Canadian Light Source

XRD Summer School

August 16 – 18, 2022

Thin Film Characterization with X-Rays

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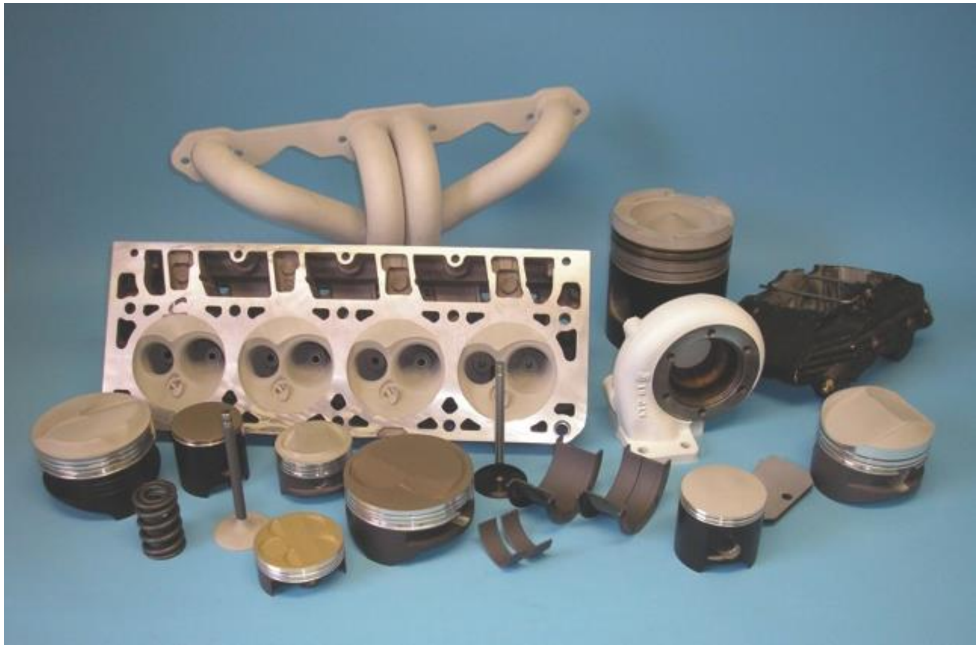
TOPICS

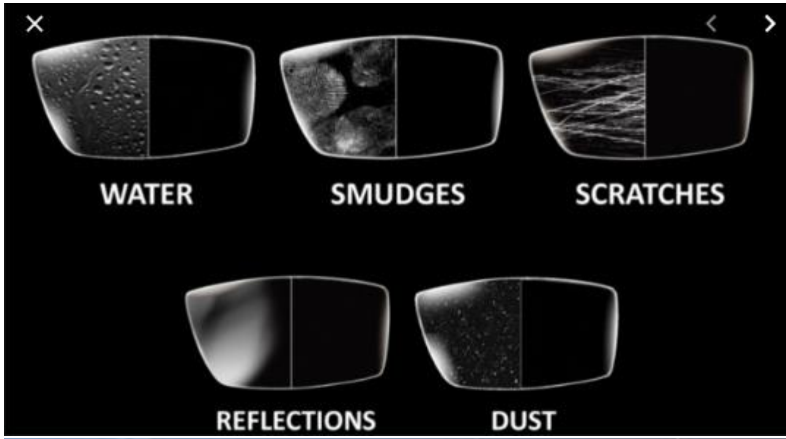
1. Motivation
2. Is the film thin?
3. X-ray Attenuation

Techniques:

a) GI-powder XRD
b) GI-single crystal XRD
c) Reflectivity
d) GISAXS

Motivation

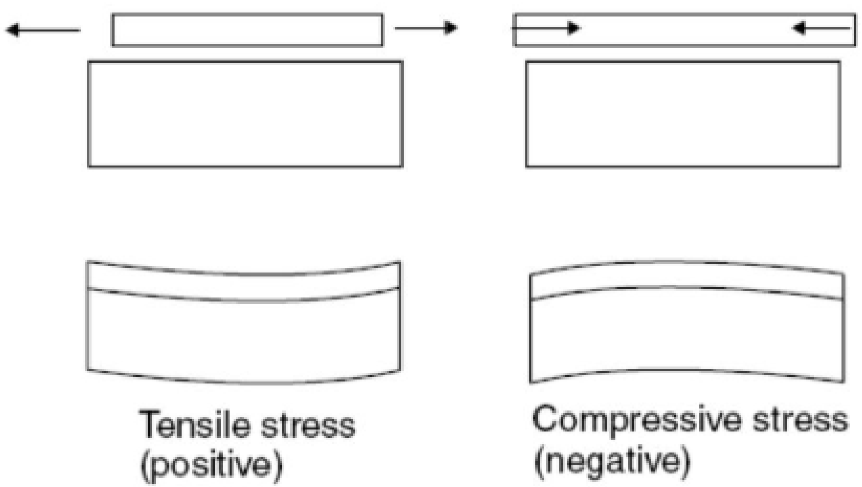


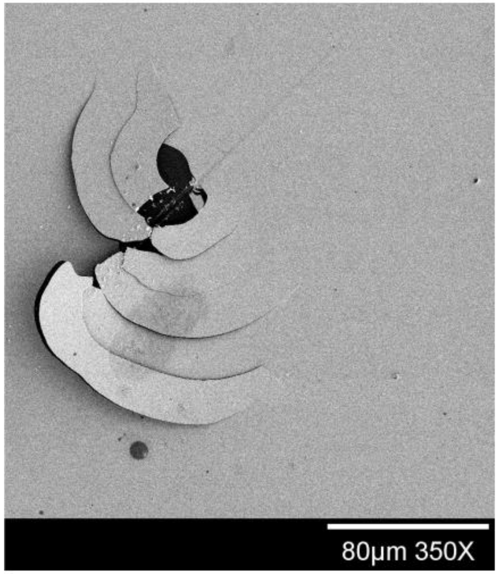


Three Most Common Issues Coatings Address:

1. Friction
2. Heat
3. Corrosion

Structure ⟷ Performance





Stress fracture patterns in ALD W/Si

What can we measure?

Small angle x-ray reflectivity

GI-SAXS

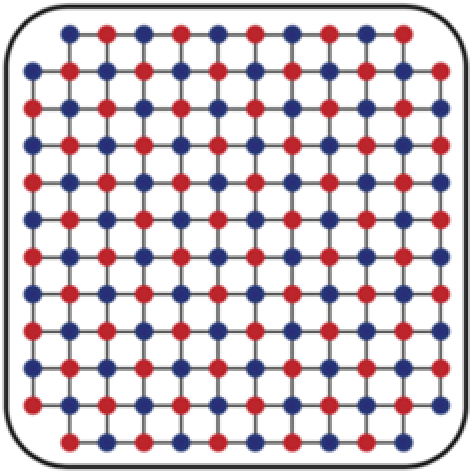
GI-WAXS -- GI – PXRD
-- GI -- RSM

Reflectivity
XRD
Pole figures

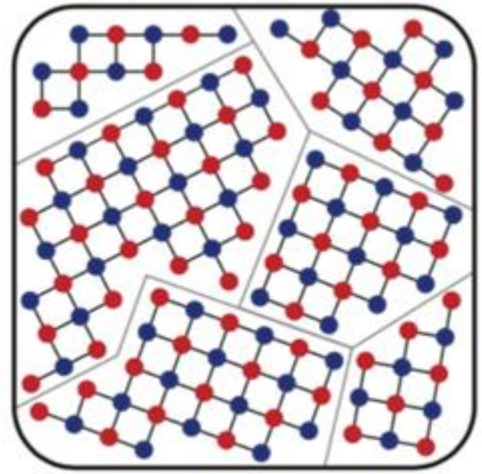
They yield information about:
✓Film thickness, roughness, porosity
✓Structure, stress, texture, defects
✓Composition, interdiffusion, gradients
✓Buried nanostructures, size, shape, ordering

What kind of films can we measure?

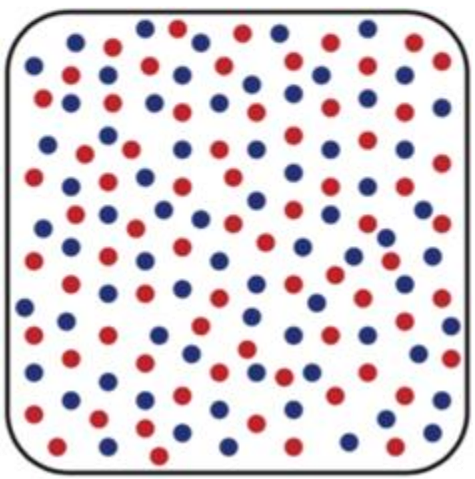
Single-crystal



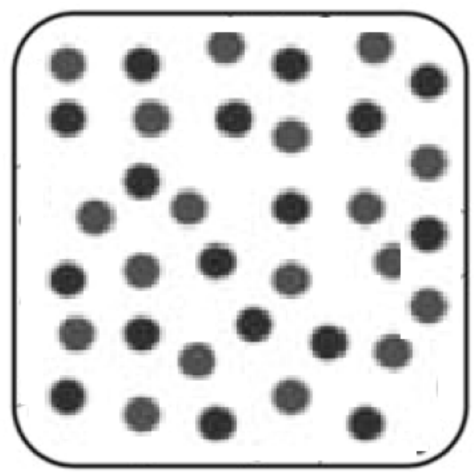
Poly-crystalline



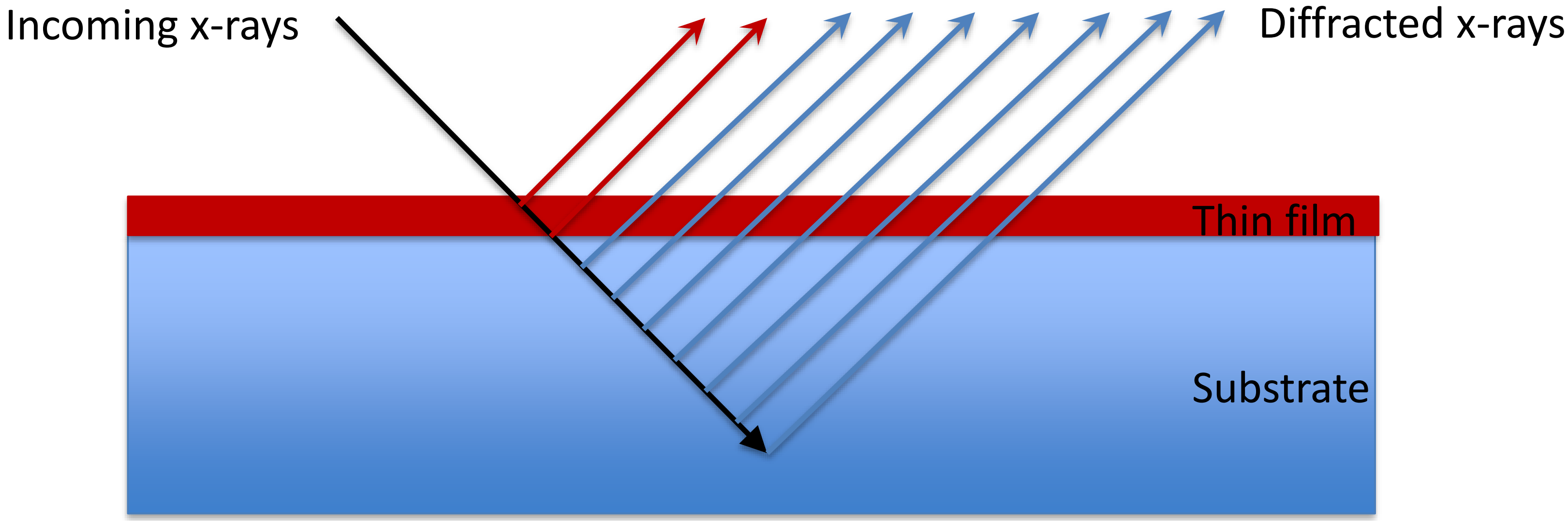
Amorphous

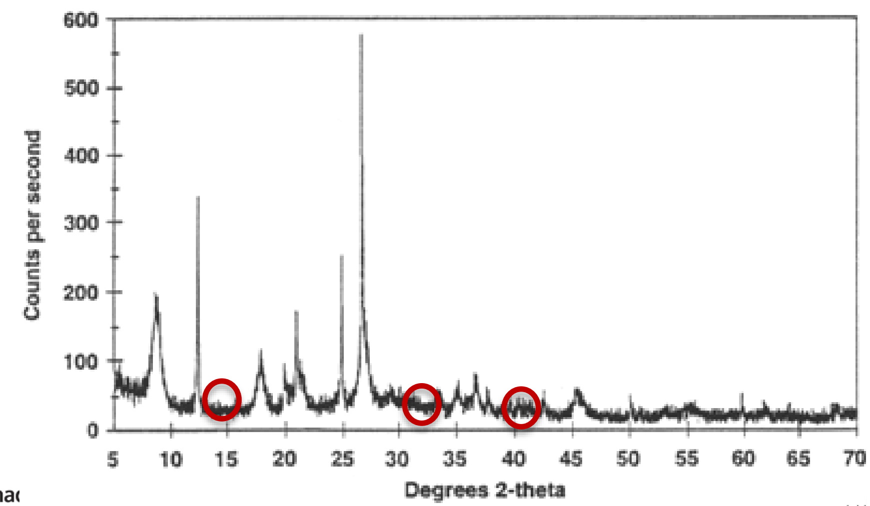


Nanostructures

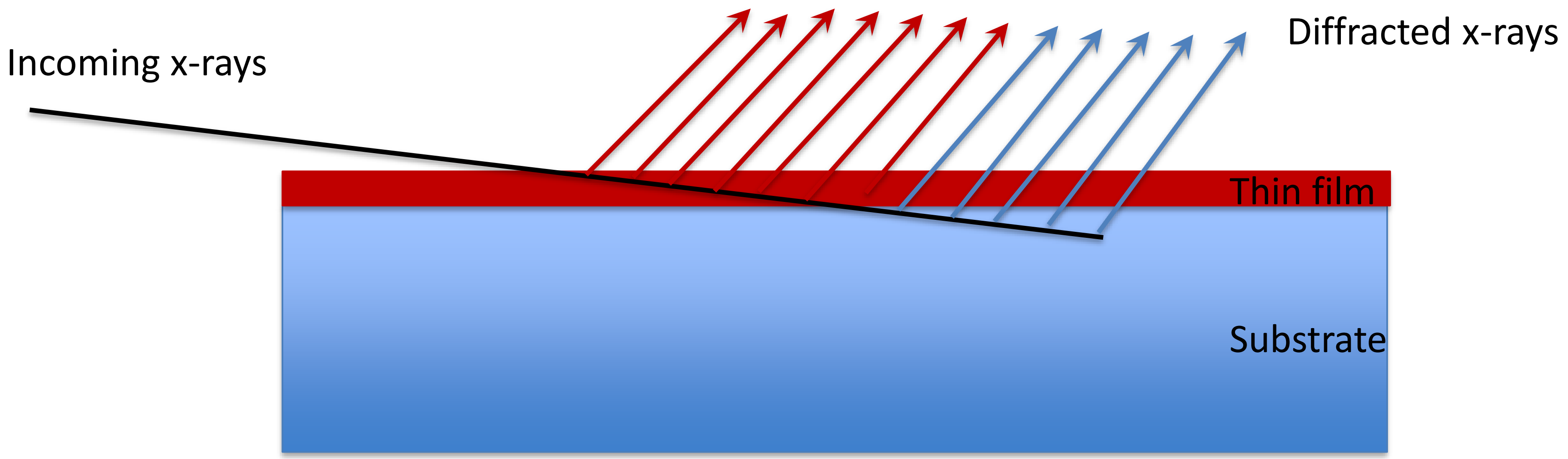


Using X-Rays to investigate thin films





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



X-Rays attenuation length

The **attenuation length** ε 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

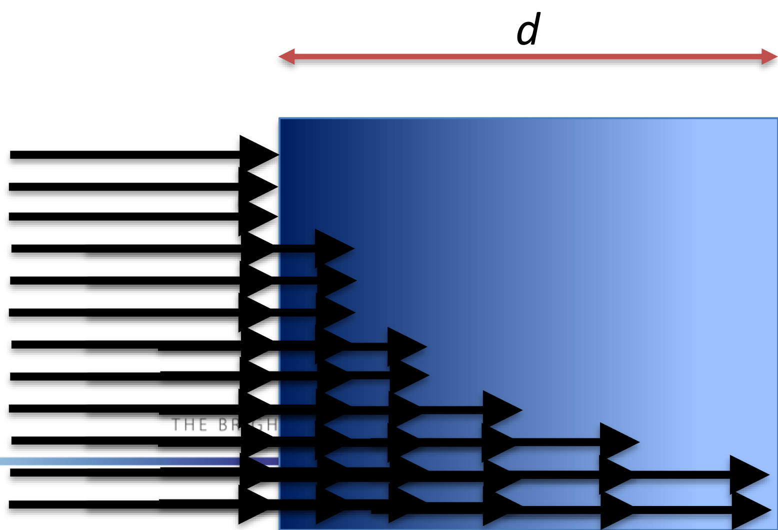
$$I = I_o\, e^{-\frac{d}{\varepsilon}}$$

The **attenuation coefficient** μ 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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www.cxro.lbl.gov

X-Ray attenuation length

CXRO THE CENTER FOR X-RAY OPTICS

BERKELEY LAB

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

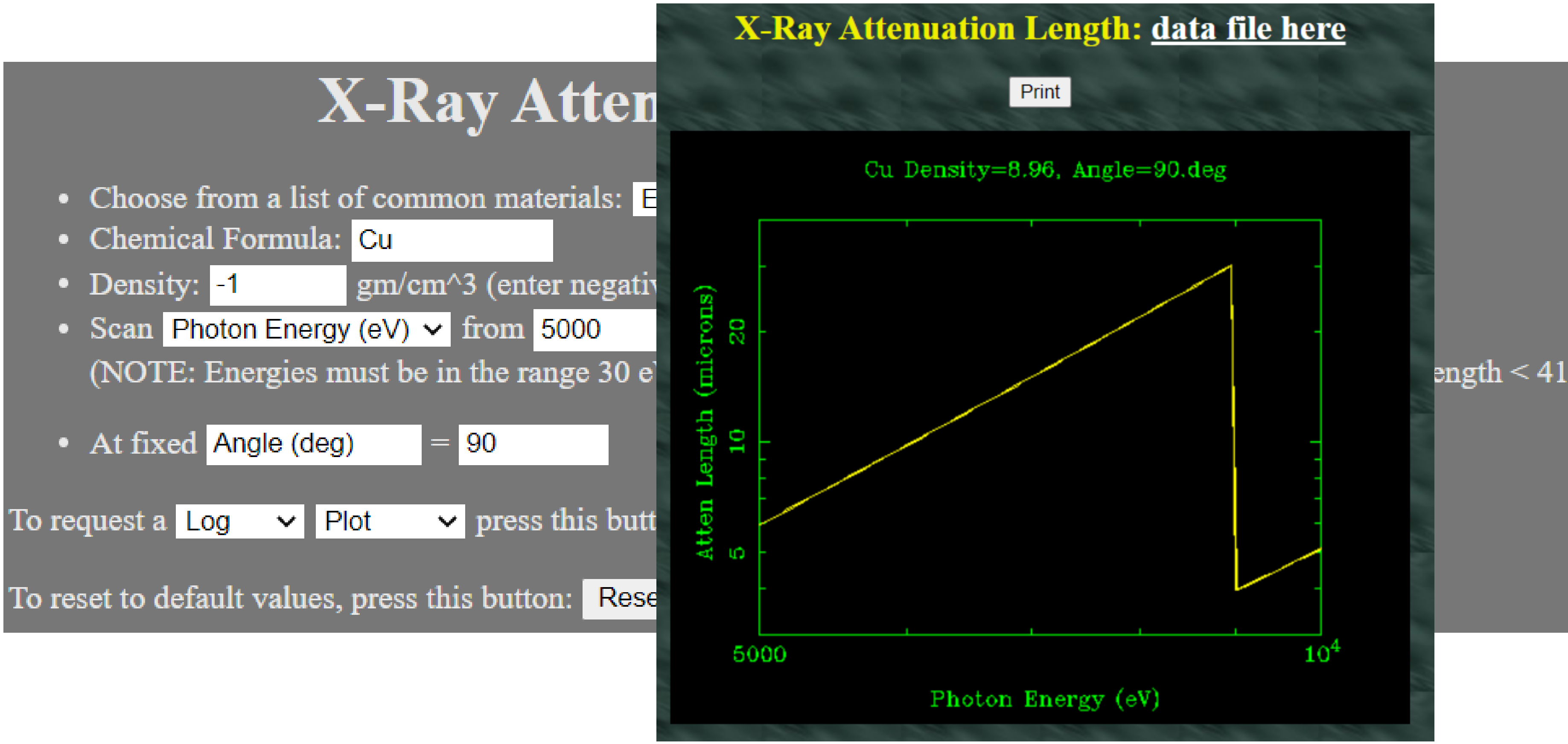
X-Ray Attenuation Length

- 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

X-Ray attenuation length

www.cxro.lbl.gov

THE CENTER FOR X-RAY OPTICS

X-Ray Database

Zone Plate Education

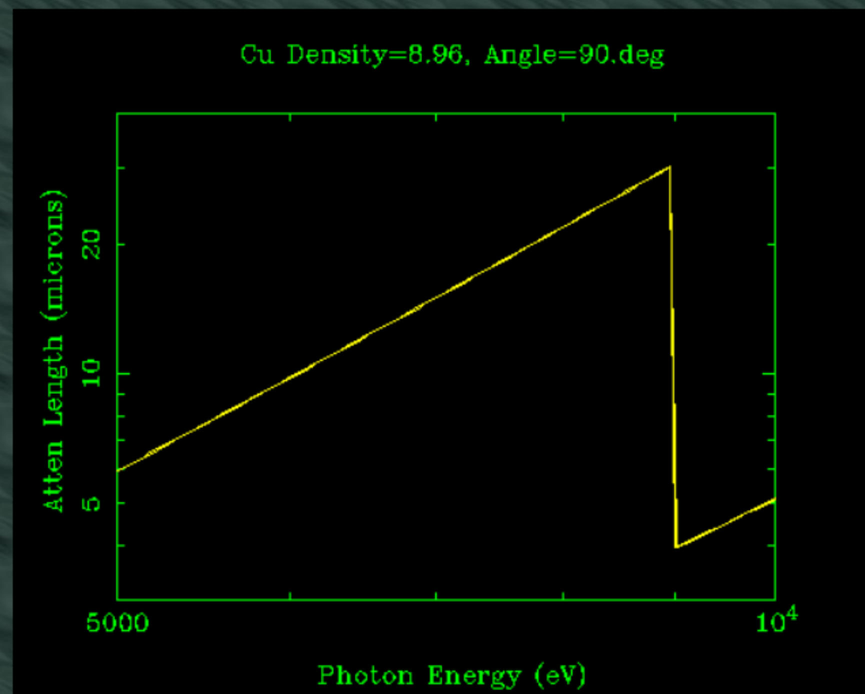
X-Ray Atten

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

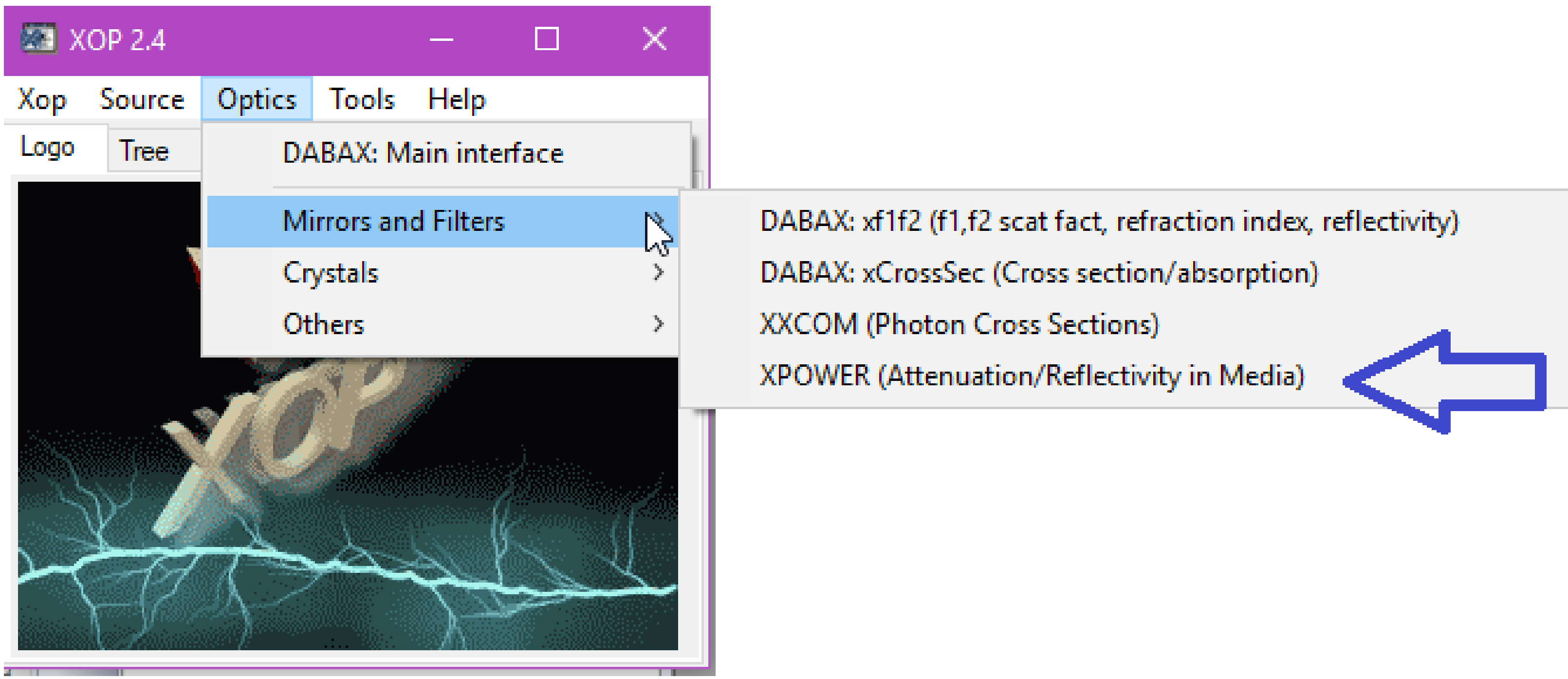
Element 29: Cu

Edge	keV
K	8.9789

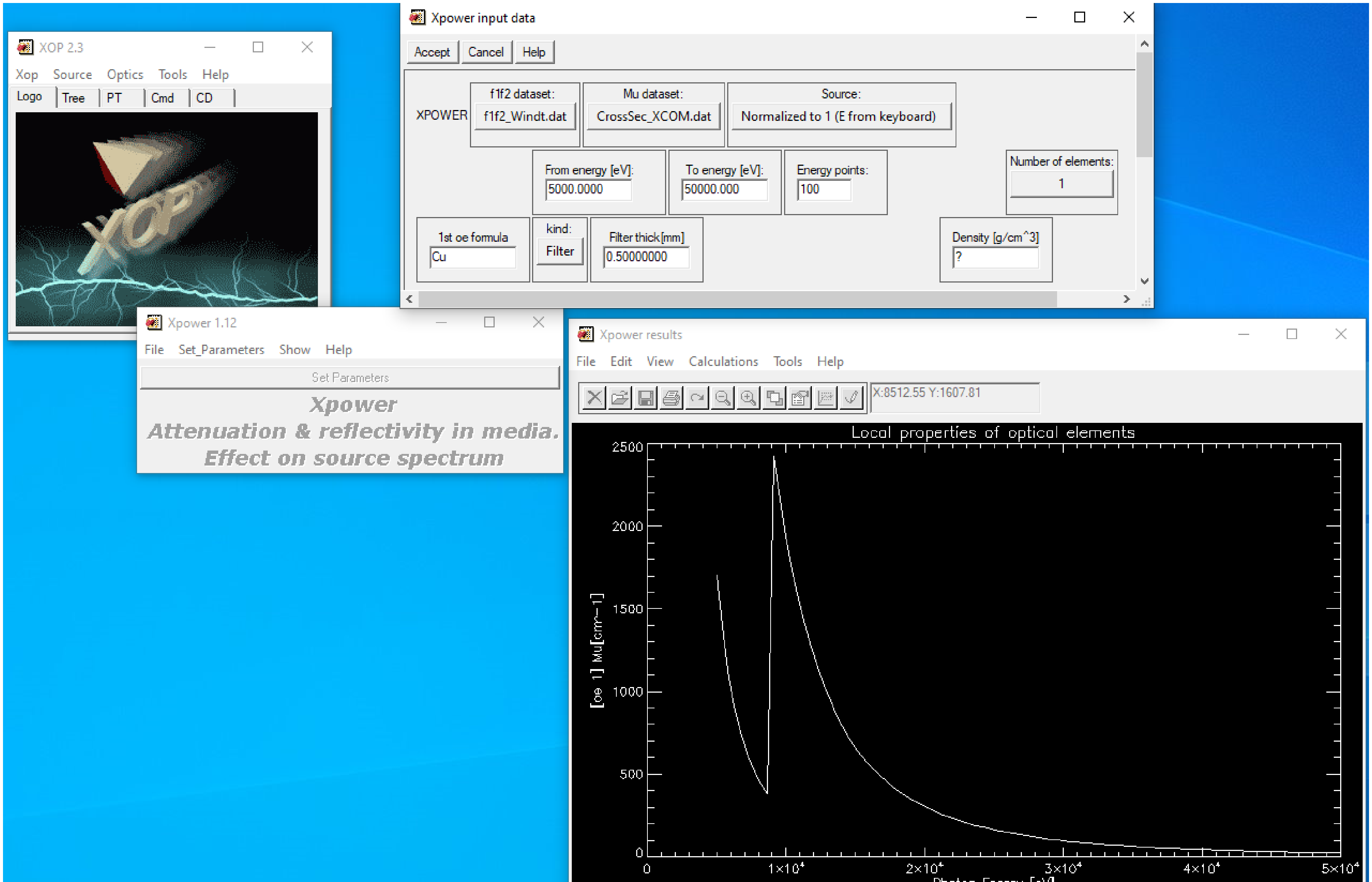
X-Ray attenuation length

XOP/XPOWER

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

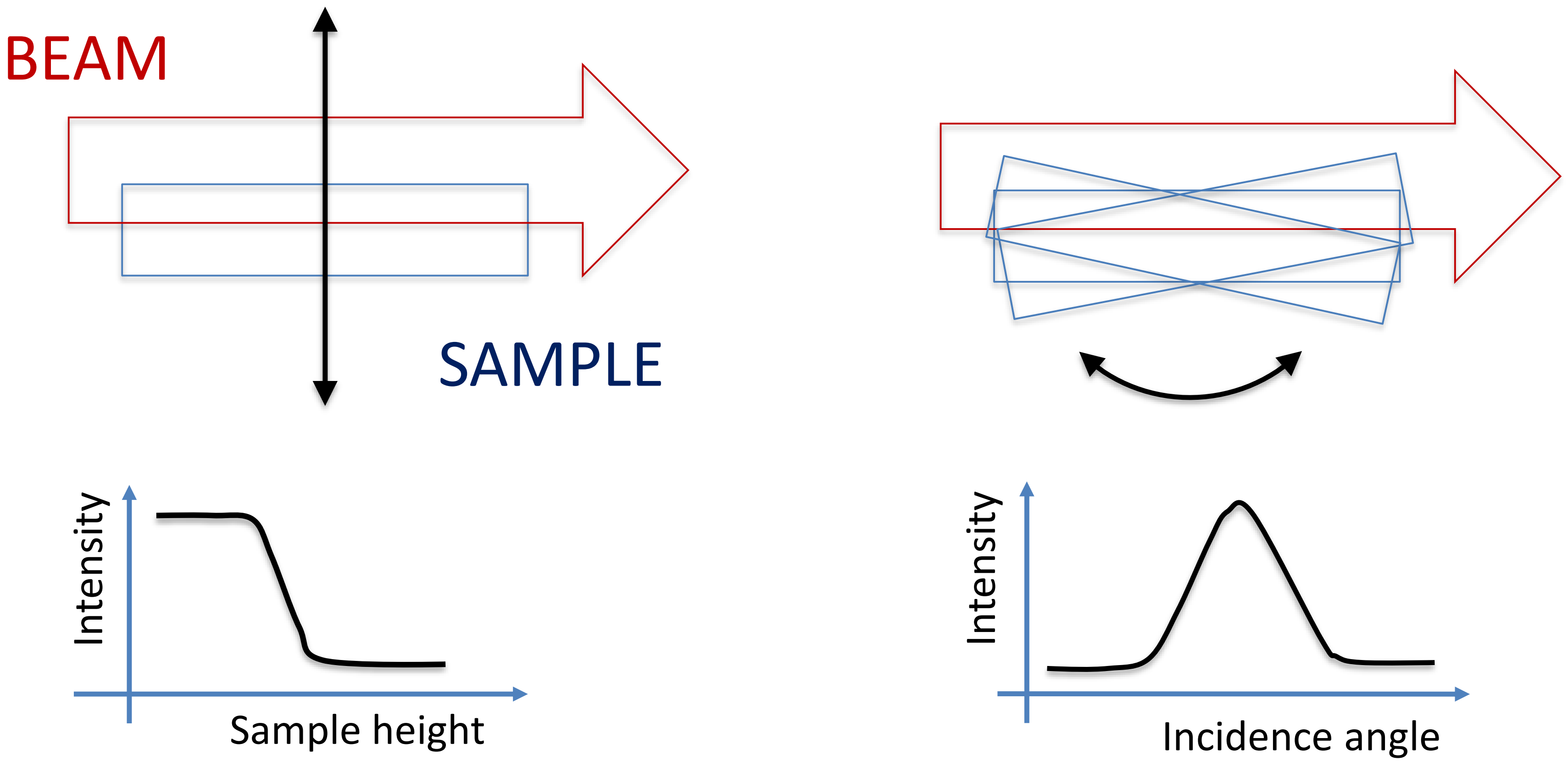


X-Ray attenuation length



How do we measure?

Sample alignment



Iterate!

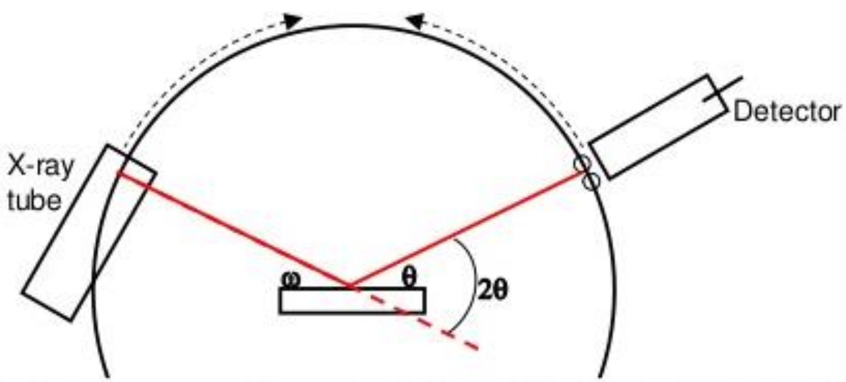
Grazing incidence diffraction

applied to

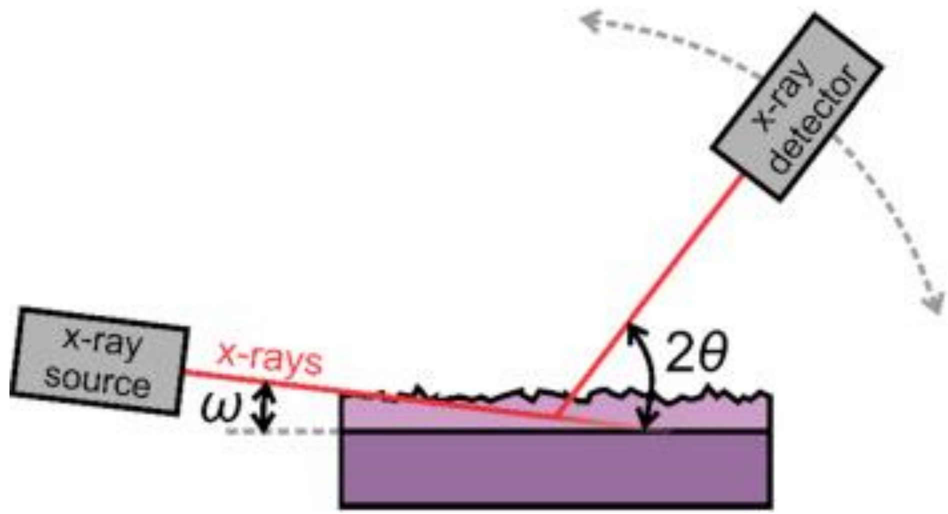
Polycrystalline films

Grazing incidence diffraction

Regular specular geometry, ω = θ



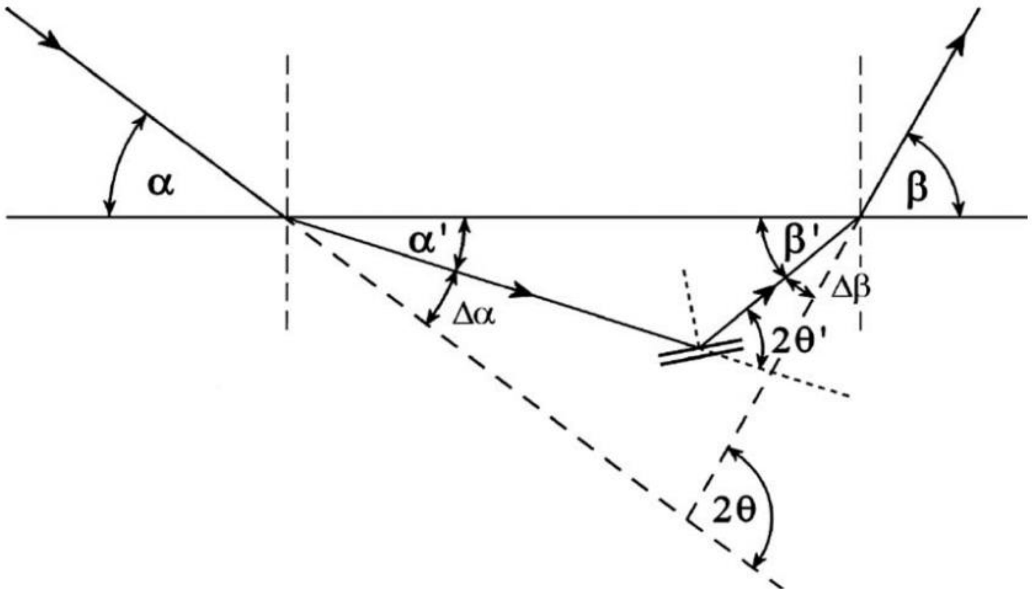
Grazing incidence geometry



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

Grazing incidence diffraction

Refraction correction

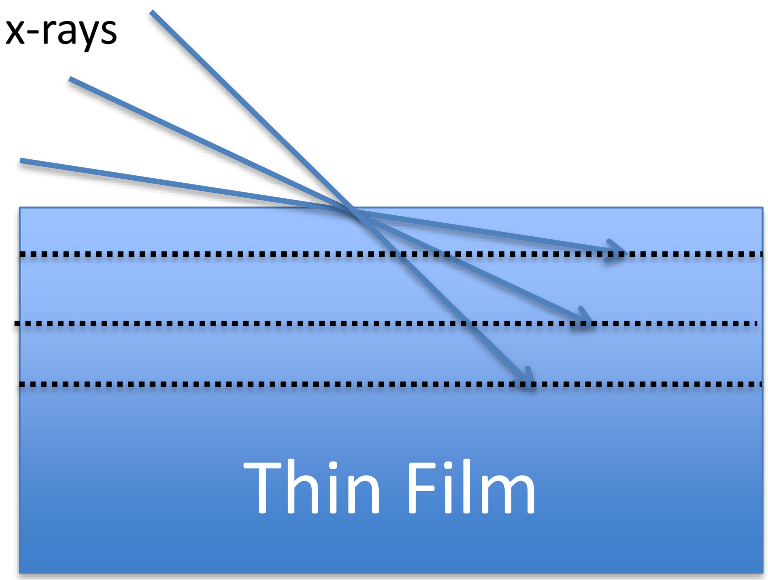


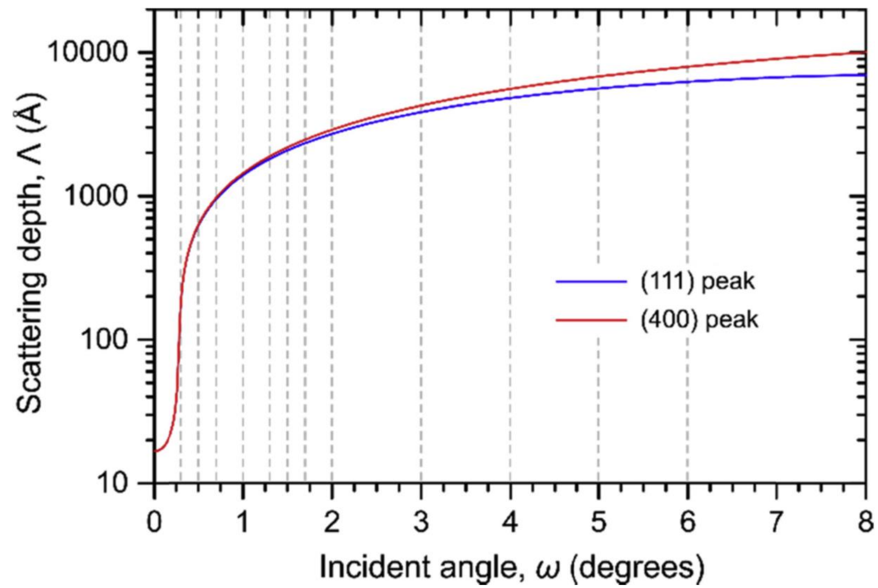
$$\Delta 2\theta = \delta[\cot\alpha + \cot(2\theta - \alpha) + 2\tan\theta]$$

Powder Diffraction **24**(S1): S11-S15, 2012

Grazing incidence diffraction

Depth sensitivity

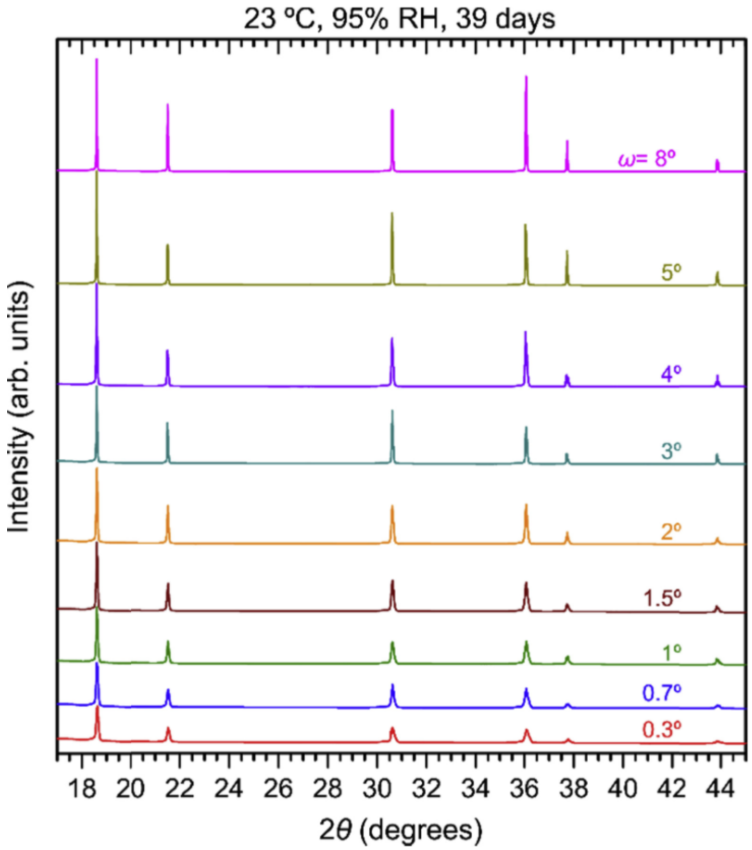


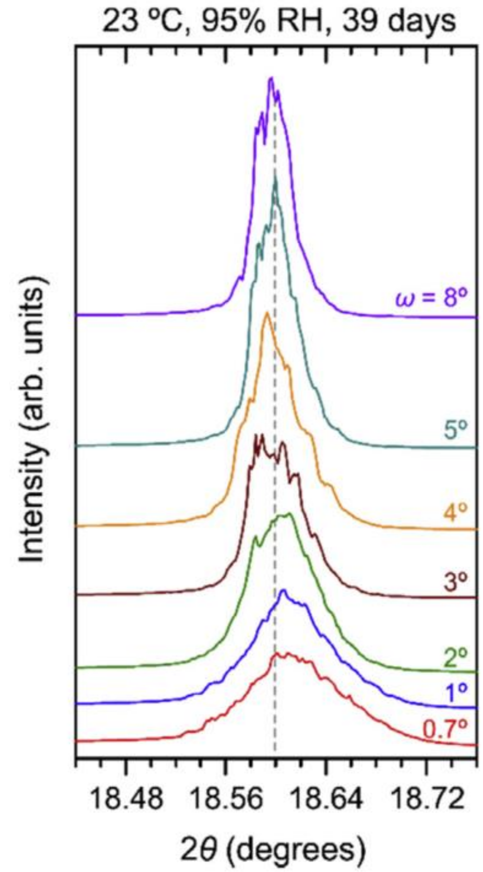


Journal of Nuclear Materials **502**: 68-75, 2018.

Grazing incidence diffraction

Uranium Oxide (UO_2) exposed to air





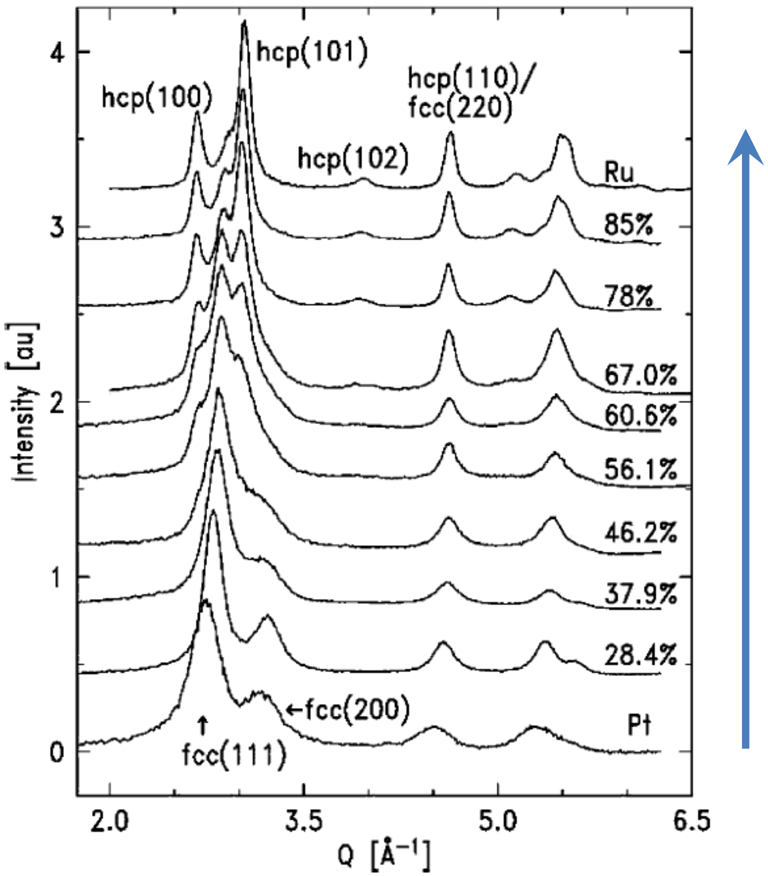
Journal of Nuclear Materials **502**: 68-75, 2018.

Grazing incidence diffraction

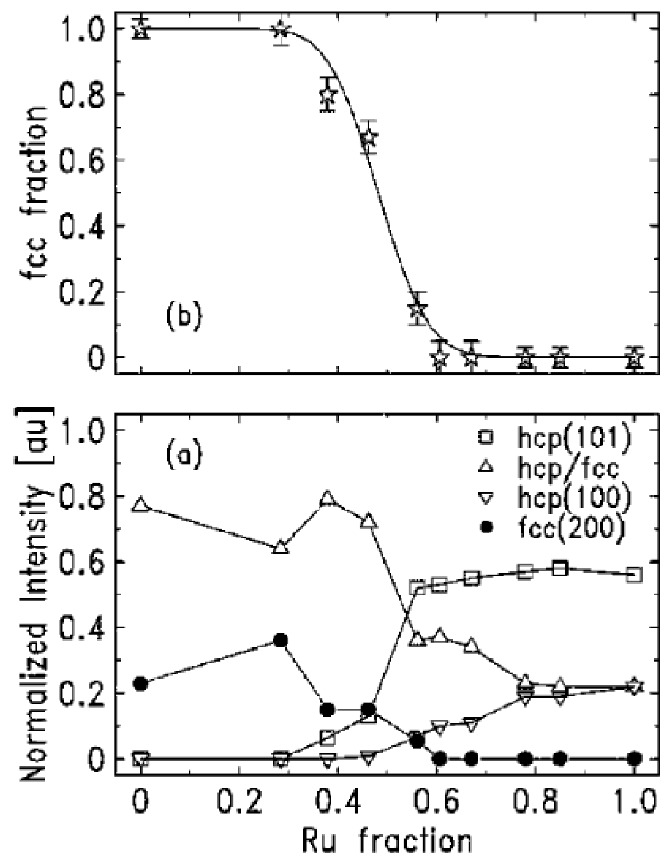
Structure and electrocatalysis of sputtered RuPt thin-film electrodes

130 Å thick

Grazing incidence x-ray diffraction



Phase diagram determination



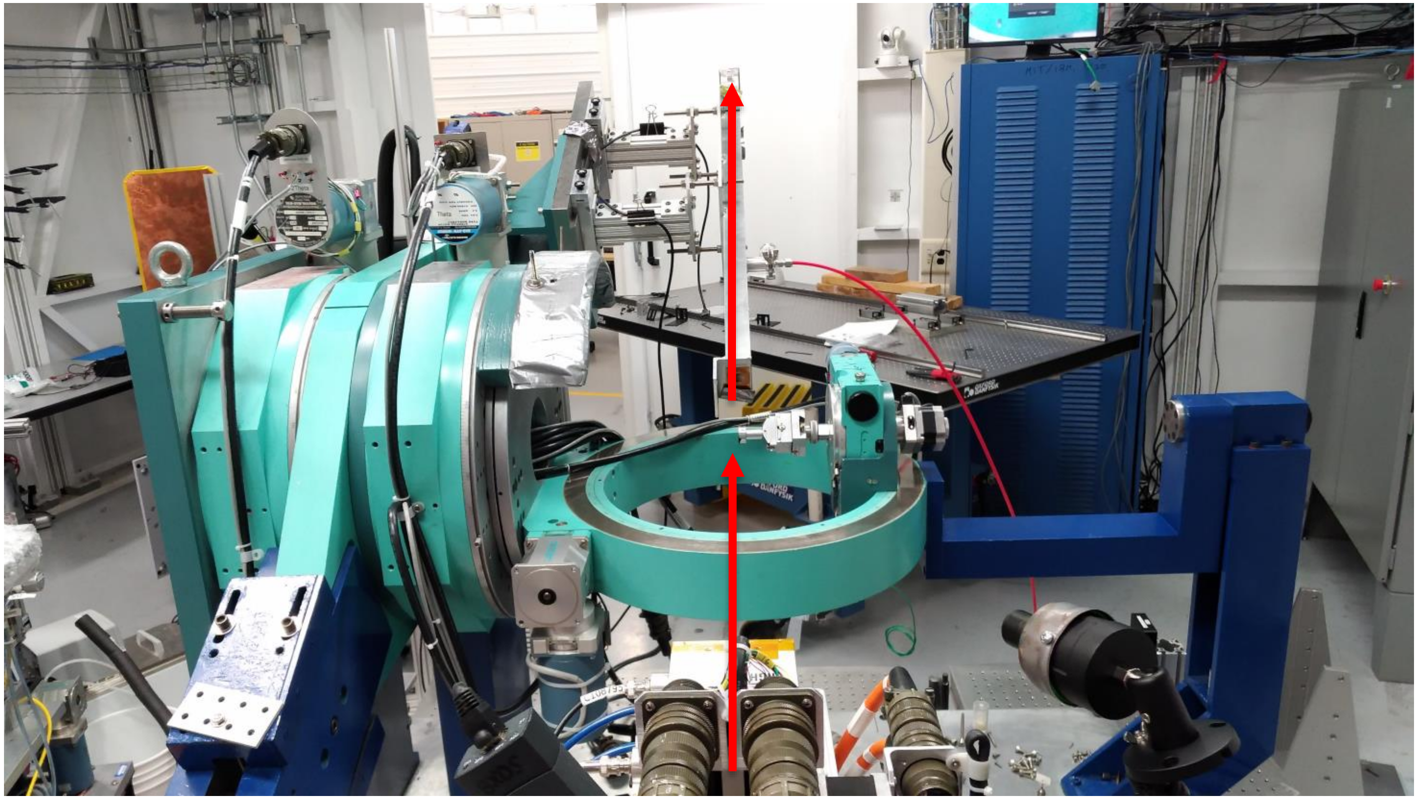
J. Phys. Chem. B **109**, 12845, 2005. Kim et al.

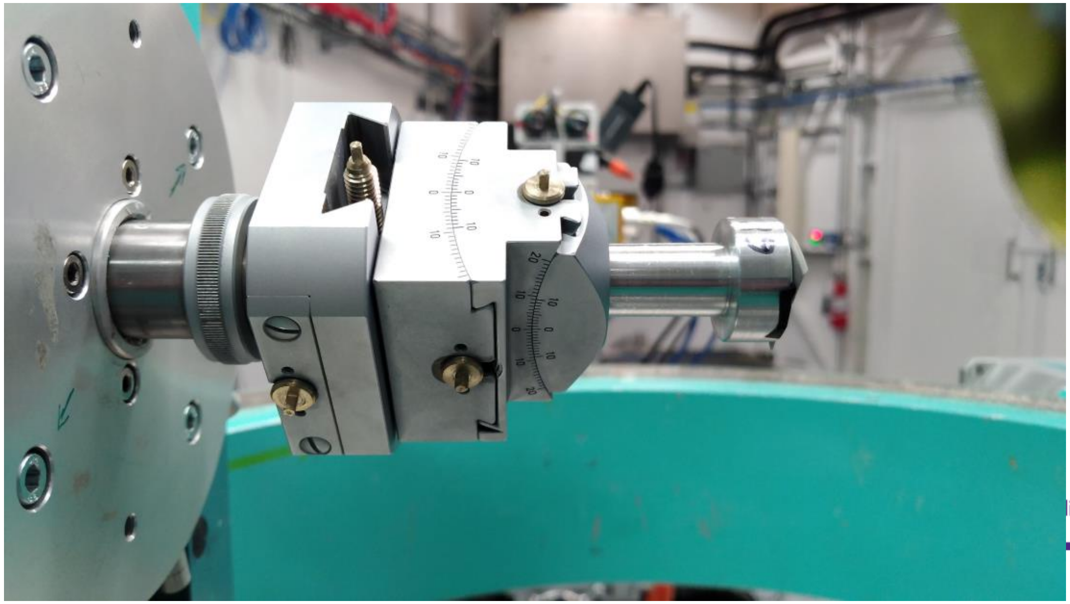
Grazing incidence diffraction

applied to

Single crystal films

GID setup





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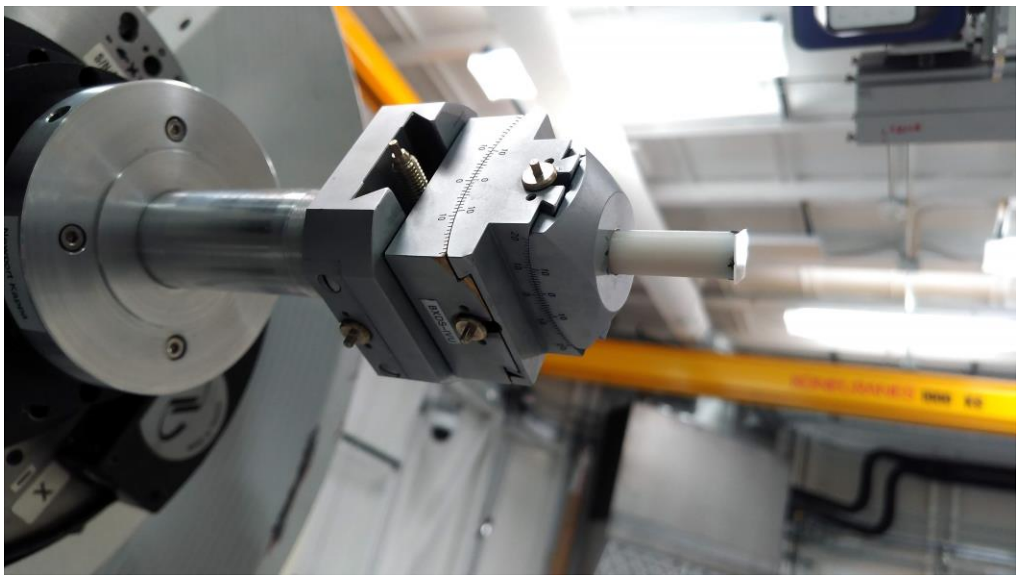
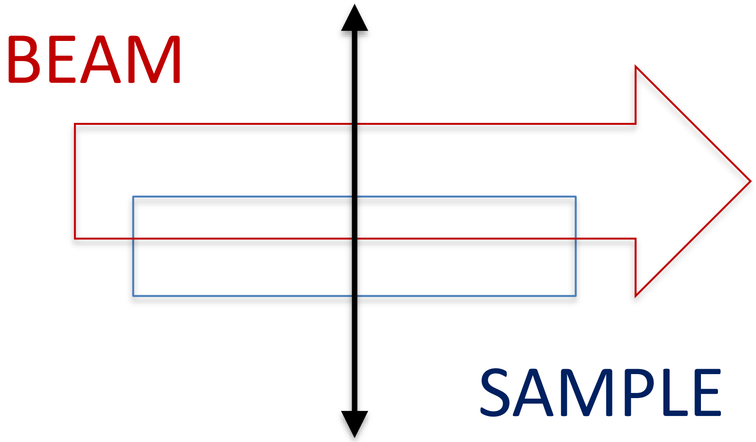
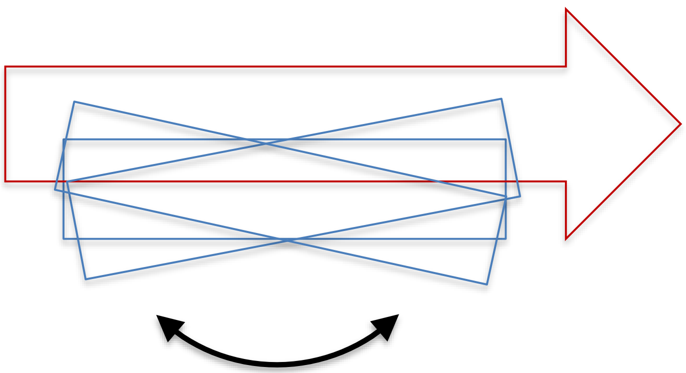
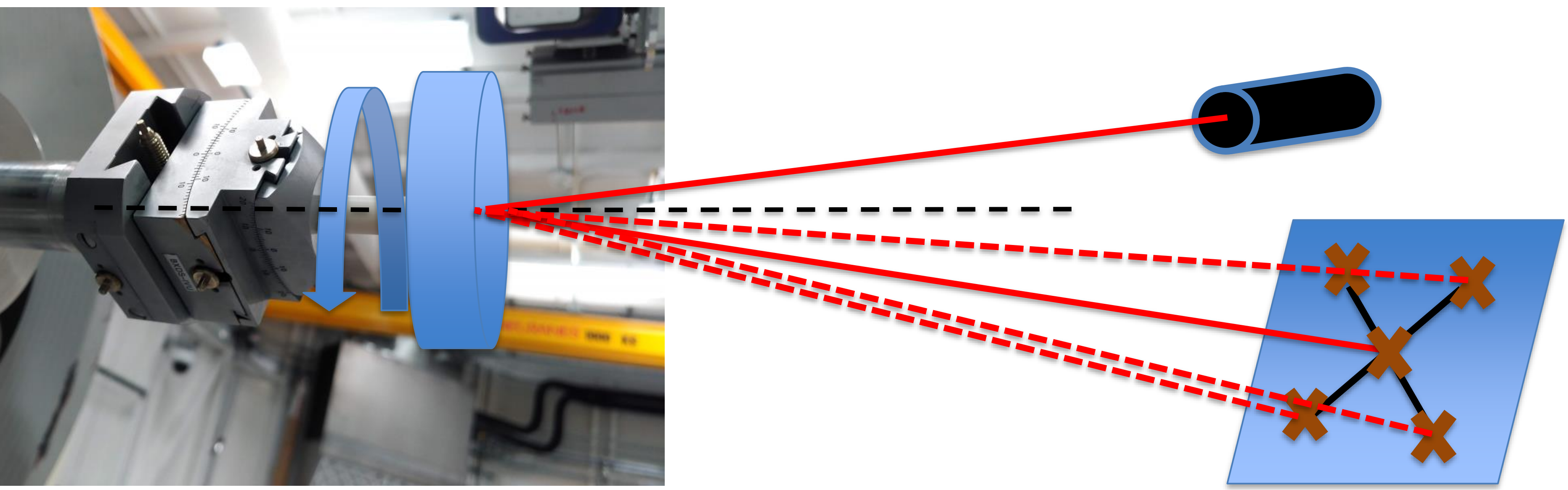
GID setup



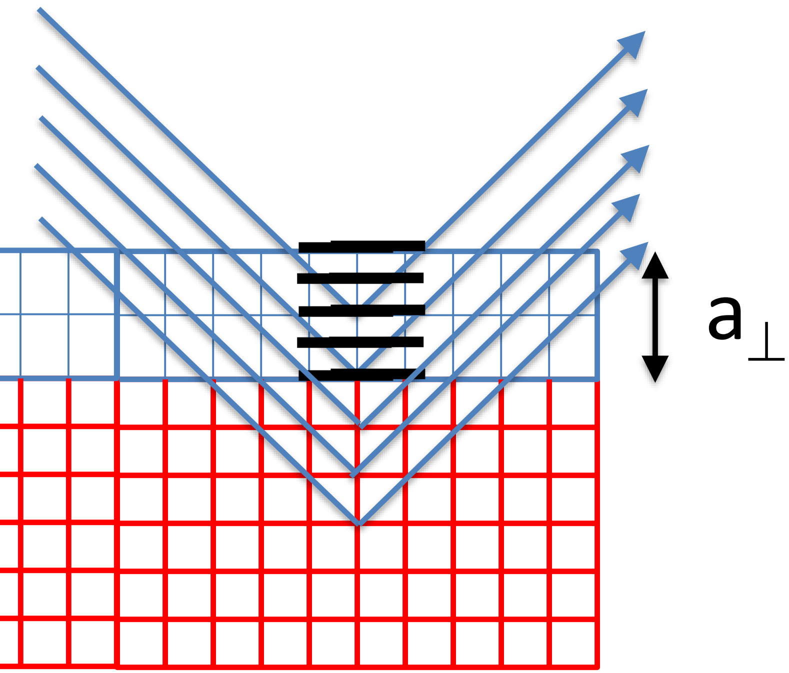
Sample alignment

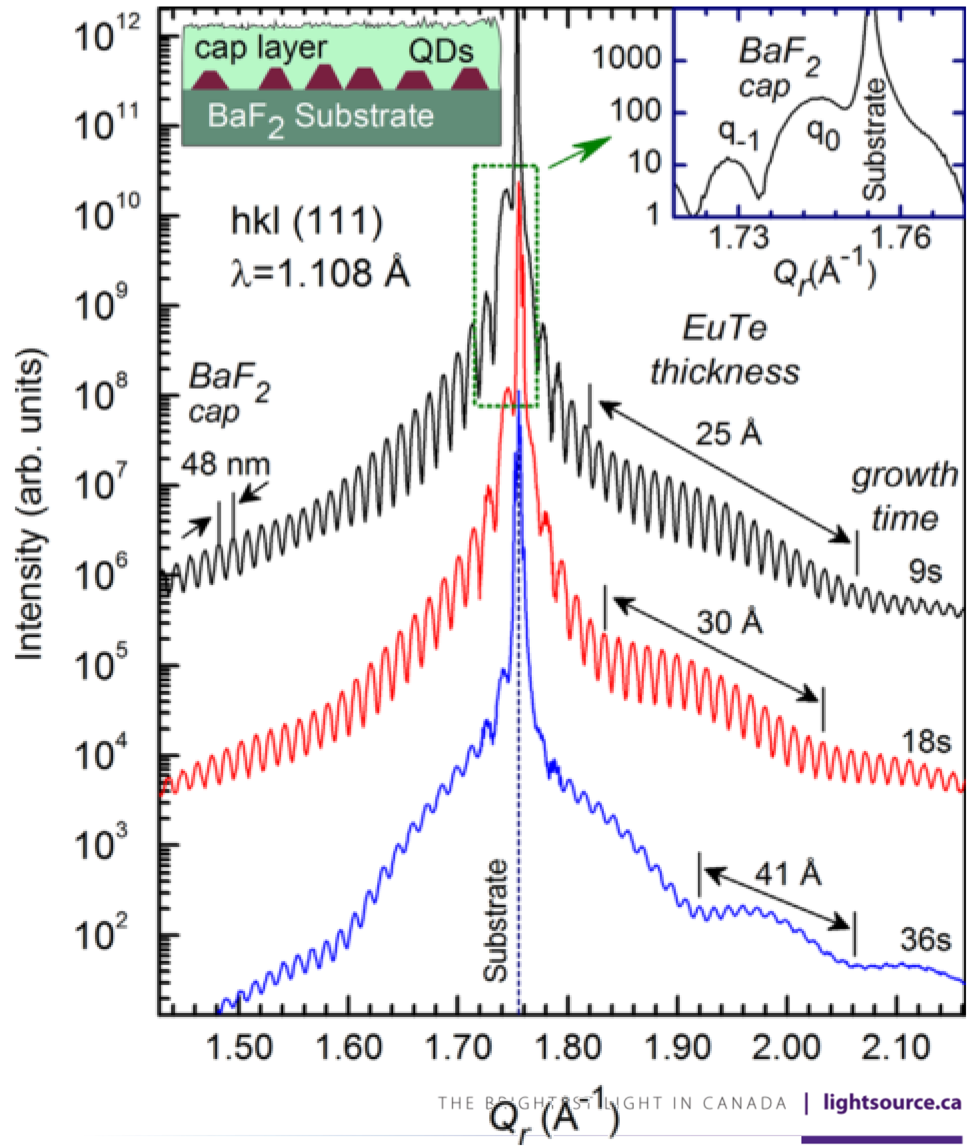






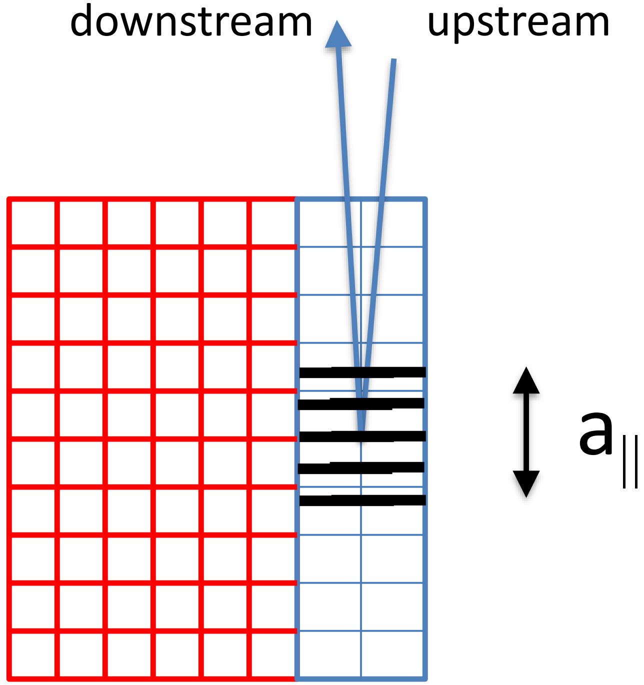
Not-Grazing incidence diffraction

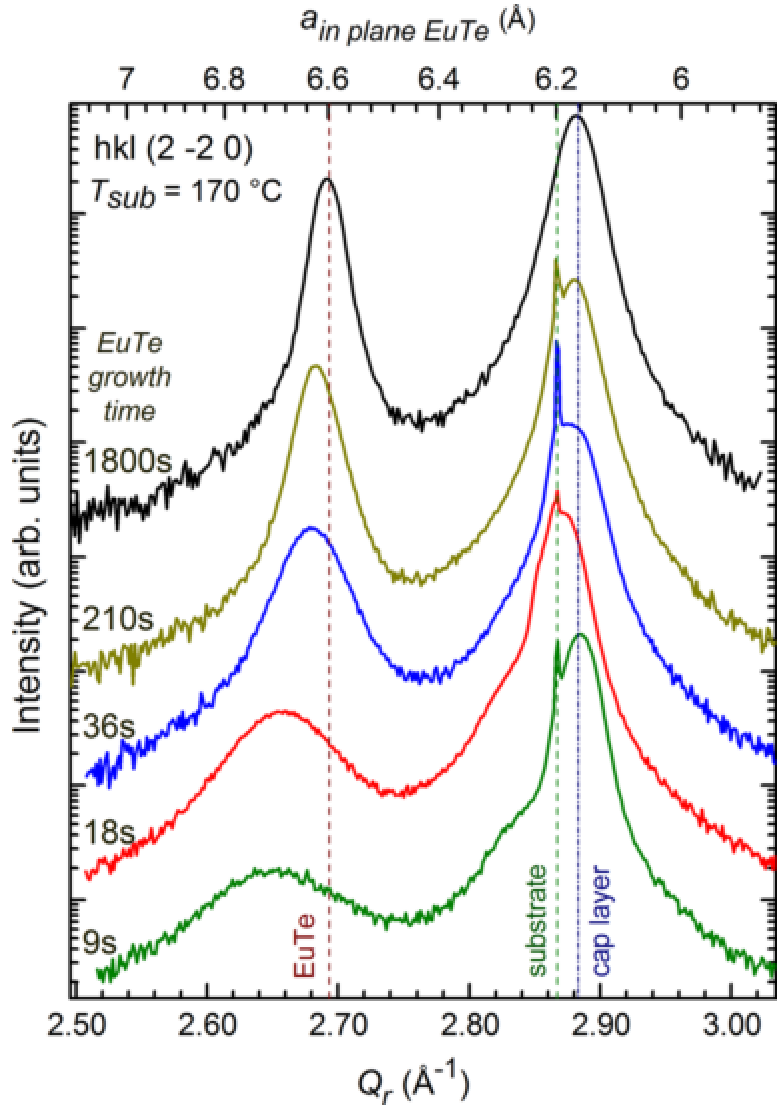




Journal of Crystal Growth **386**(0): 139-145, 2014

Grazing incidence diffraction





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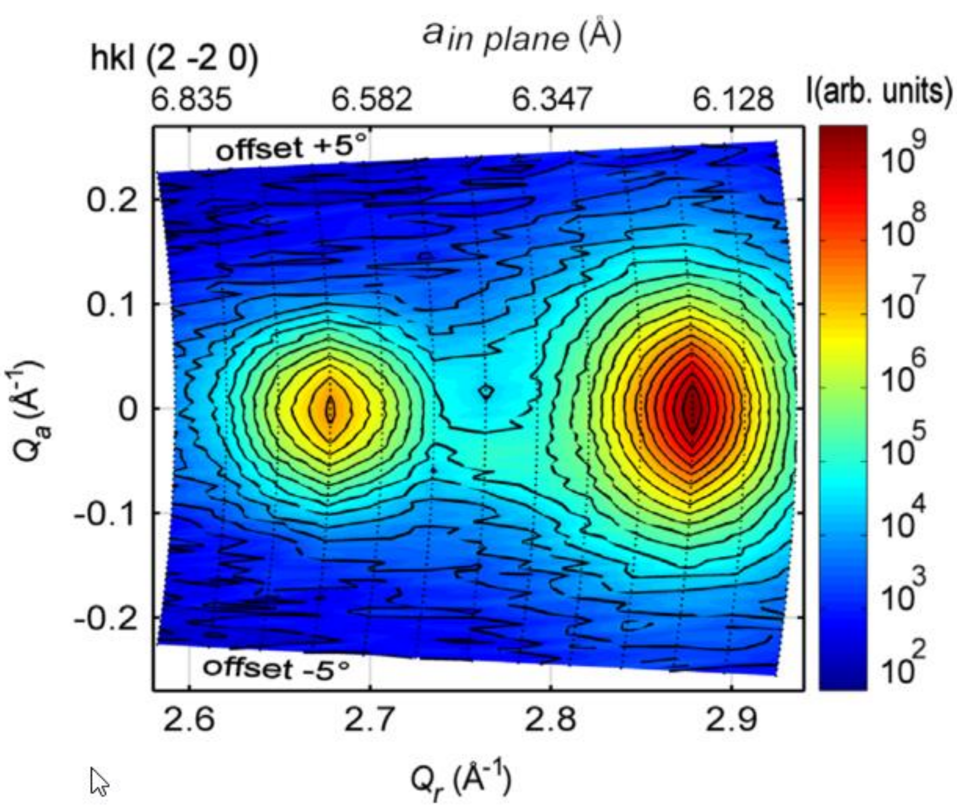
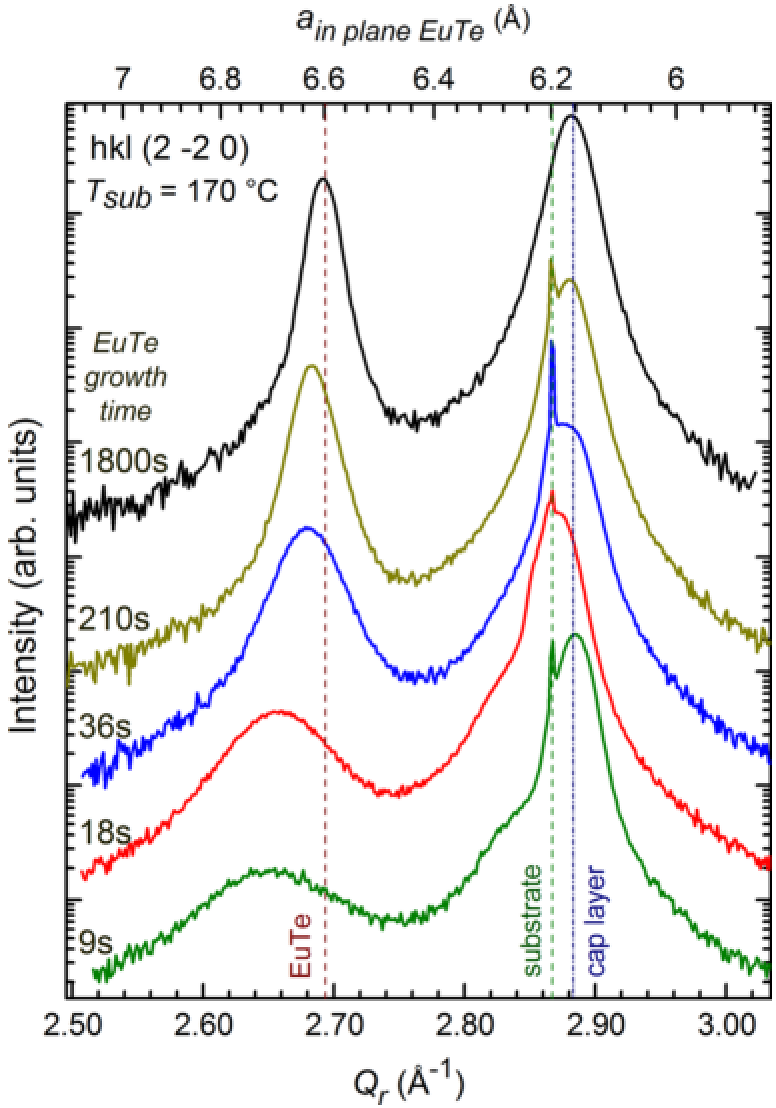
Grazing incidence diffraction





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

Small angle x-ray reflectivity

Single crystal films

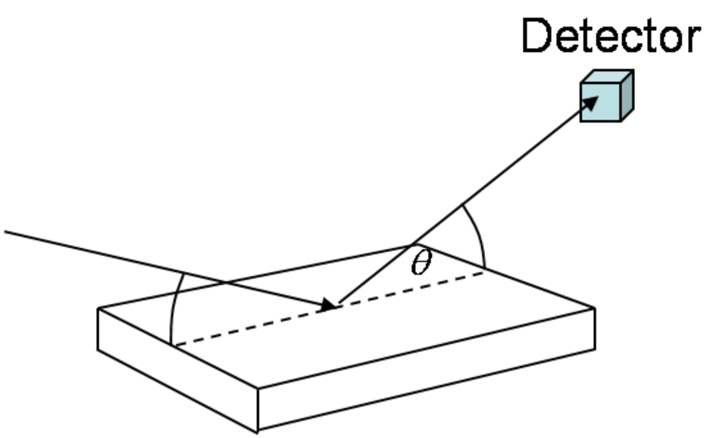
Polycrystalline films

Amorphous films

Small angle X-Ray reflectivity

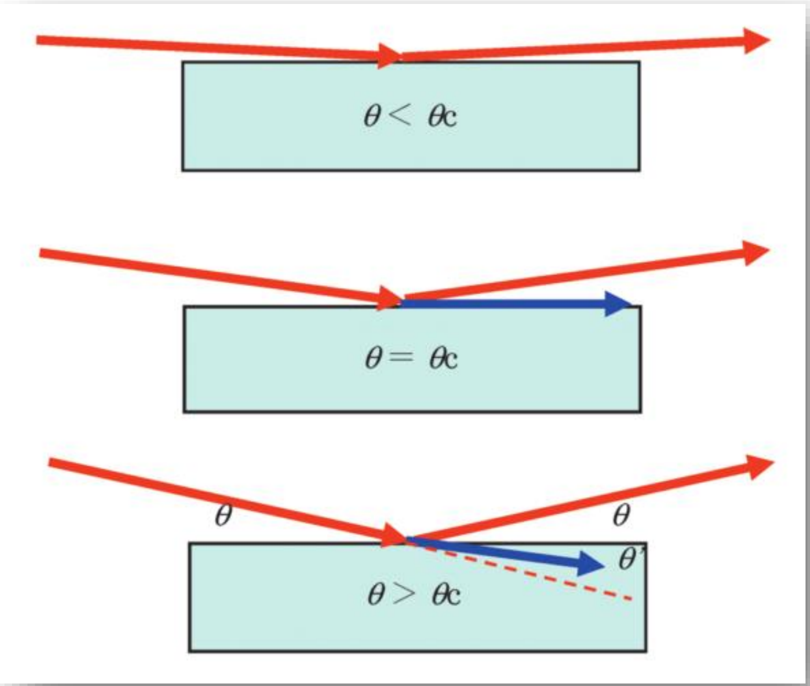
- Reflectivity yields information about the
  - Thicknesses
  - Density / porosity
  - Roughness of the interfaces

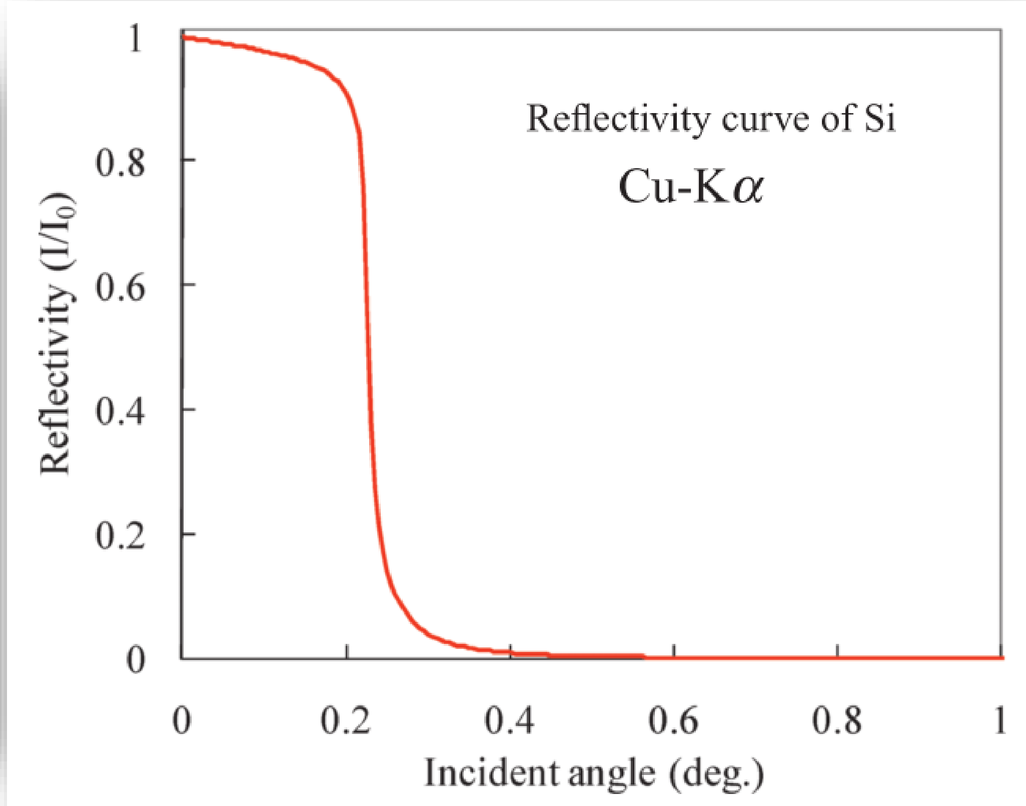
- Other names:
  - X-ray specular reflectivity
  - X-ray reflectometry
  - XRR



No diffraction!

Small angle X-Ray reflectivity

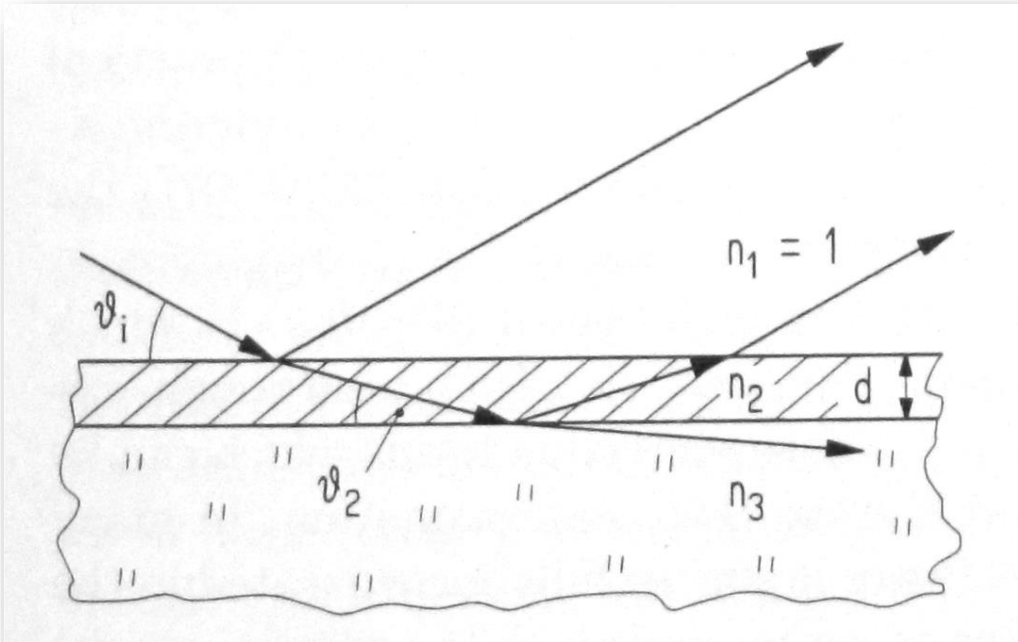




$$\theta_c \sim \lambda\sqrt{\rho}$$

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

Small angle X-Ray reflectivity



Snell's law

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

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

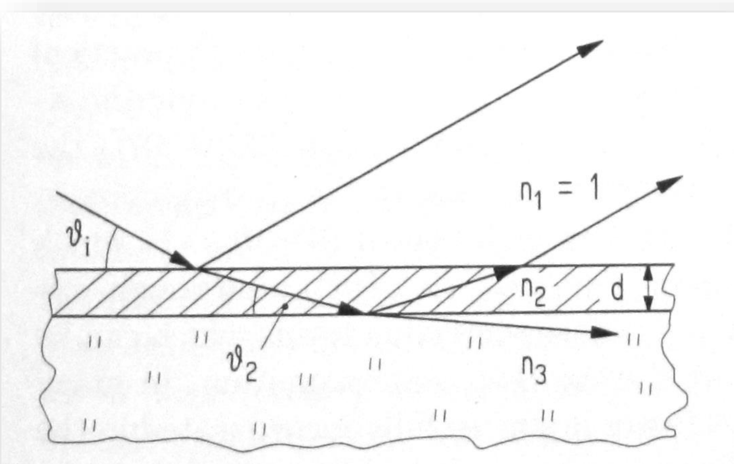
Gibaud 2013 – X-ray reflectivity chapter

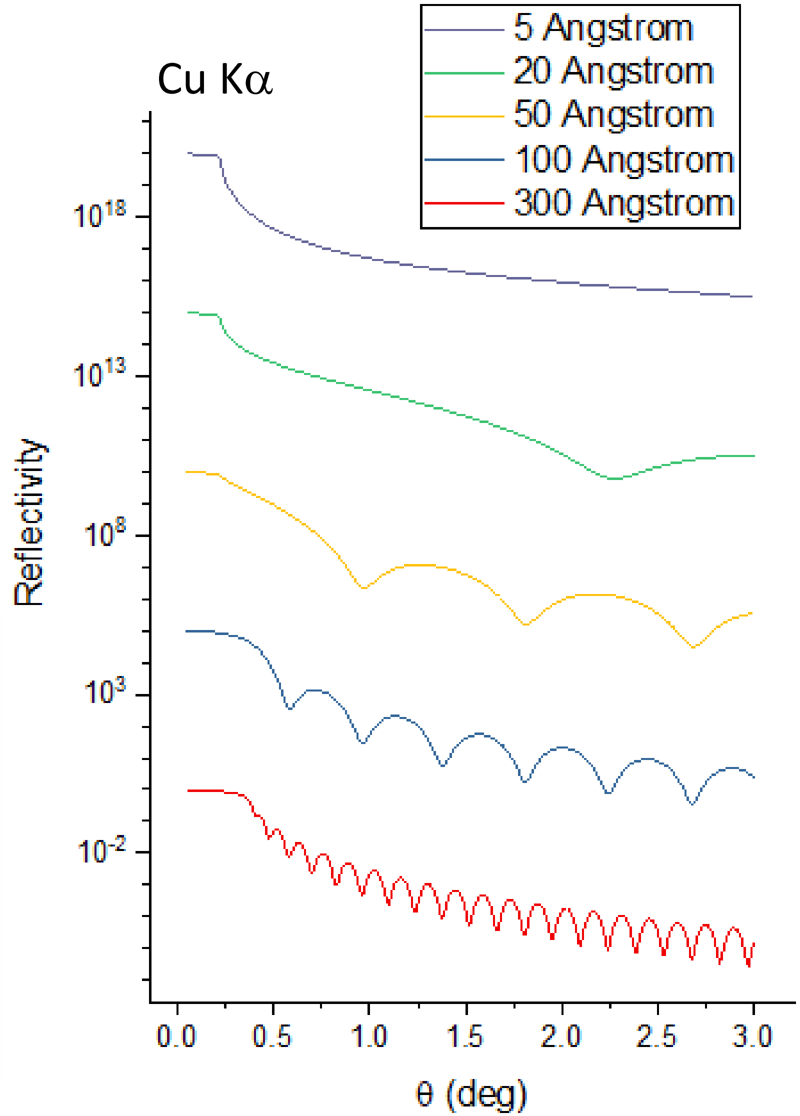
Small angle X-Ray reflectivity

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

Kiessig fringes

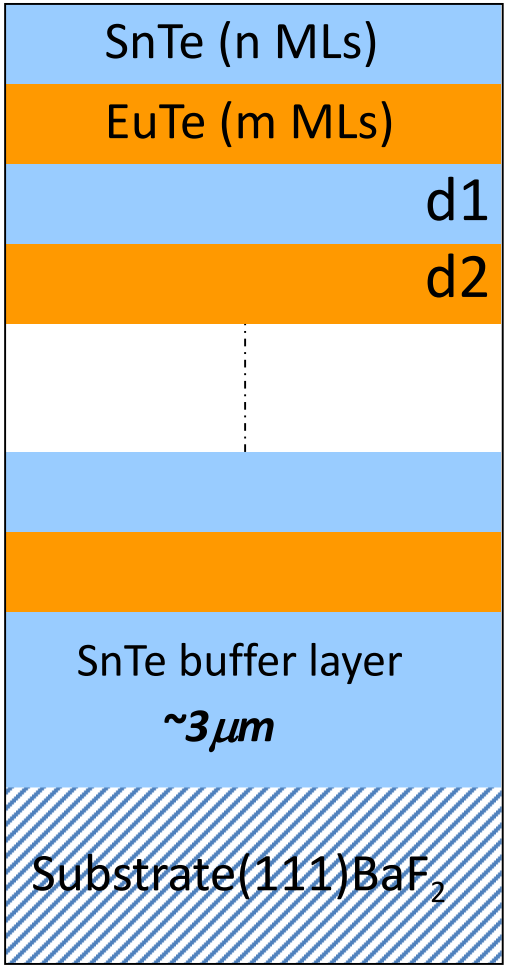
$$d = \frac{\lambda}{2\Delta\theta_r}$$



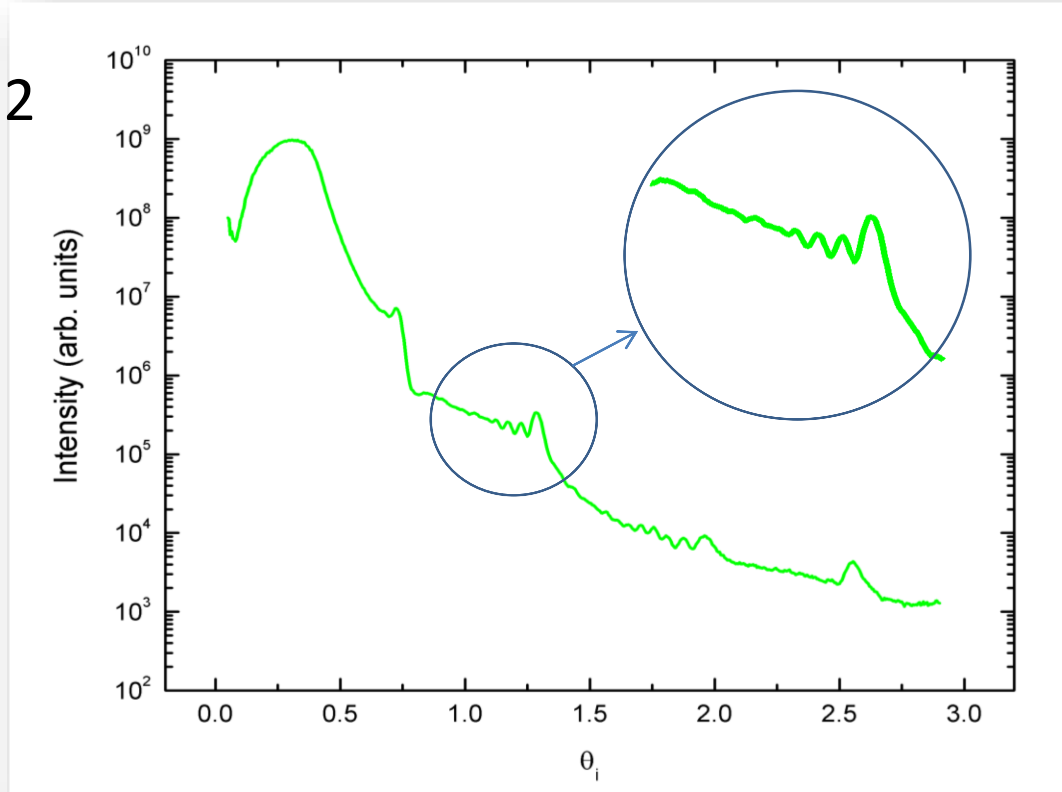


$$\frac{1.54\cdot \text{Angstrom}}{2\cdot 0.01\cdot \text{deg}} = 0.4\ \mu\text{m}$$

Small angle X-Ray reflectivity



D=d1+d2



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

Kiessig fringes spacing:

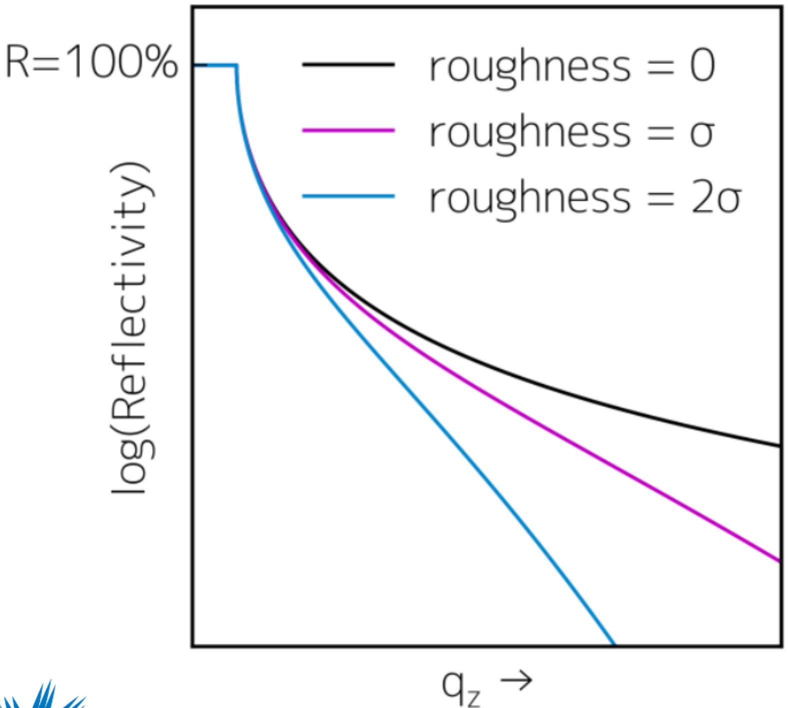
0.61 deg ~ 83 Å (SL period)

0.05 deg ~ 994.9 Å (Stack thickness)

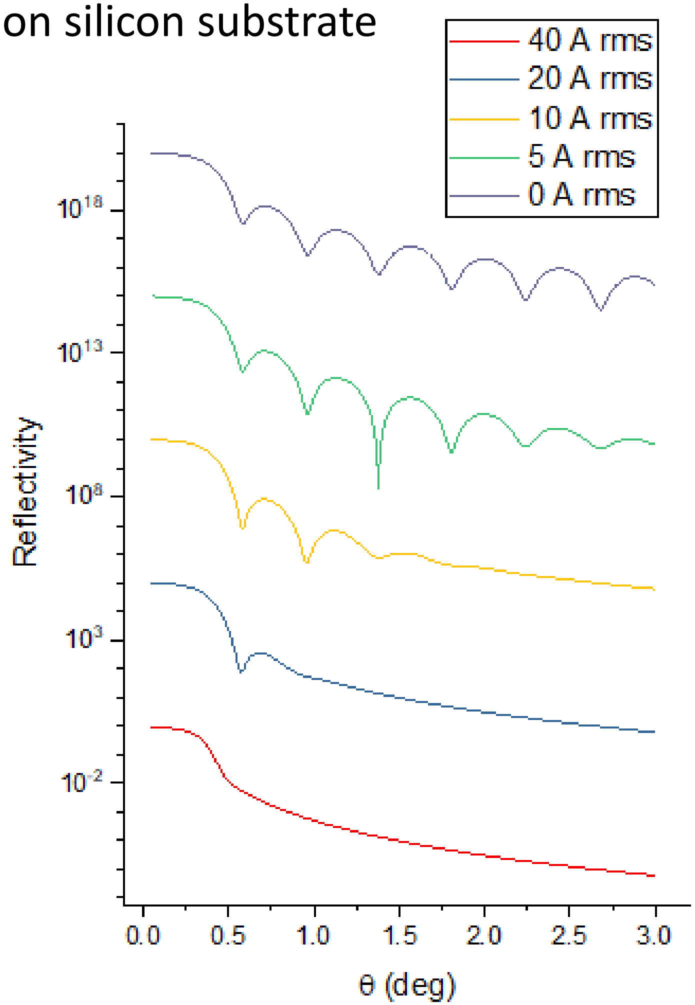
Small angle X-Ray reflectivity

Surface roughness

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

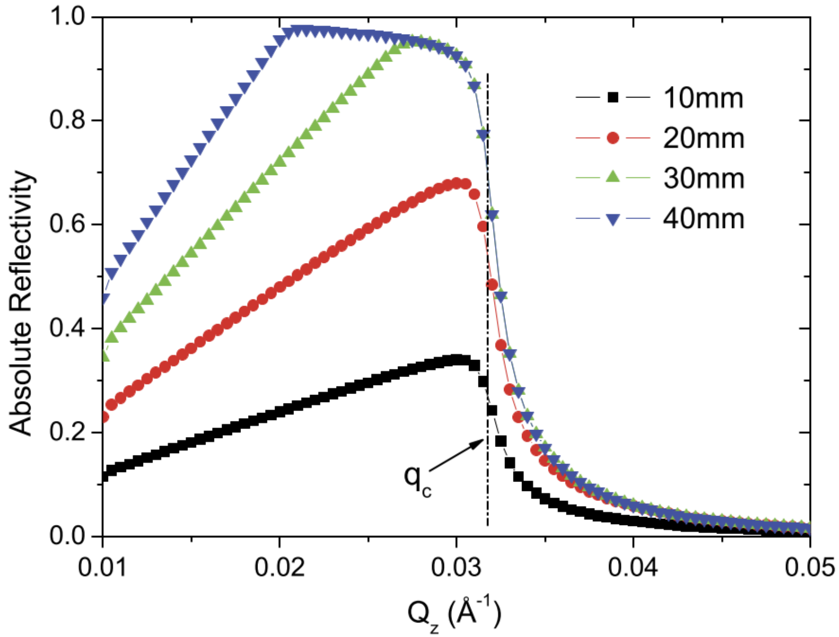


100 Angstrom chromium layer on silicon substrate



Small angle X-Ray reflectivity

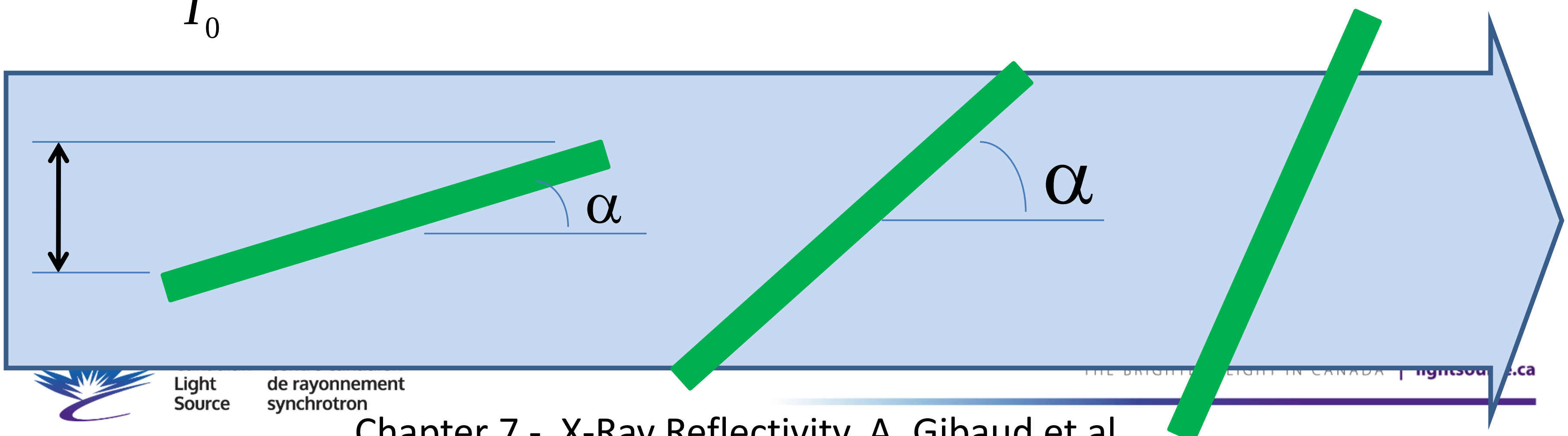
Footprint correction



Beam footprint length:

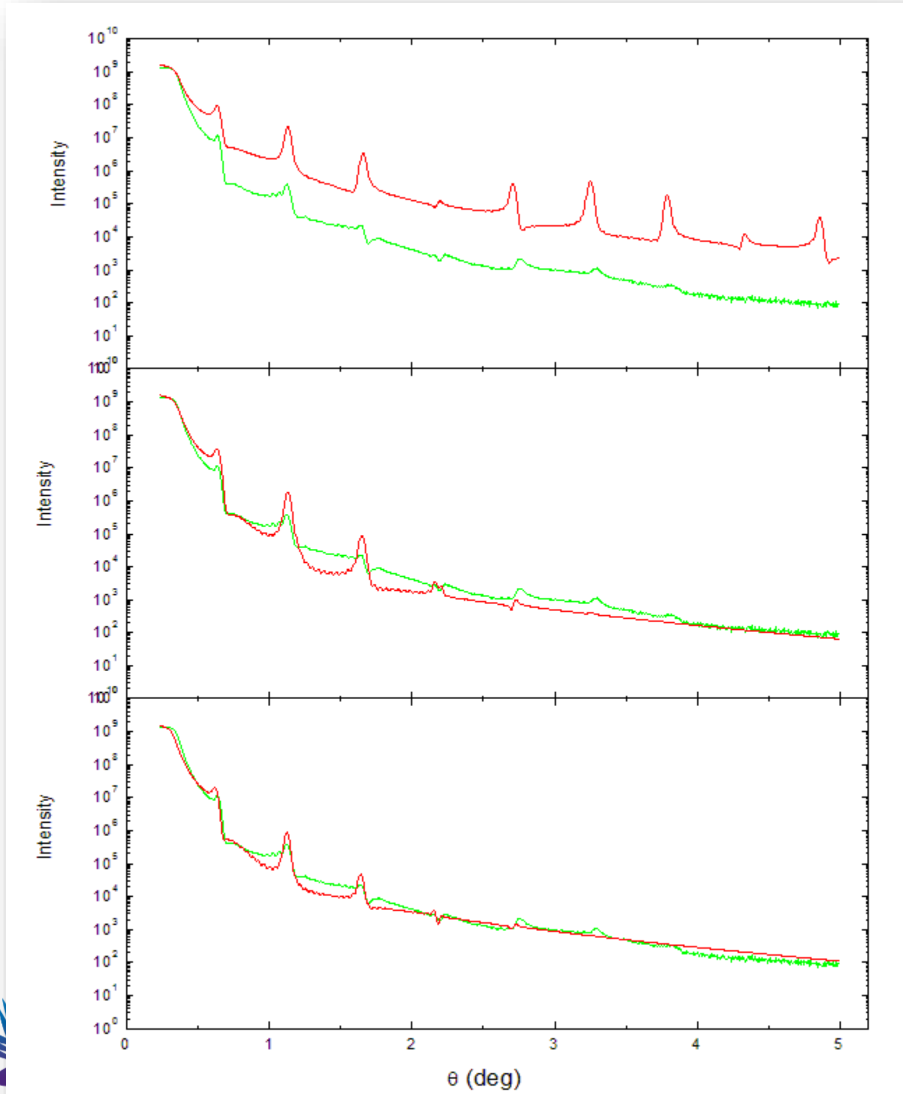
$$F = \frac{t}{\sin(\alpha)}$$

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



Small angle X-Ray reflectivity

Fits to the measurement



Smooth interfaces

Rough interfaces

Lower densities
(porous sample?)

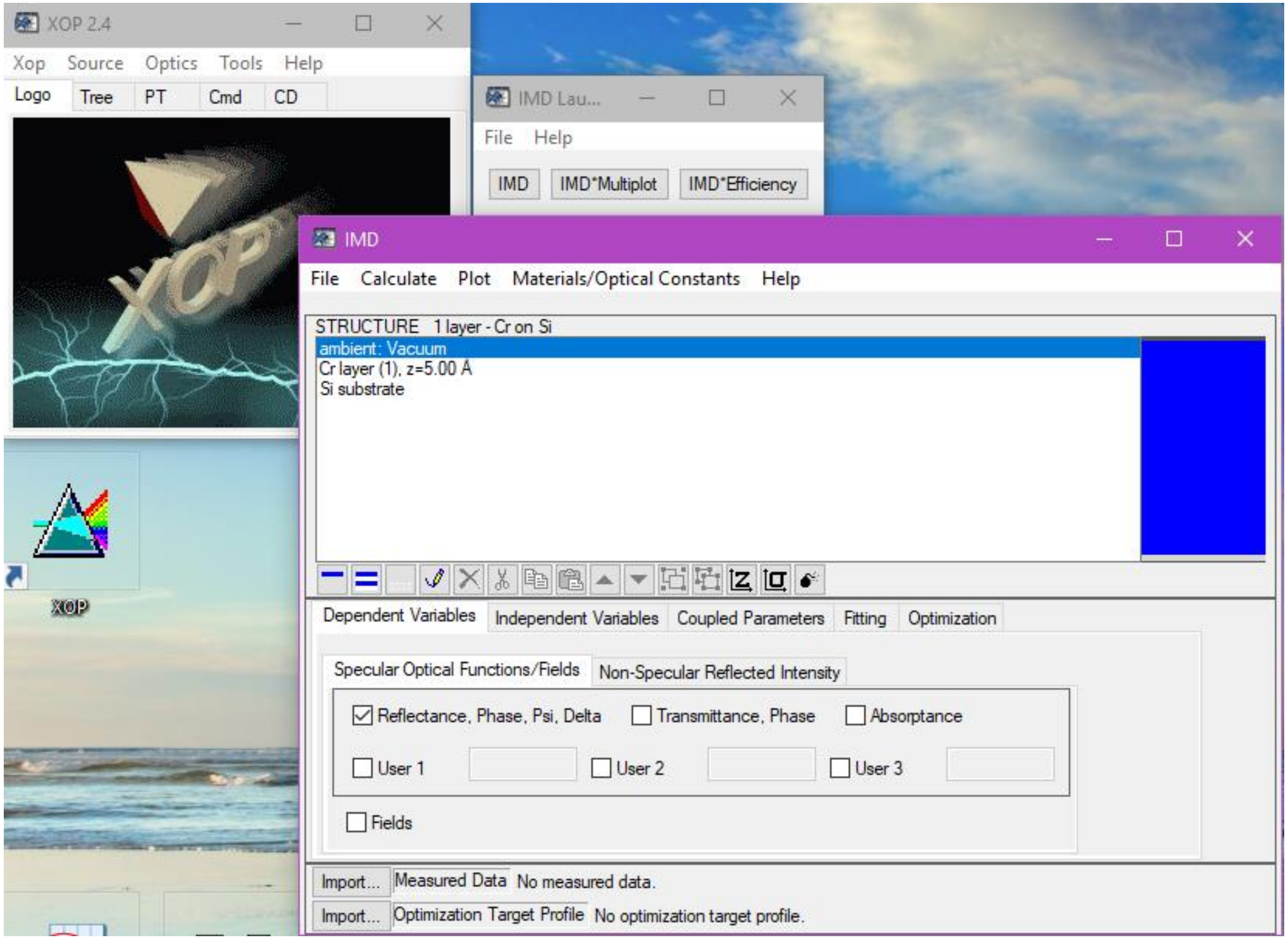
Oxide layer cap!

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

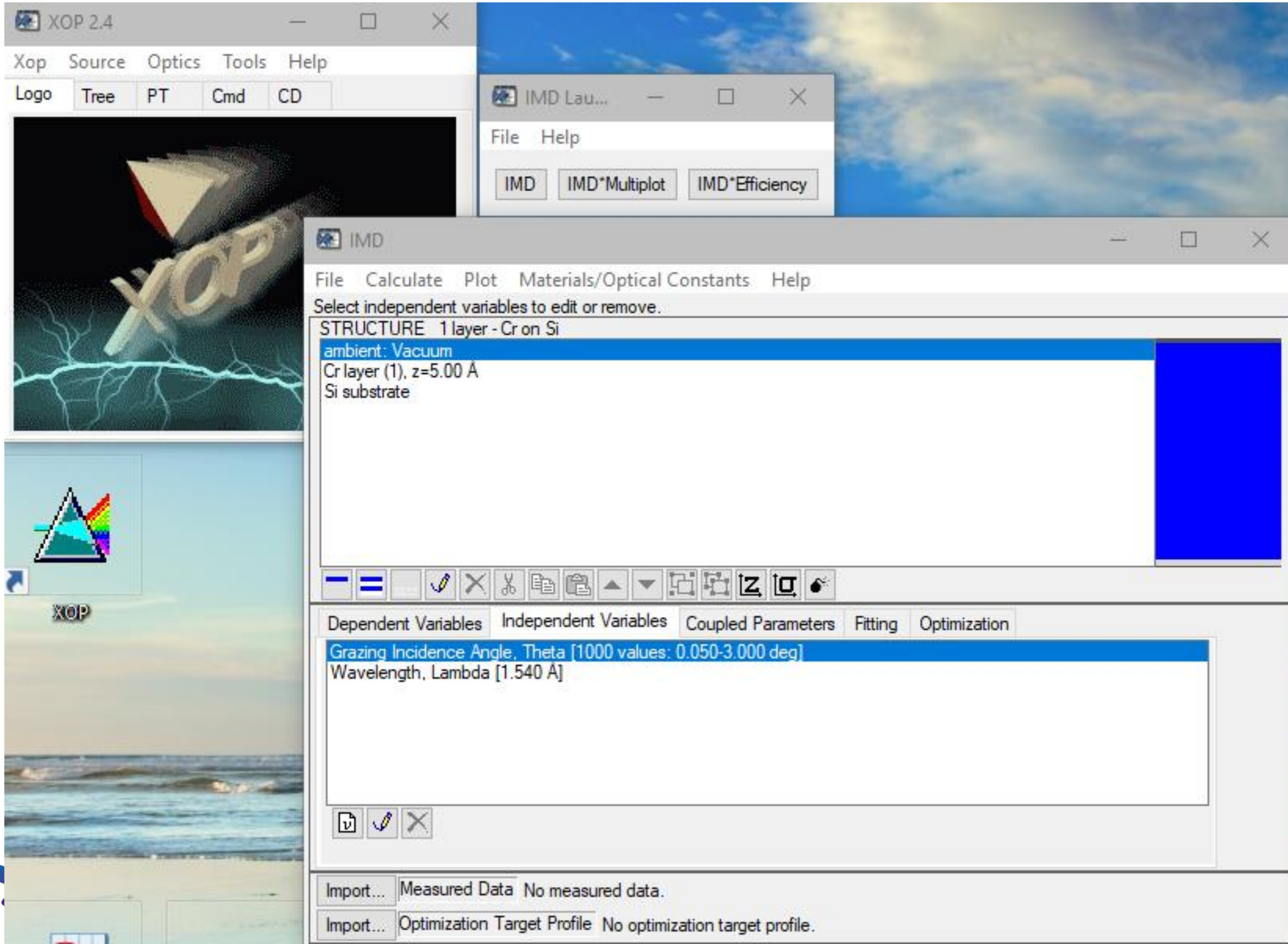
IMD/XOP to simulate x-ray reflectivity



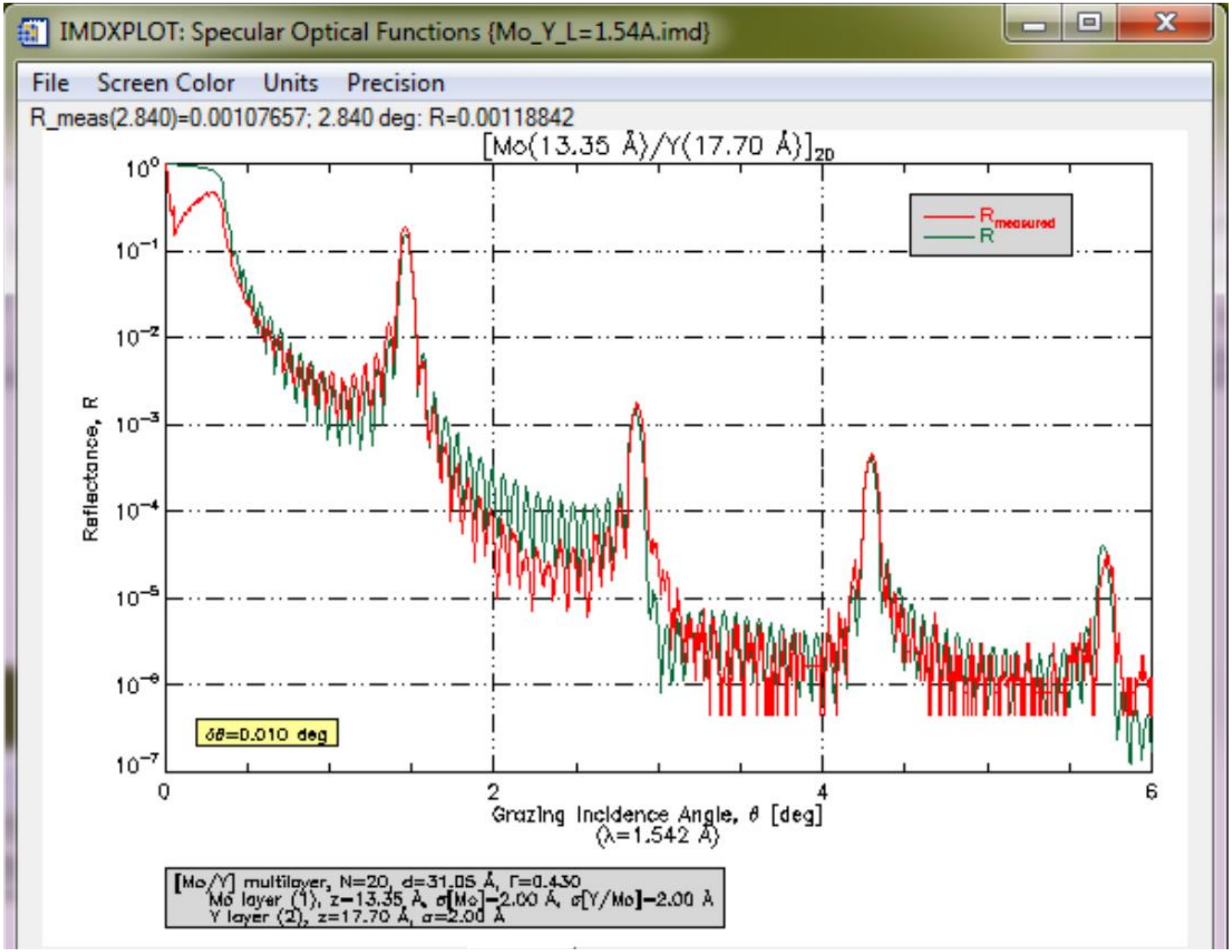
https://www.aps.anl.gov/Science/Scientific-Software/XOP

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

IMD/XOP to simulate x-ray reflectivity



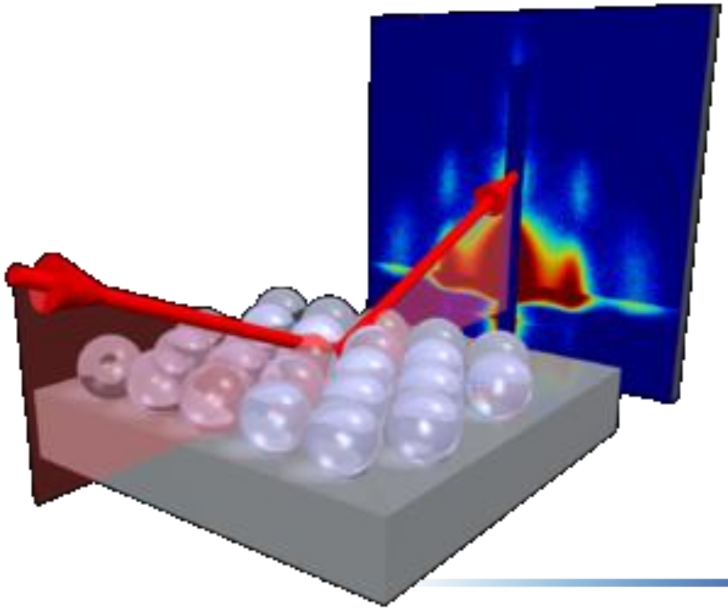
IMD/XOP to simulate x-ray reflectivity



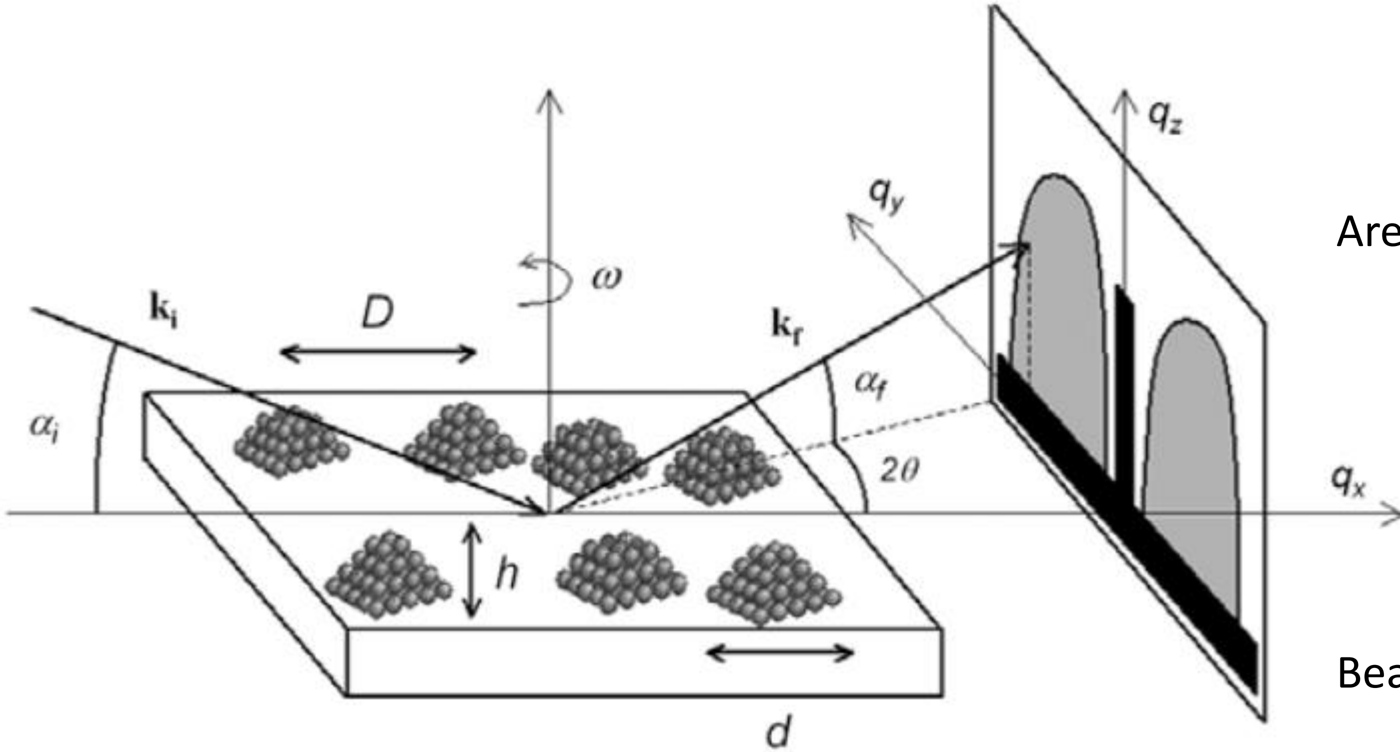
Grazing incidence

Small angle X-ray scattering

GISAXS



GISAXS measurements

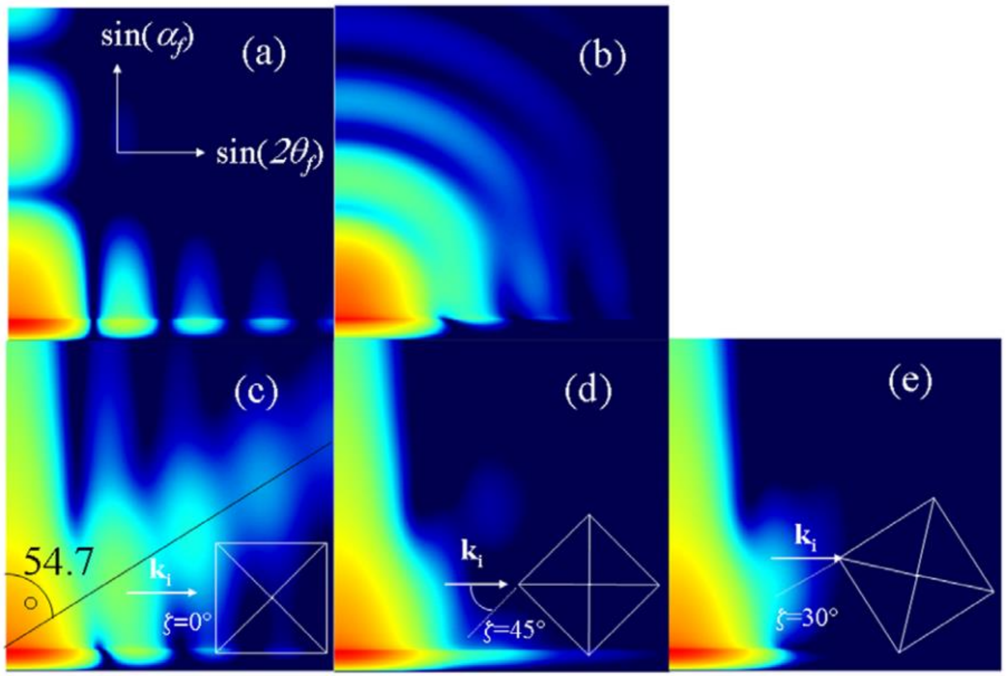


Area detector

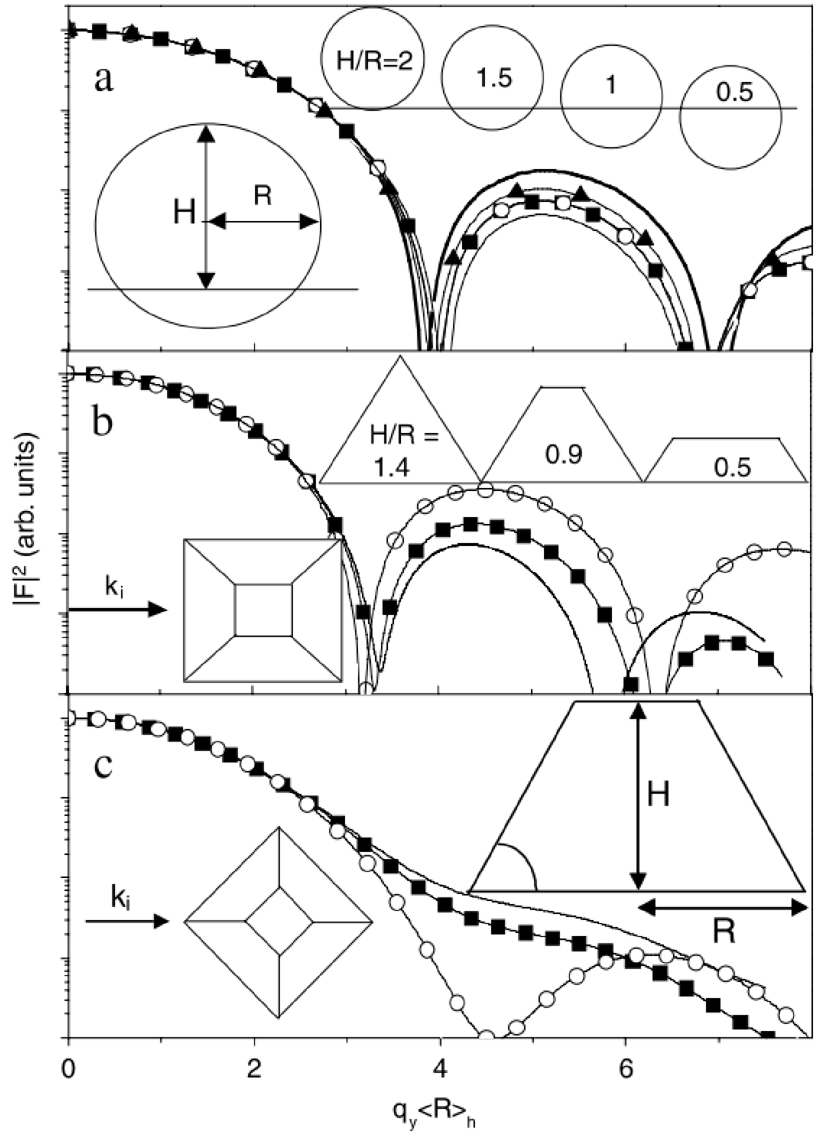
Beam stop

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

GISAXS



q_y



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

Modelling software

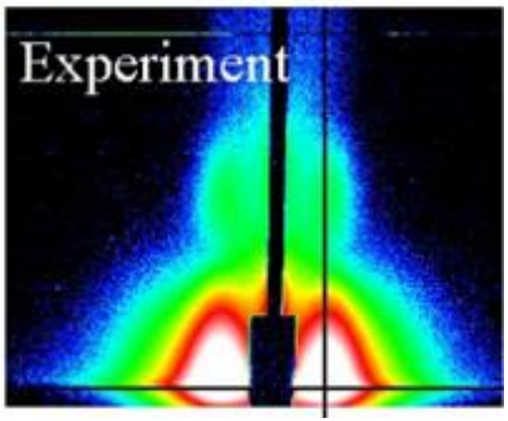
- R. Lazzari, IsGISAXS: A program for grazing-incidence small-angle X-ray scattering analysis of supported islands, J. Appl. Crystallogr. 35 (2002) 406–421.
- http://www.insp.jussieu.fr/oxydes/IsGISAXS/isgisaxs.htm

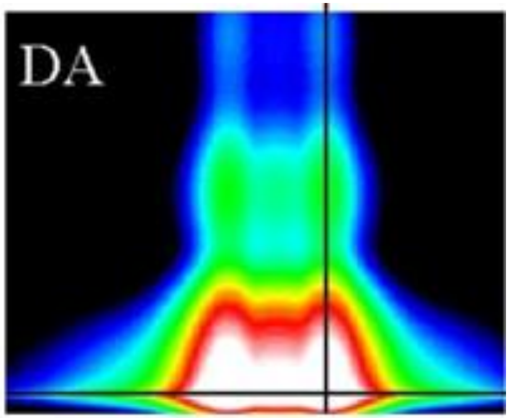
- Jiang, Z. (2015). "GIXSGUI: a MATLAB toolbox for grazing-incidence X-ray scattering data visualization and reduction, and indexing of buried three-dimensional periodic nanostructured films." Journal of Applied Crystallography **48**(3): 917-926.
- https://www.aps.anl.gov/Science/Scientific-Software/GIXSGUI

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

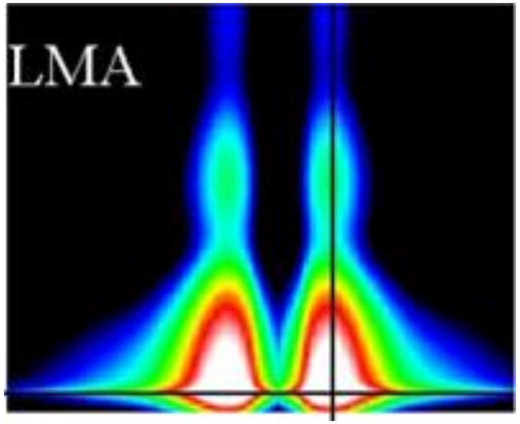
IsGISAXS

Pd islands on MgO(100)

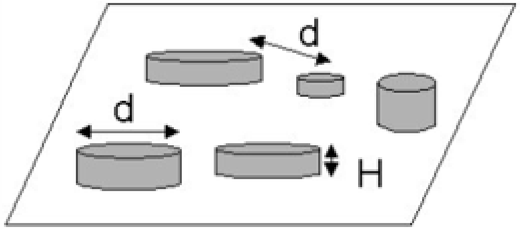




Decoupling Approximation (DA)



Local Monodisperse Approximation (LMA)

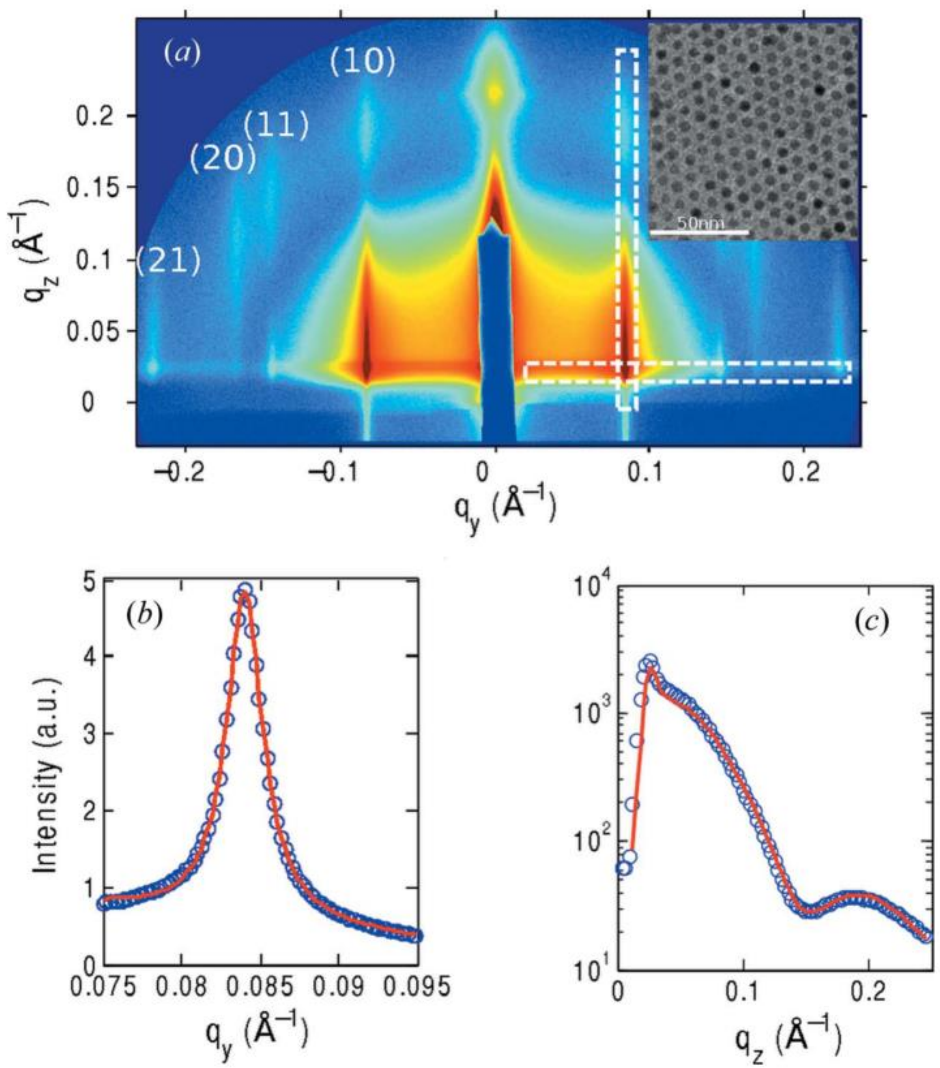


PARAMETERS :
cylinder
D = 20.7 nm
d = 10.2 nm
H = 6.6 nm
σ_R = 1.3
σ_H = 1.1

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

GISAXS

Spherical gold nanoparticles in silicon



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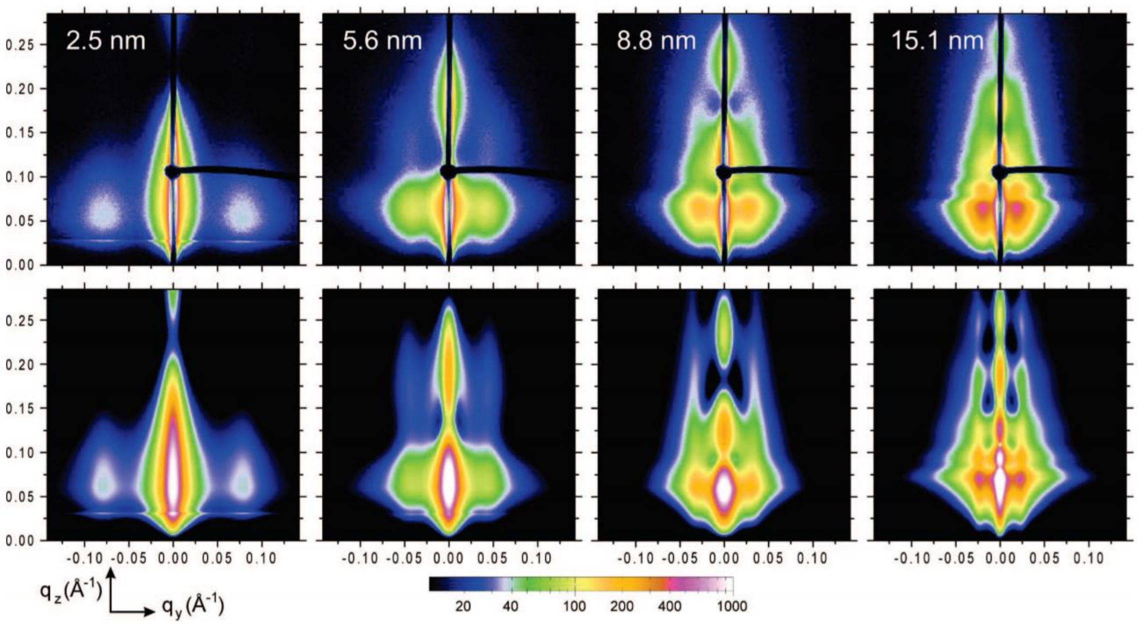
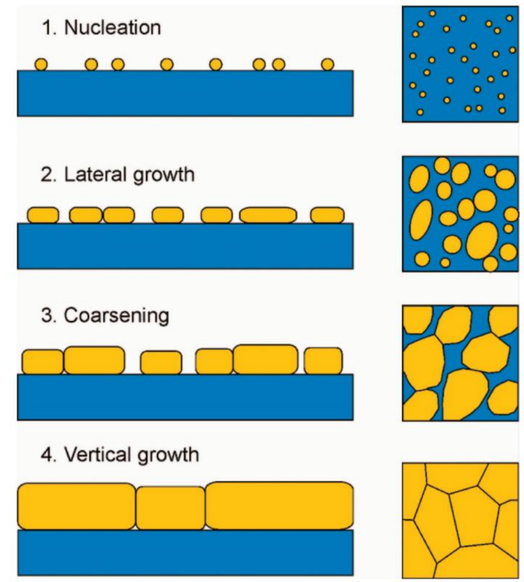
Journal of Applied Crystallography **48**(3): 917-926, 2015

In Situ GISAXS

Gold film growth on conducting polymer





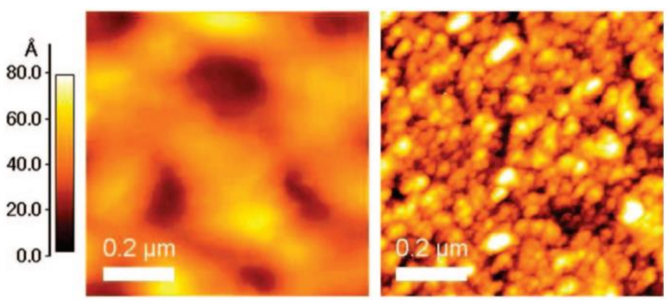
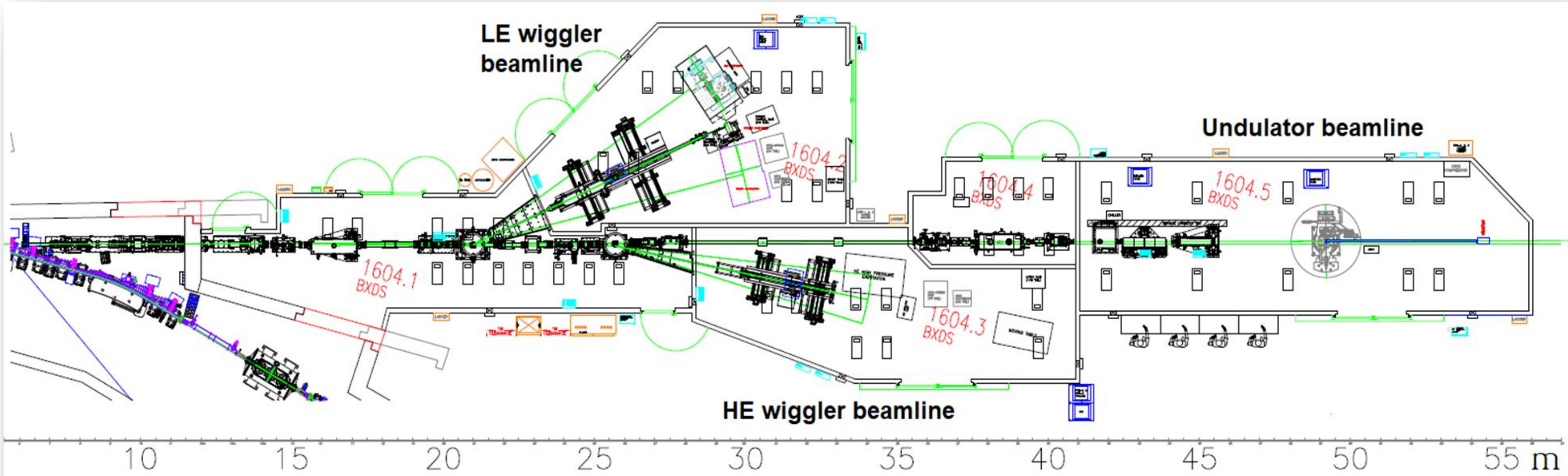


Table 1. Morphological Parameters Extracted from Simulation of the Data by Use of a Model Consisting of Parallelepiped and Spheroid Particle Geometries To Describe the Cluster Shape[a]

t (min)	d_0 (nm)	d (nm)	r_p (nm)	σ_p (nm)	h_p (nm)	r_s (nm)	σ_s (nm)	h_s (nm)	D (nm)	ω (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

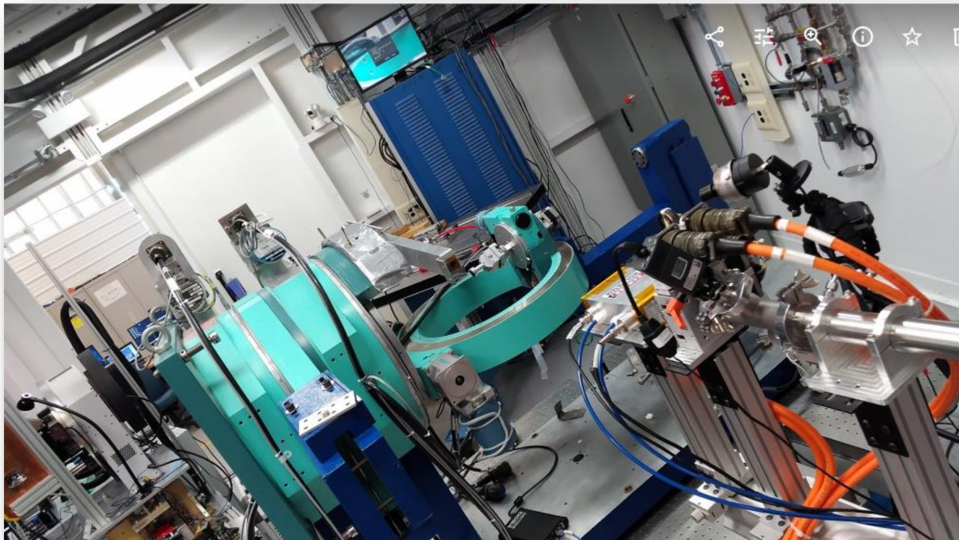
Beamlines energy range

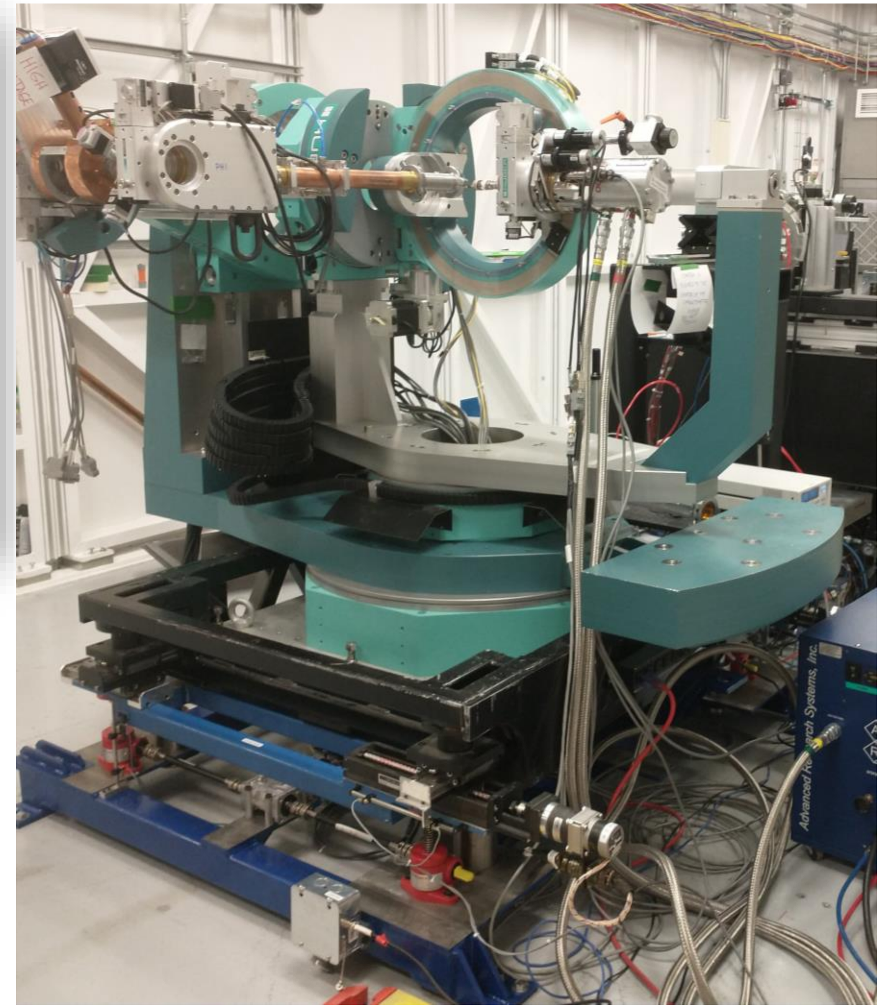
Lower energy wiggler beamline: 7 – 22 keV

Undulator beamline: 5 – 24 keV

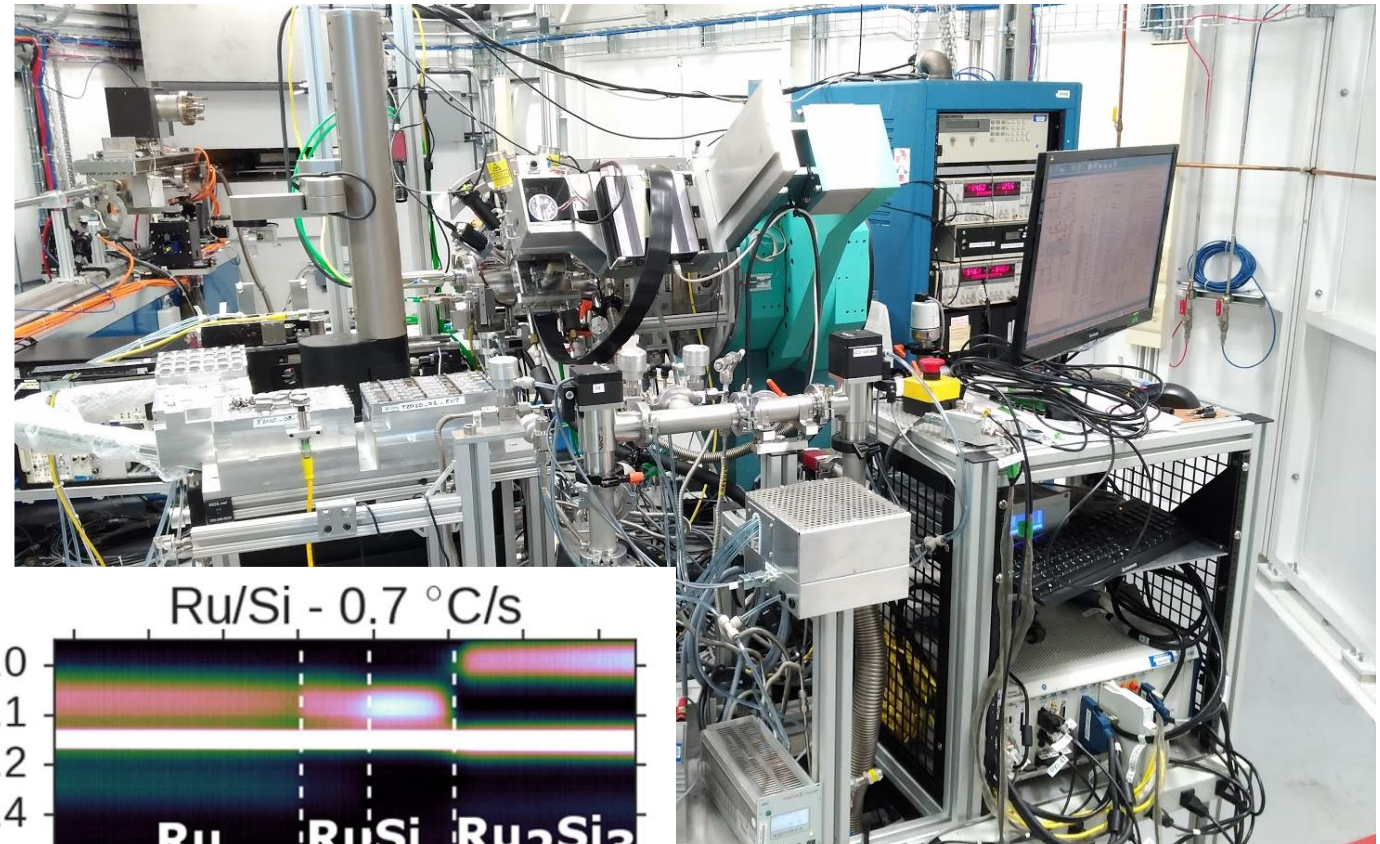
Higher Energy wiggler beamline: 20 – 95 keV

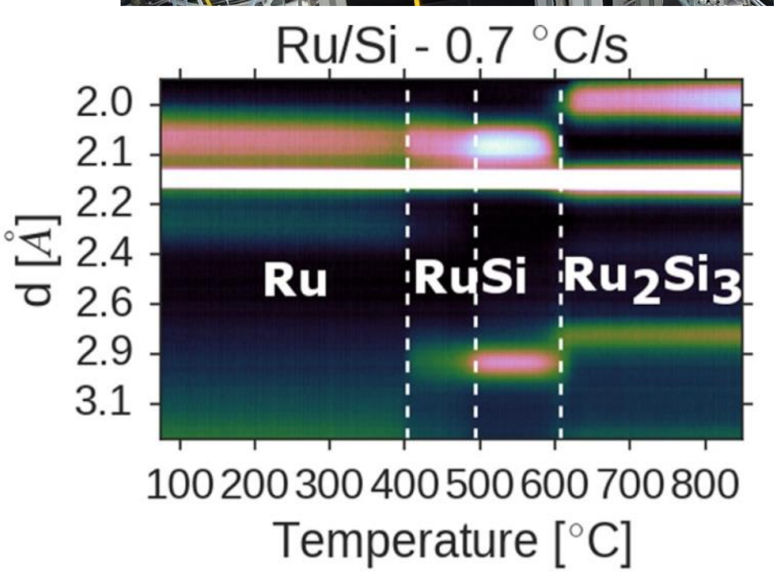
Thin film characterization at the Brockhouse sector





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

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Brockhouse Diffraction Sector Beamlines

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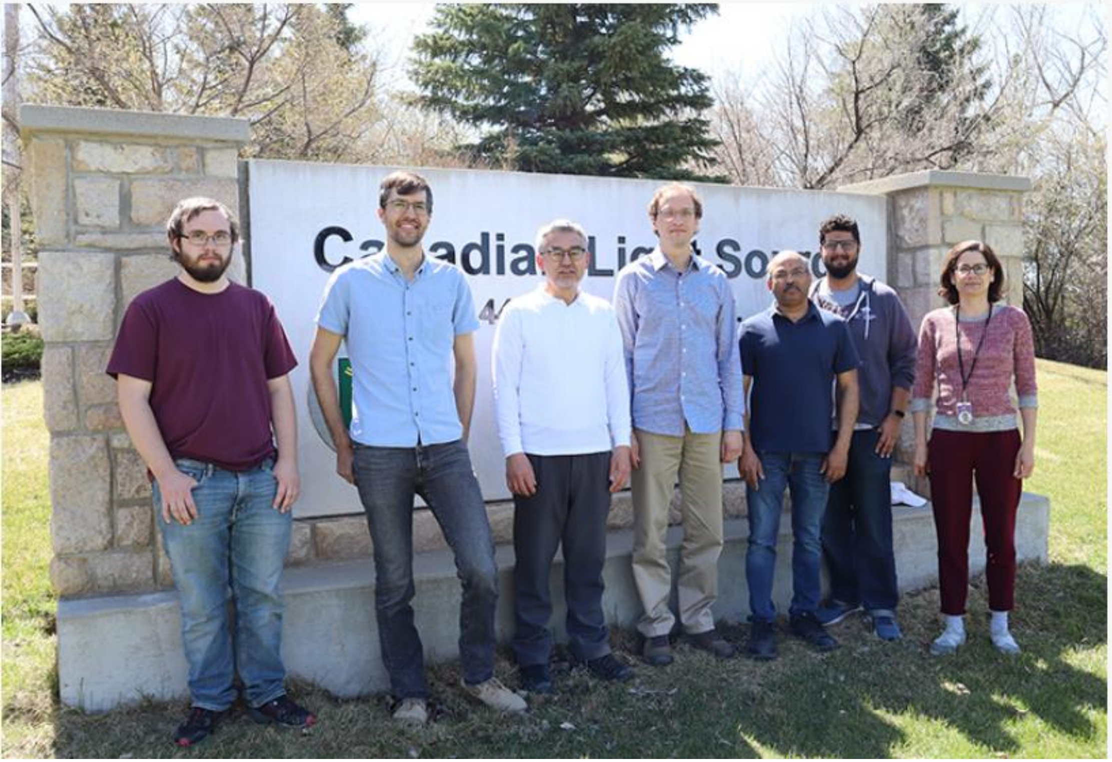

Welcome to the Brockhouse homepage. We provide a wide range of complementary diffraction and scattering techniques to fully characterize your materials.

- 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

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