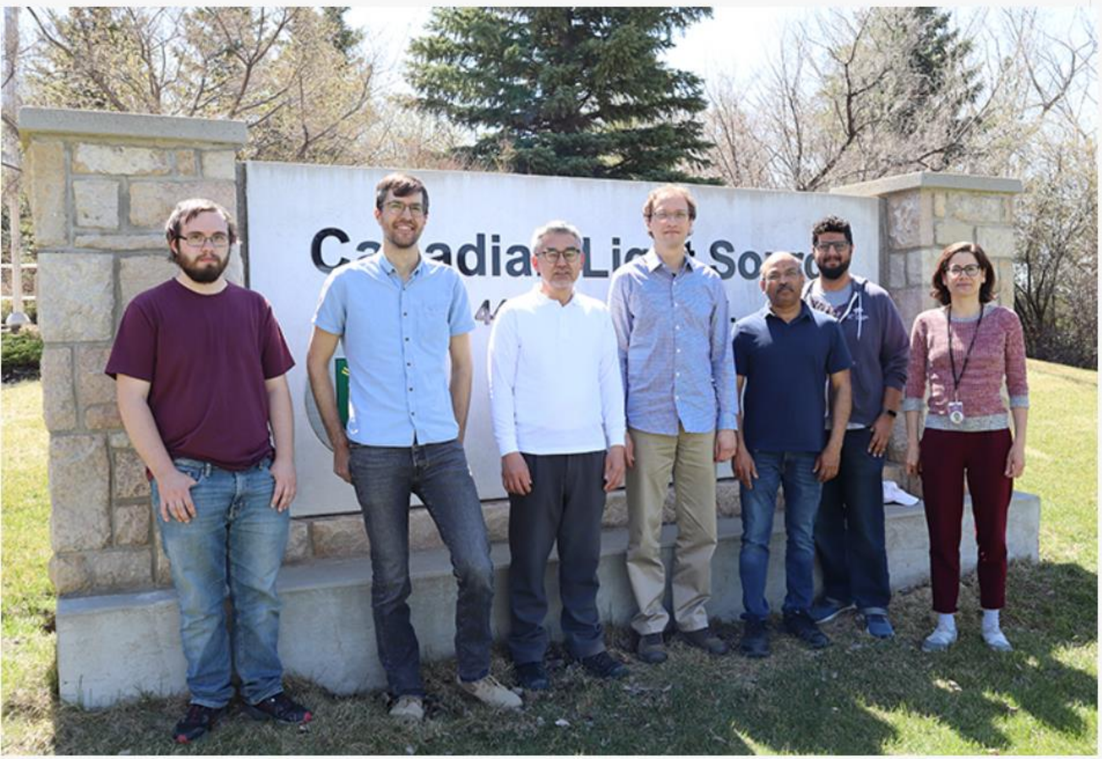
Roughness probe

# BXDS – Brockhouse X-ray Diffraction and Scattering for materials science

brockhouse.lightsource.ca

**Brockhouse Diffraction Sector Beamlines**

Home | Beamlines | User Guide | Contact Us | Workshops



Welcome to the Brockhouse homepage. We provide a wide range of complementary diffraction and scattering techniques to fully characterize your materials.

- High resolution powder diffraction
- Pair distribution function (PDF)
- High energy diffraction for in-situ studies
- Reciprocal space mapping
- Small/wide angle X-ray scattering (SAXS/WAXS)
- High pressure crystallography
- X-ray reflectivity
- Grazing incidence diffraction (GID)
- Anomalous diffraction and magnetic diffraction

# Conclusions

If you have a sample… → measure XRD!

If it is a very thin film… → try one of the techniques with grazing incidence geometry

They yield information about:

- ✓ Structure / texture / stress
- ✓ Defects
- ✓ Thickness
- ✓ Roughness
- ✓ Composition, interdiffusion, gradients
- ✓ Size, morphology, ordering
- ✓ How does it perform under real working conditions?

  →Come to a synchrotron and perform in-situ experiments!

# Further reading

- Thin Film Analysis by X-Ray Scattering, by Mario Birkholz, 2006

- Surface Science Techniques
  - Chapter 6: Grazing incidence X-Ray diffraction by Osami Sakata and Masashi Nakamura
  - Chapter 7: X-Ray Reflectivity by Gibaud, Chebil and Beuvier

- Renaud, G., et al. (2009). "Probing surface and interface morphology with Grazing Incidence Small Angle X-Ray Scattering." Surface Science Reports **64**(8): 255-380

# Acknowledgments

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