Canadian Powder Diffraction workshop 13

Thin Film Characterization with X-Rays

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October 26–30, 2020

CPDW 13

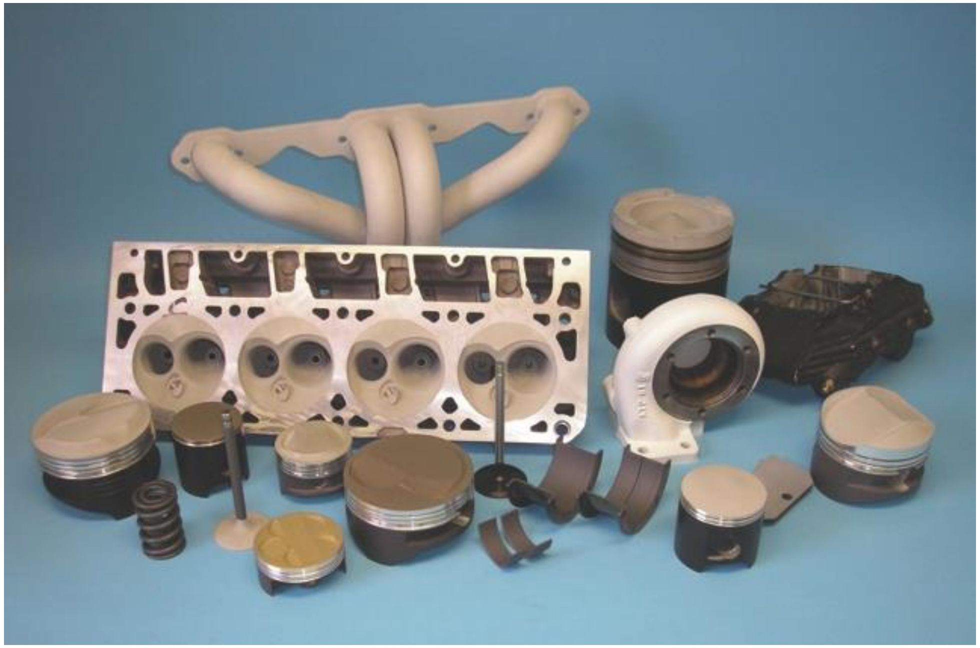
TOPICS

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

Techniques:

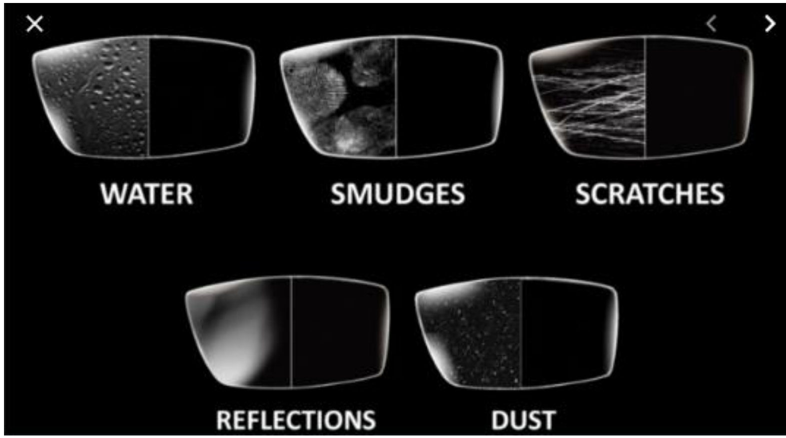
a) GI-powder XRD
b) GI-single crystal XRD
c) Reflectivity
d) GISAXS

Motivation

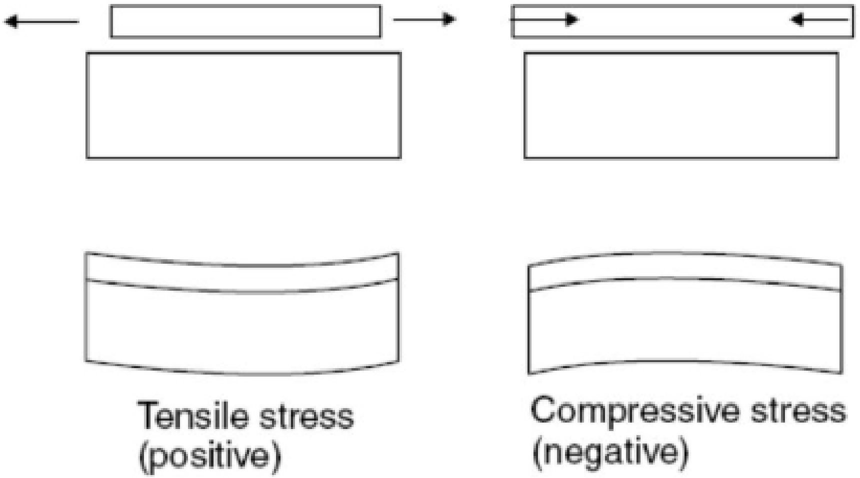


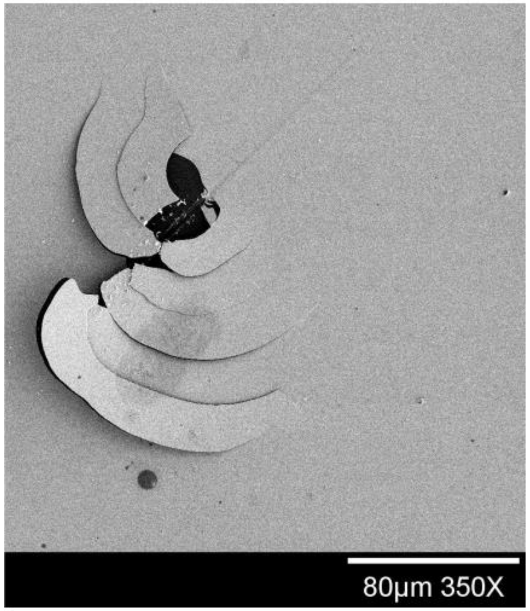
Three Most Common Issues Coatings Address:

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



Structure ↔ Performance





Stress fracture patterns in ALD W/Si

What can we measure?

Small angle x-ray reflectivity

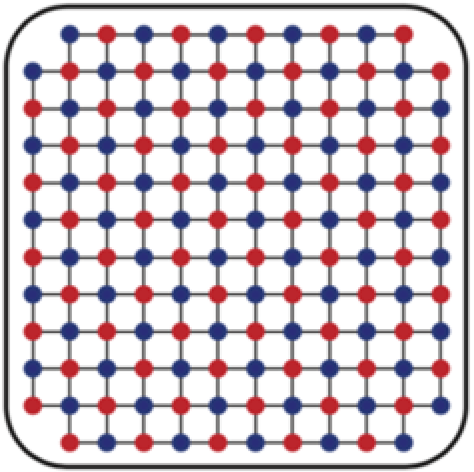
GI-SAXS

GI-WAXS -- GI – PXRD
-- GI -- RSM

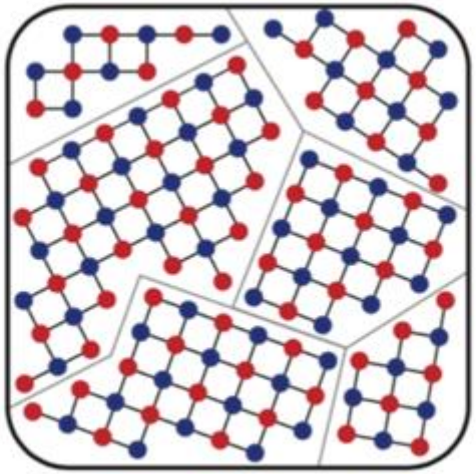
Reflectivity
XRD
Pole figures

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

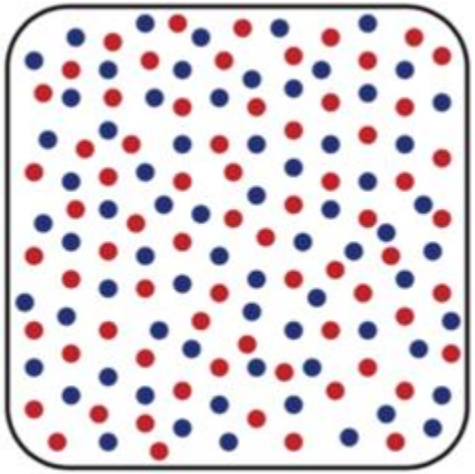
What kind of films can we measure?



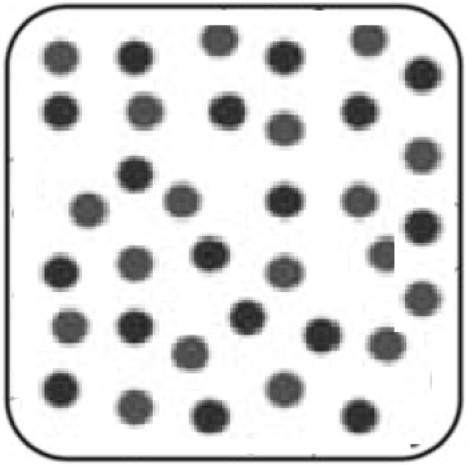
Single-crystal



Poly-crystalline

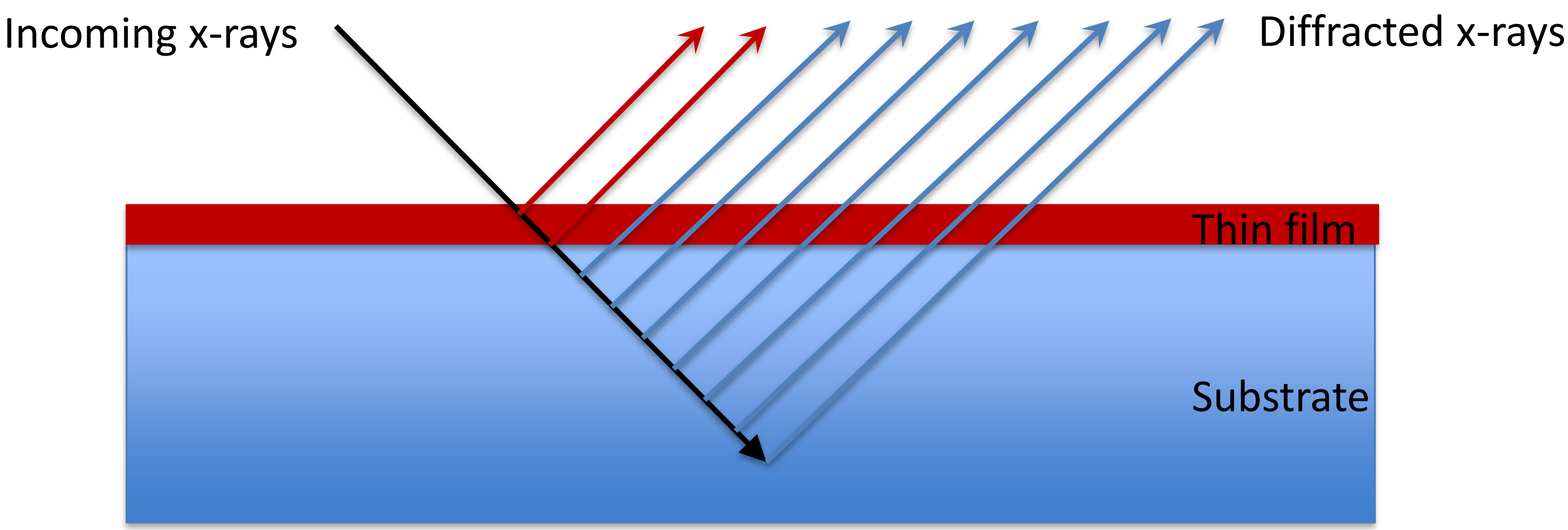


Amorphous



Nanostructures

Using X-Rays to investigate thin films

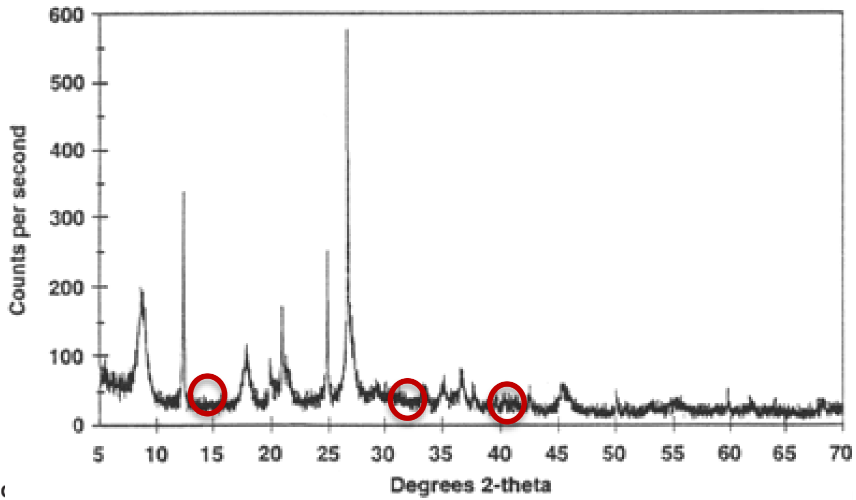


Incoming x-rays

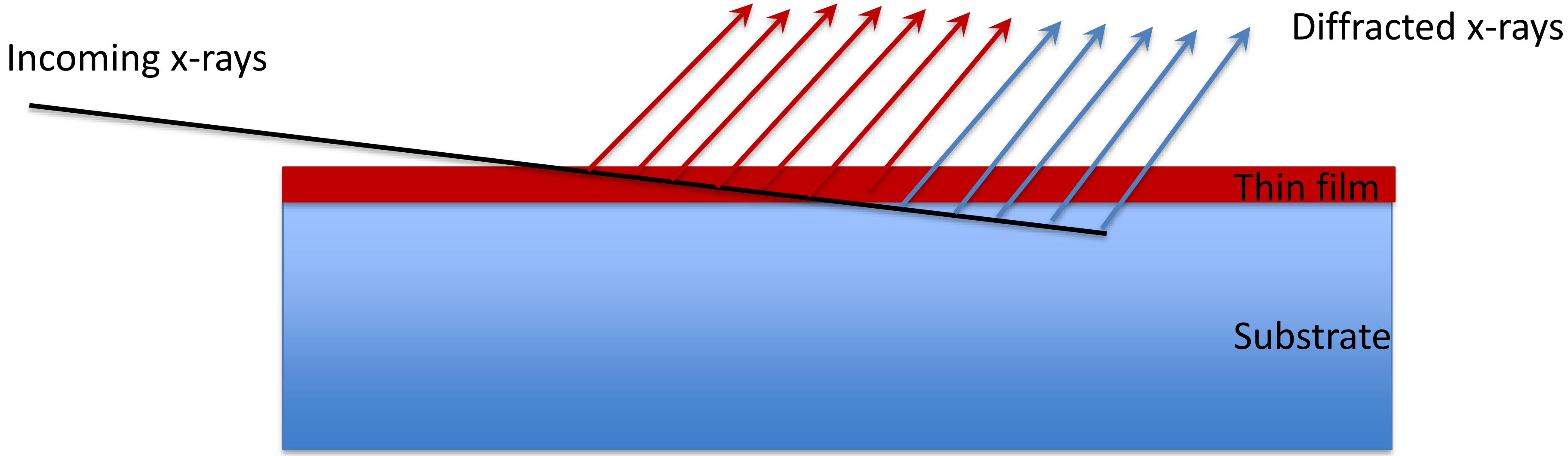
Diffracted x-rays

Thin film

Substrate



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

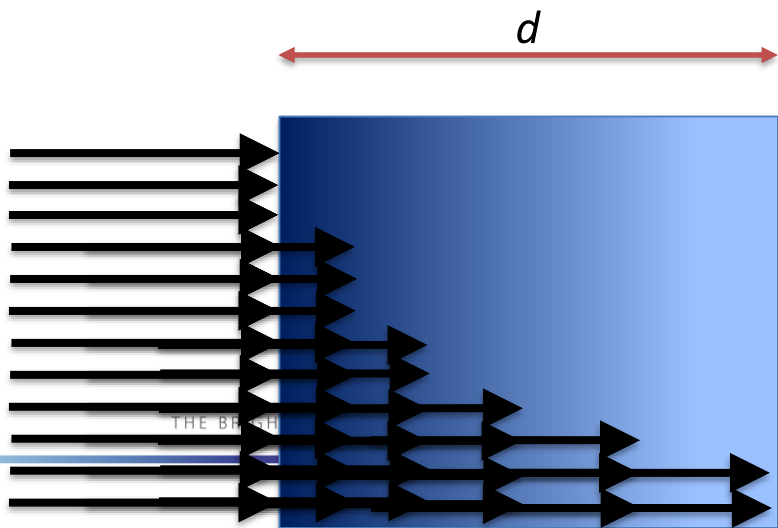
$$I = I_o\, e^{-\frac{d}{\varepsilon}}$$

The **attenuation coefficient** μ is simply the inverse of the attenuation length

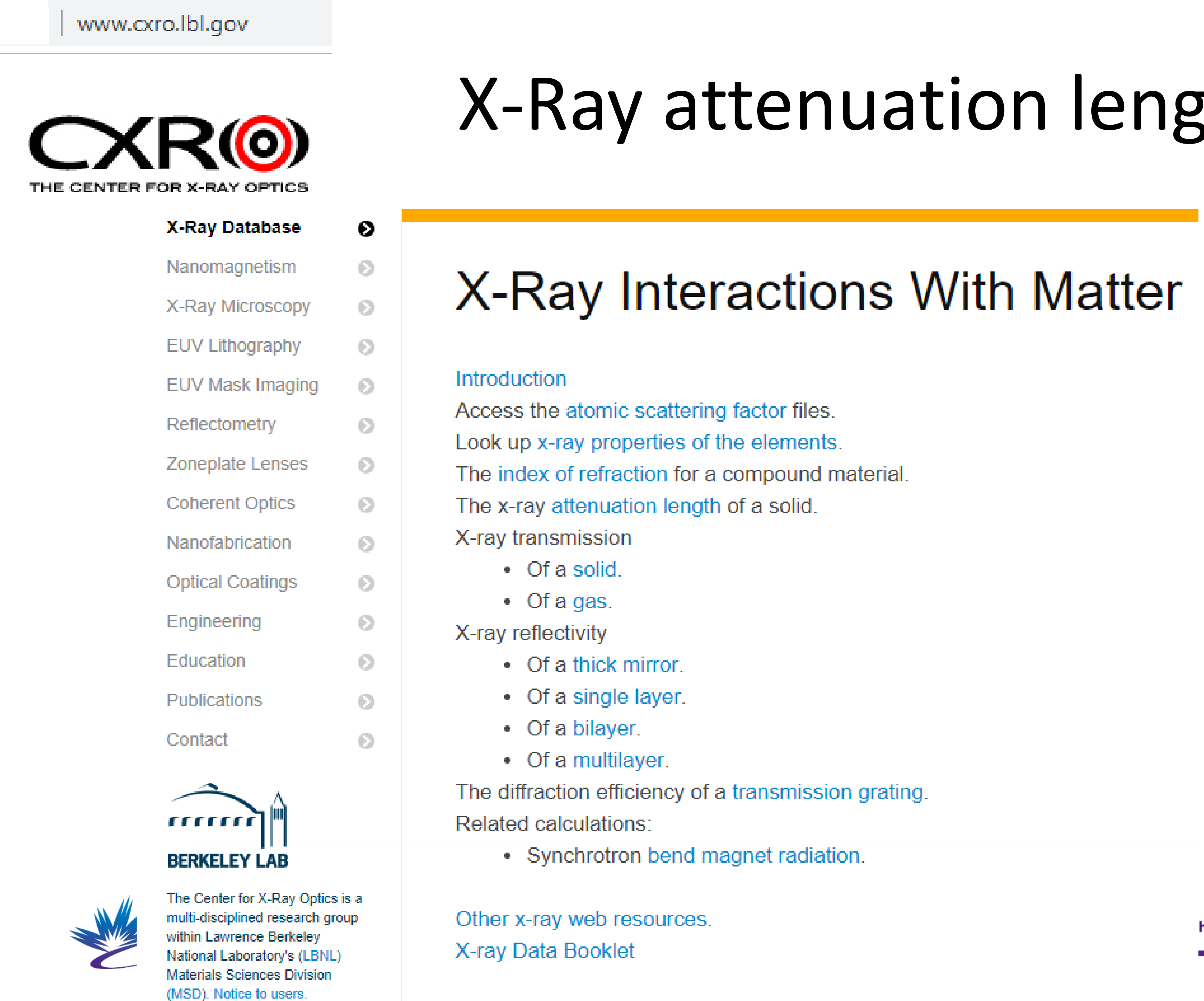
$$I = I_o\, e^{-\mu . d}$$

Where to find attenuation lengths of materials:

- CXRO
- XOP/XPOWER
- …



X-Ray attenuation length



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.

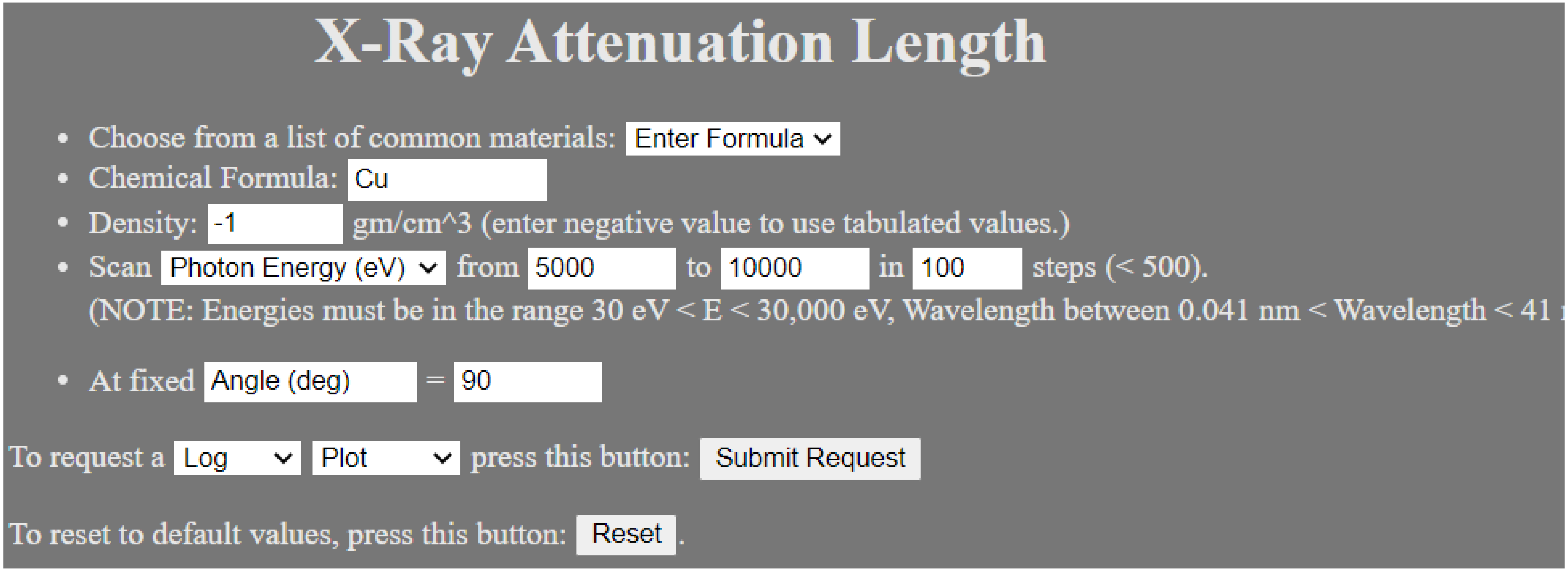
Related calculations:

- Synchrotron bend magnet radiation.

Other x-ray web resources.

X-ray Data Booklet

X-Ray attenuation length



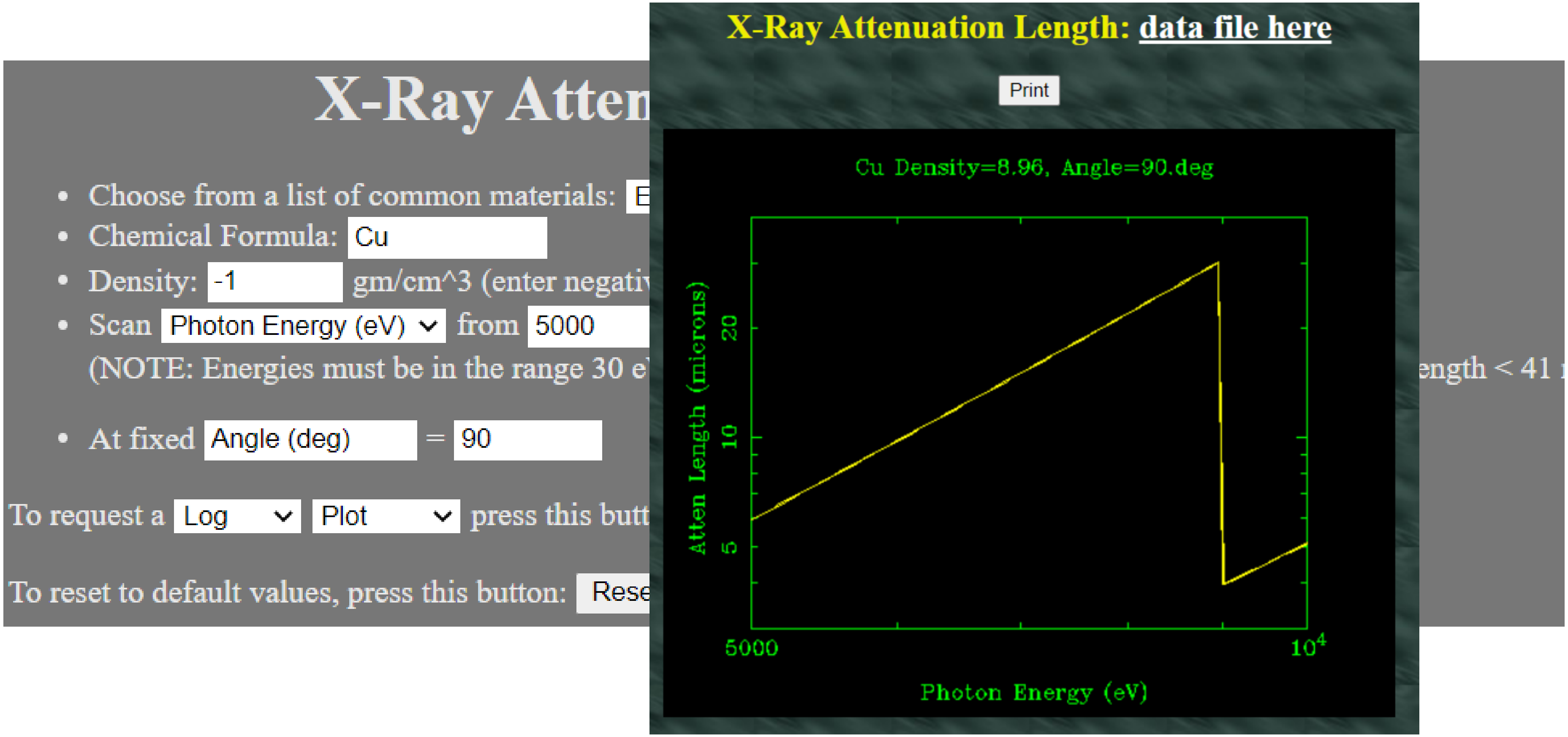
X-Ray Attenuation Length

- 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



X-Ray Atten

- Choose from a list of common materials: E
- Chemical Formula: Cu
- Density: -1 gm/cm^3 (enter negativ
- Scan Photon Energy (eV) from 5000

  (NOTE: Energies must be in the range 30 e … ength < 41
- At fixed Angle (deg) = 90

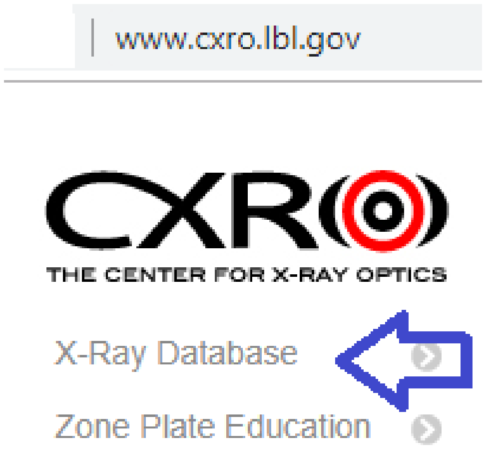
To request a Log Plot press this butt

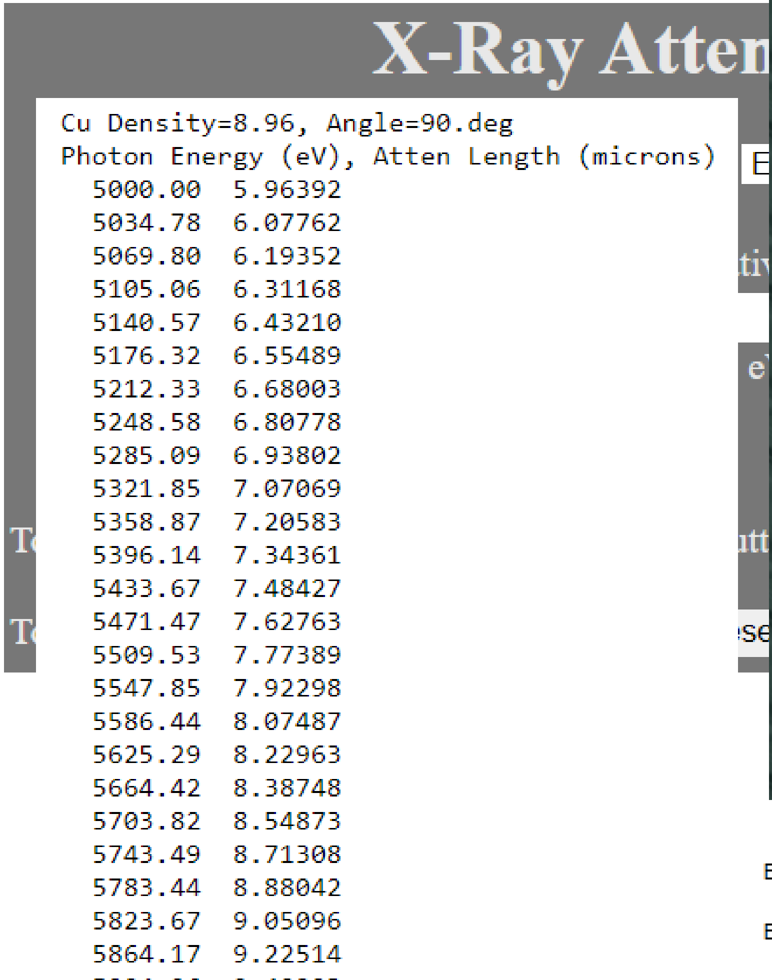
To reset to default values, press this button: Rese

X-Ray Attenuation Length: data file here

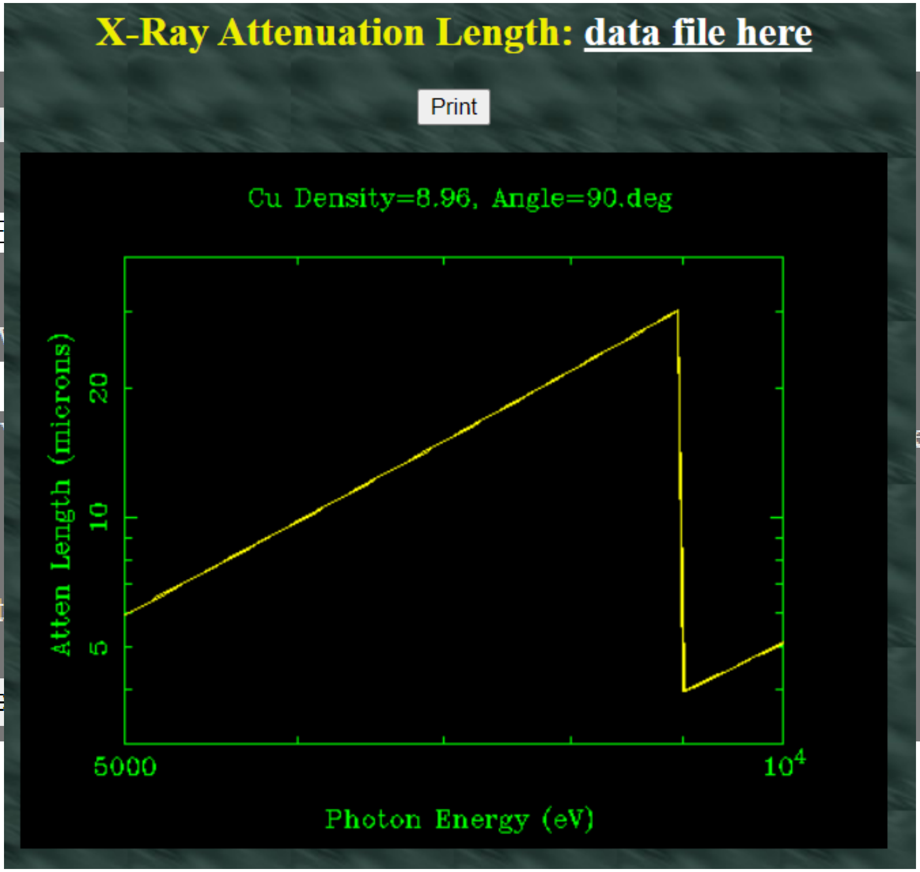
```
Element 29: Cu

Edge          keV
  K         8.9789
```

X-Ray attenuation length





```
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
```



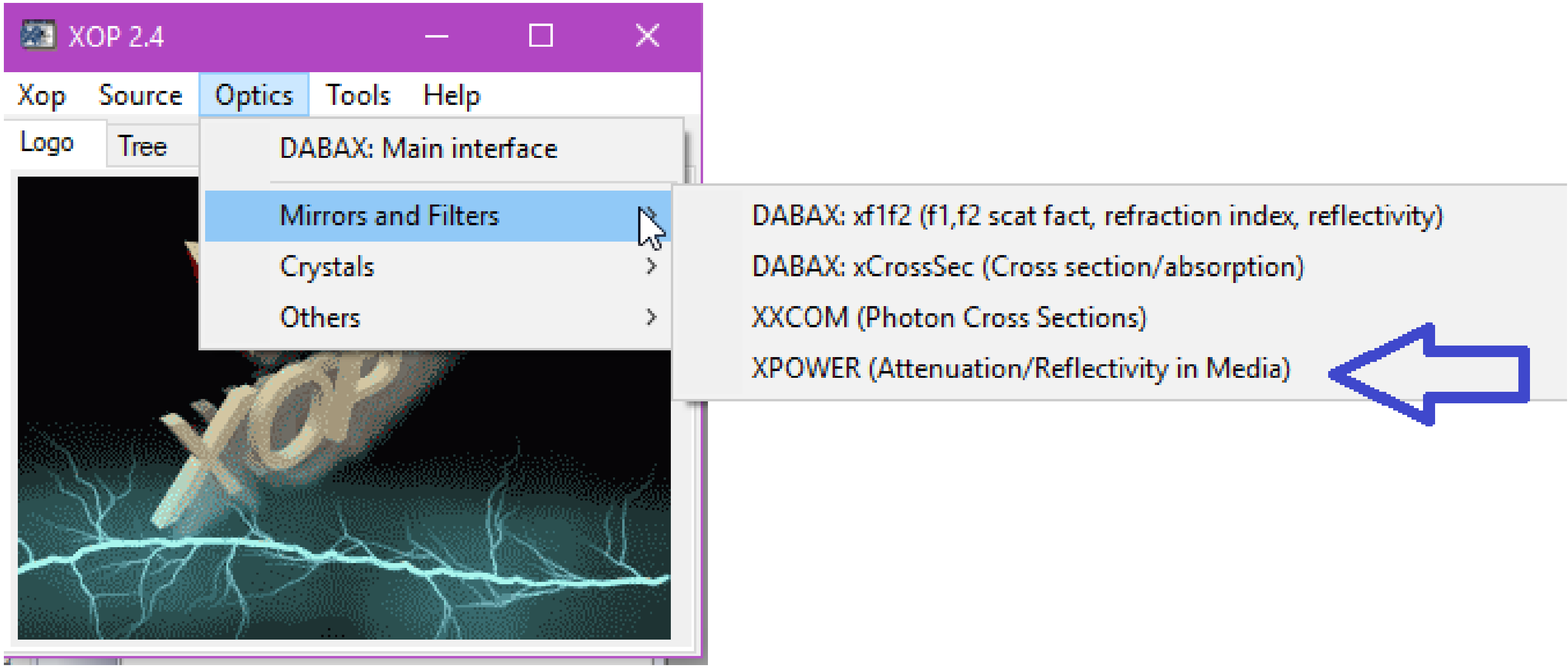
X-Ray Attenuation Length: data file here

```
Element 29: Cu

Edge        keV
 K        8.9789
```

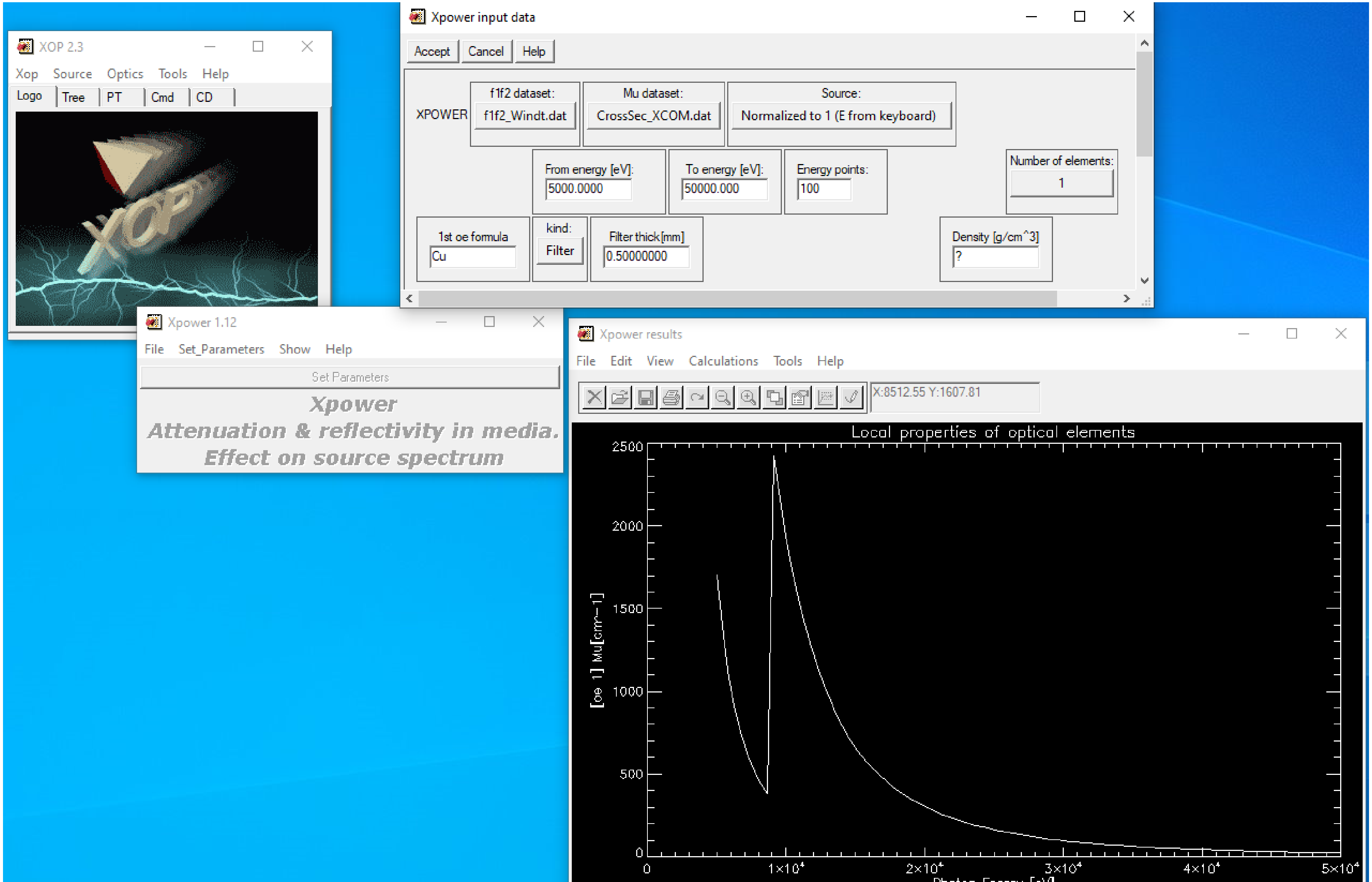
X-Ray attenuation length

XOP/XPOWER

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



X-Ray attenuation length



f1f2 dataset: f1f2_Windt.dat

Mu dataset: CrossSec_XCOM.dat

Source: Normalized to 1 (E from keyboard)

From energy [eV]: 5000.0000

To energy [eV]: 50000.000

Energy points: 100

Number of elements: 1

1st oe formula: Cu

kind: Filter

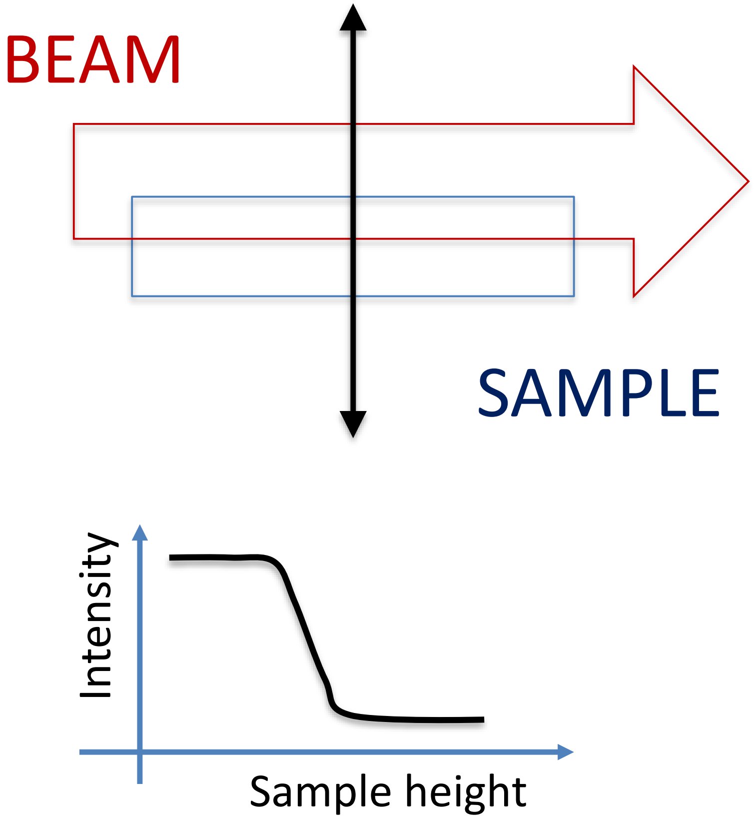
Filter thick[mm]: 0.50000000

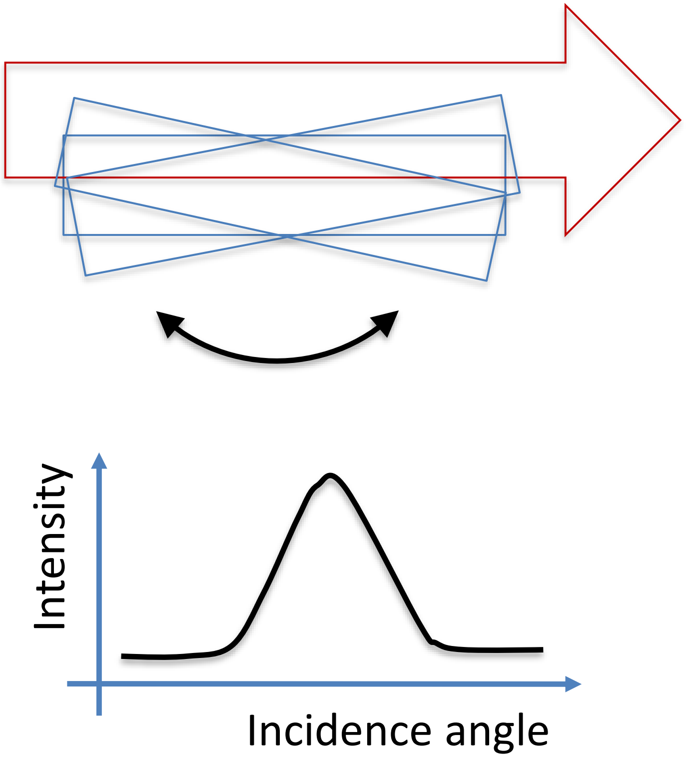
Density [g/cm^3]: ?

X:8512.55 Y:1607.81

How do we measure?

Sample alignment





Iterate!

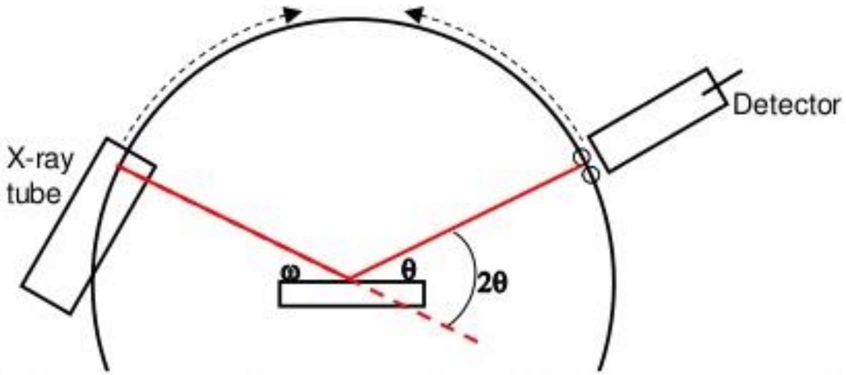
Grazing incidence diffraction

applied to

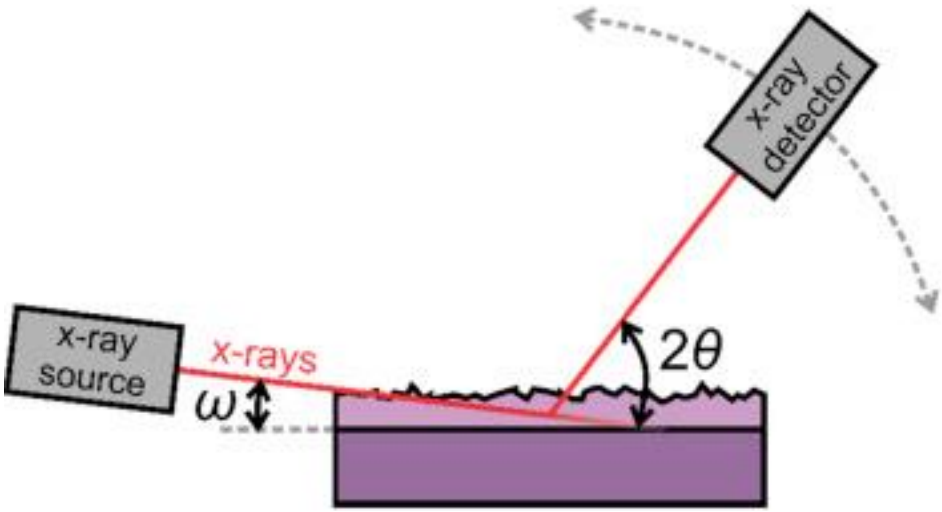
Polycrystalline films

Grazing incidence diffraction

Regular specular geometry, $\omega = \theta$



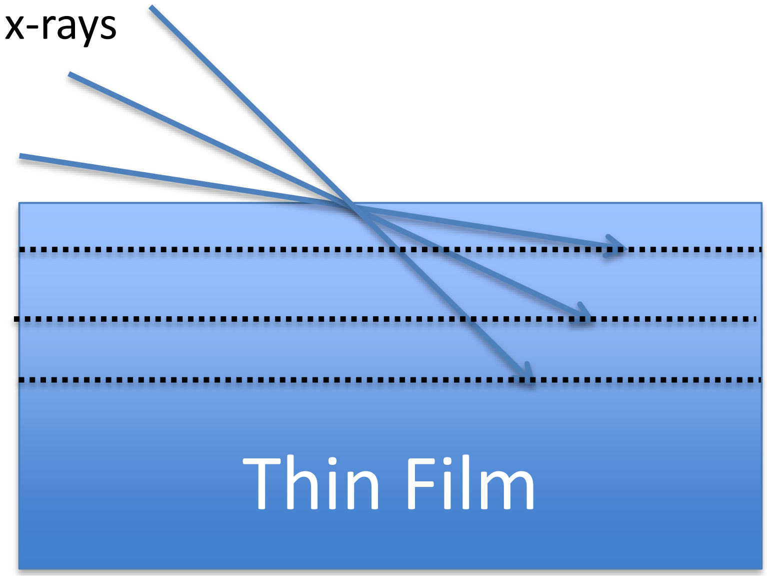
Grazing incidence geometry

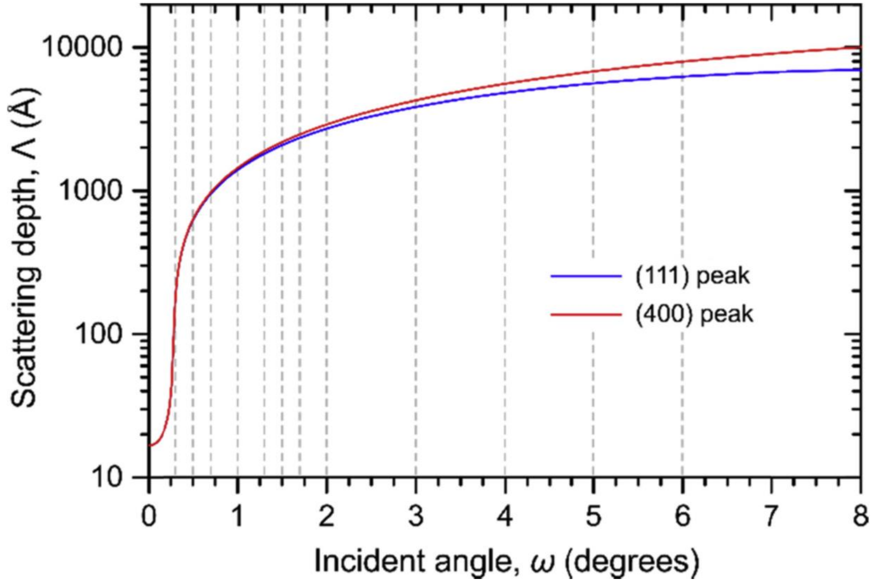


https://www.sciencedirect.com/science/article/pii/S0022311517313946

Grazing incidence diffraction

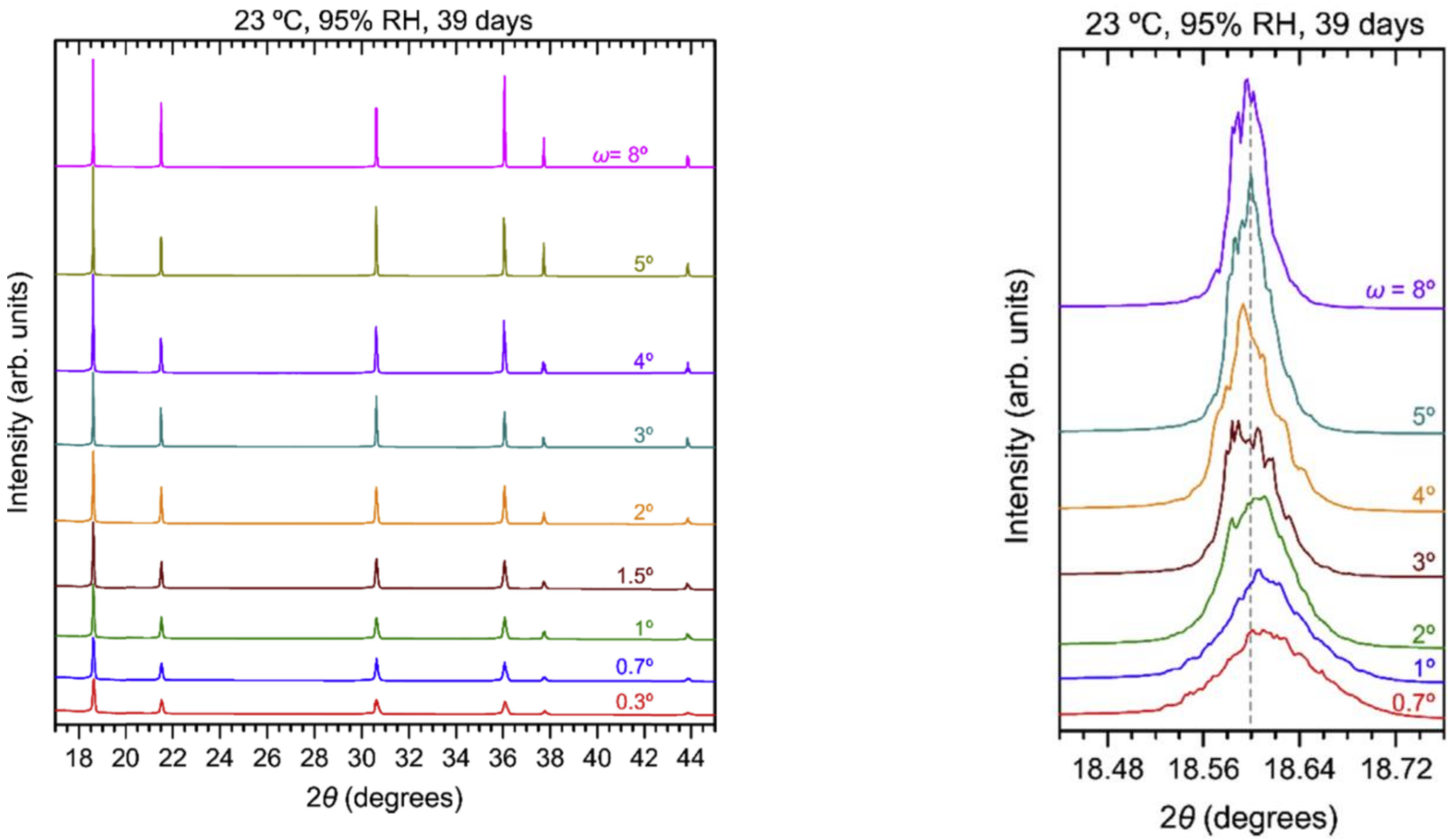
Depth sensitivity





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

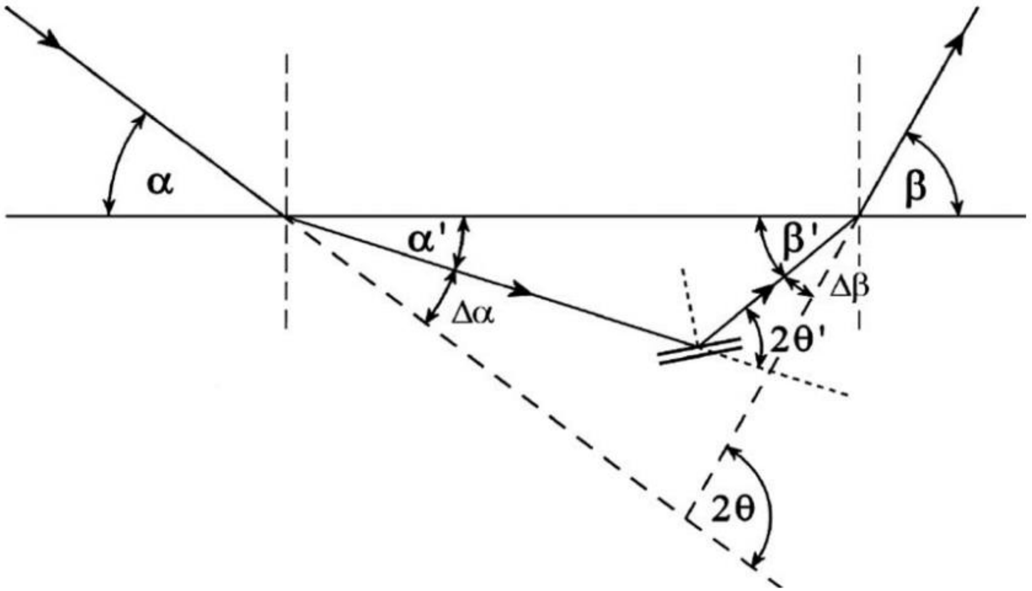
Grazing incidence diffraction



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

Grazing incidence diffraction

Refraction correction



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

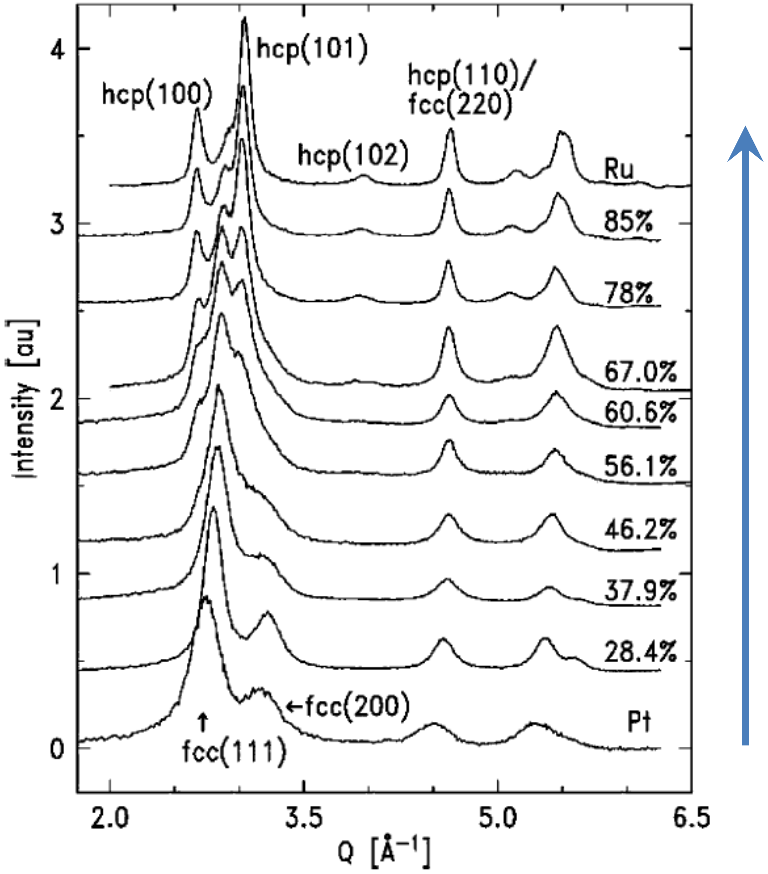
Powder Diffraction **24**(S1): S11-S15, 2012

Grazing incidence diffraction

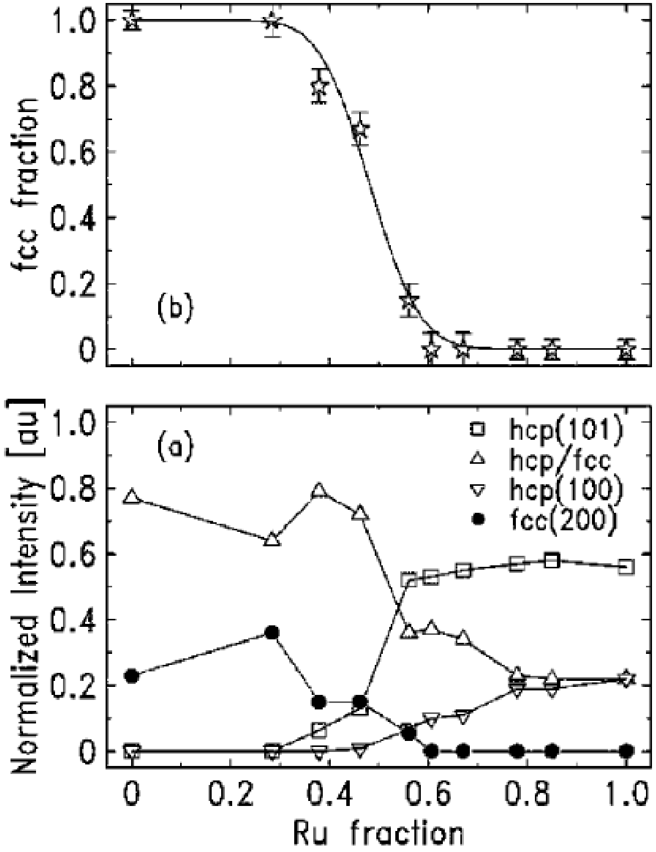
Structure and electrocatalysis of sputtered RuPt thin-film electrodes

130 Å thick

Grazing incidence x-ray diffraction



Phase diagram determination



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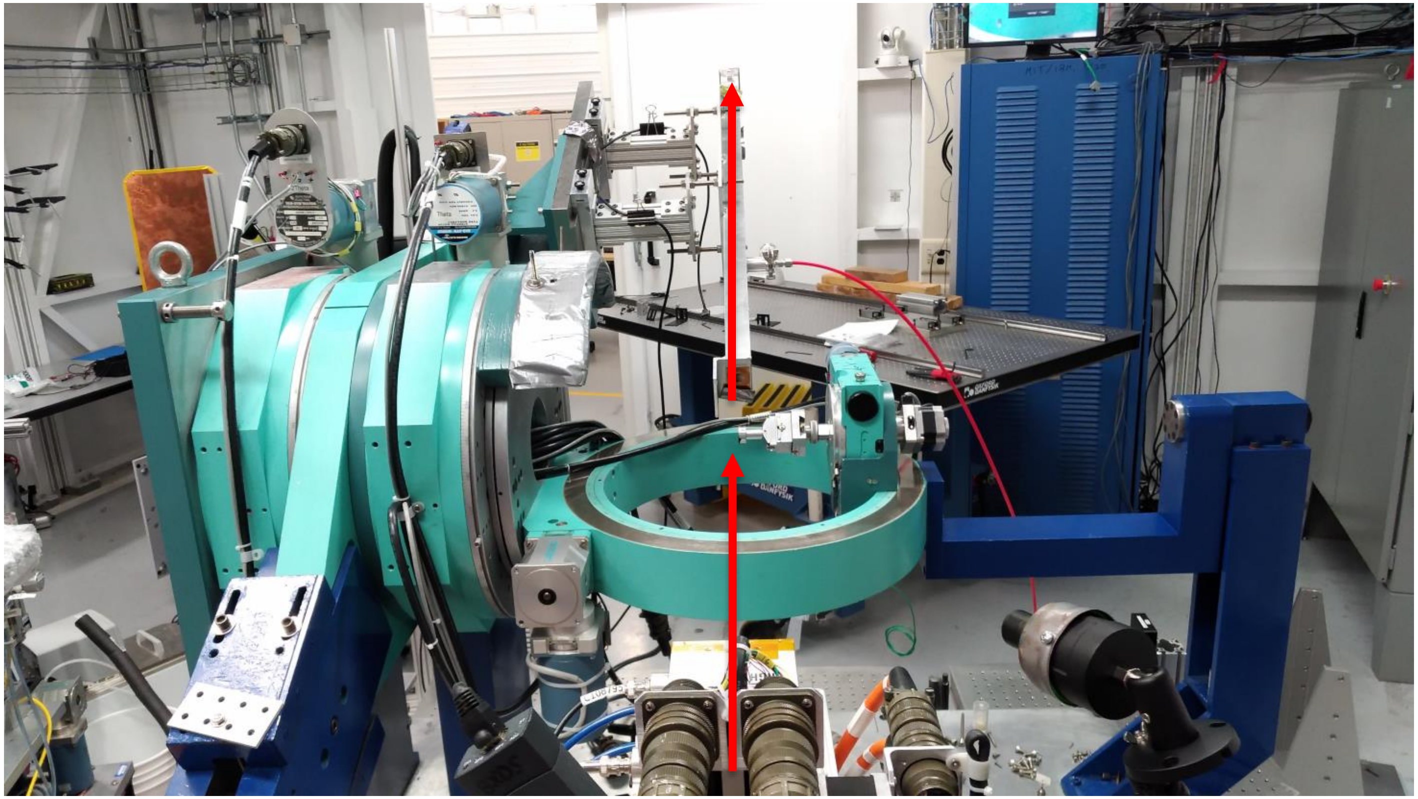
J. Phys. Chem. B **109**, 12845, 2005. Kim et al.

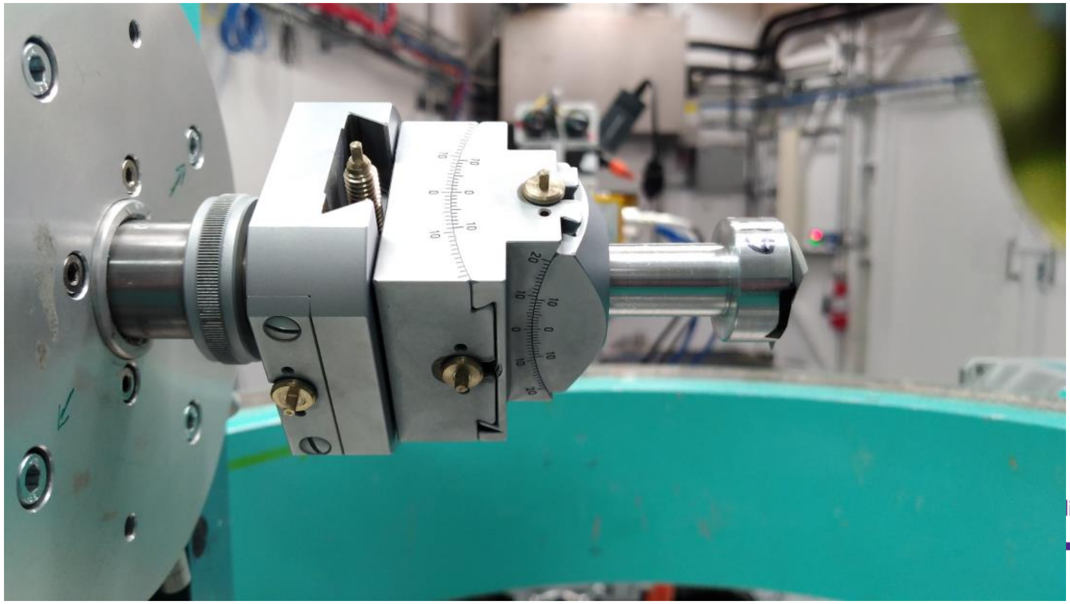
Grazing incidence diffraction

applied to

Single crystal films

GID setup





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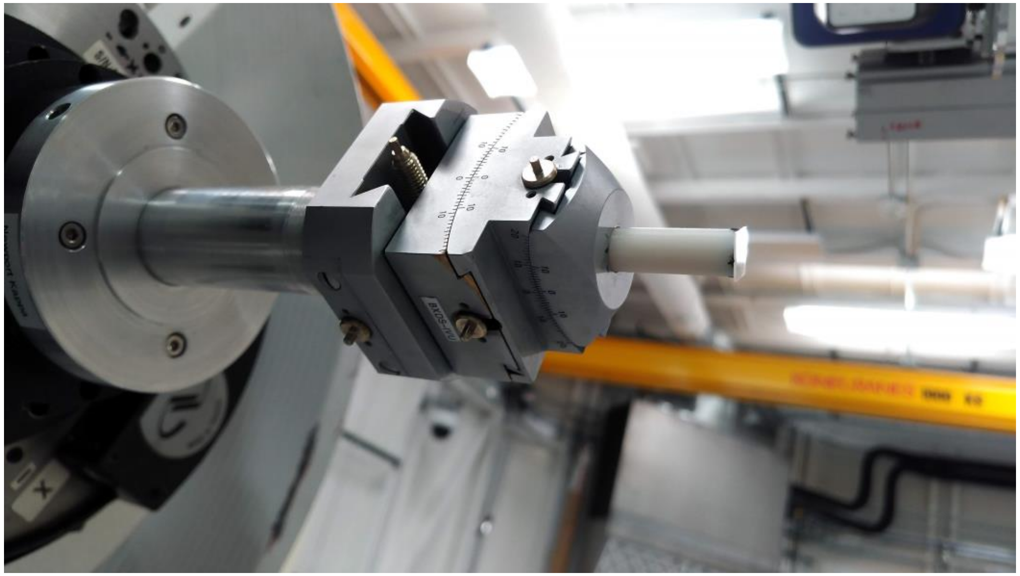
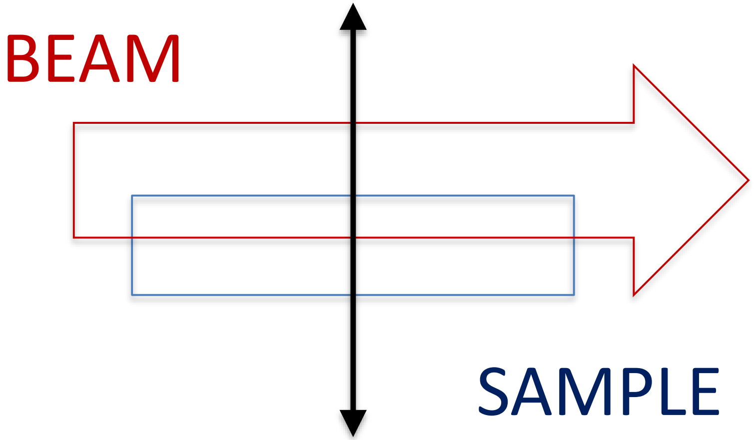
GID setup

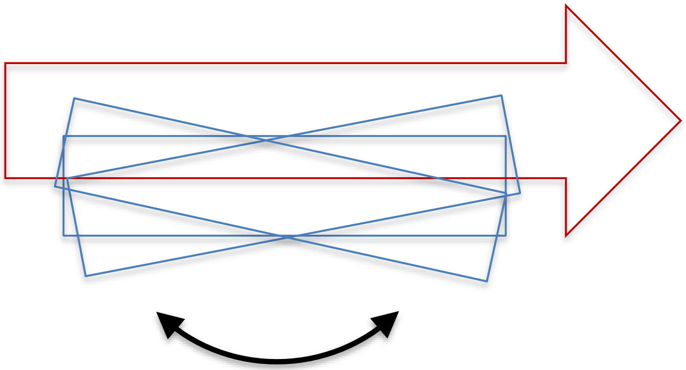


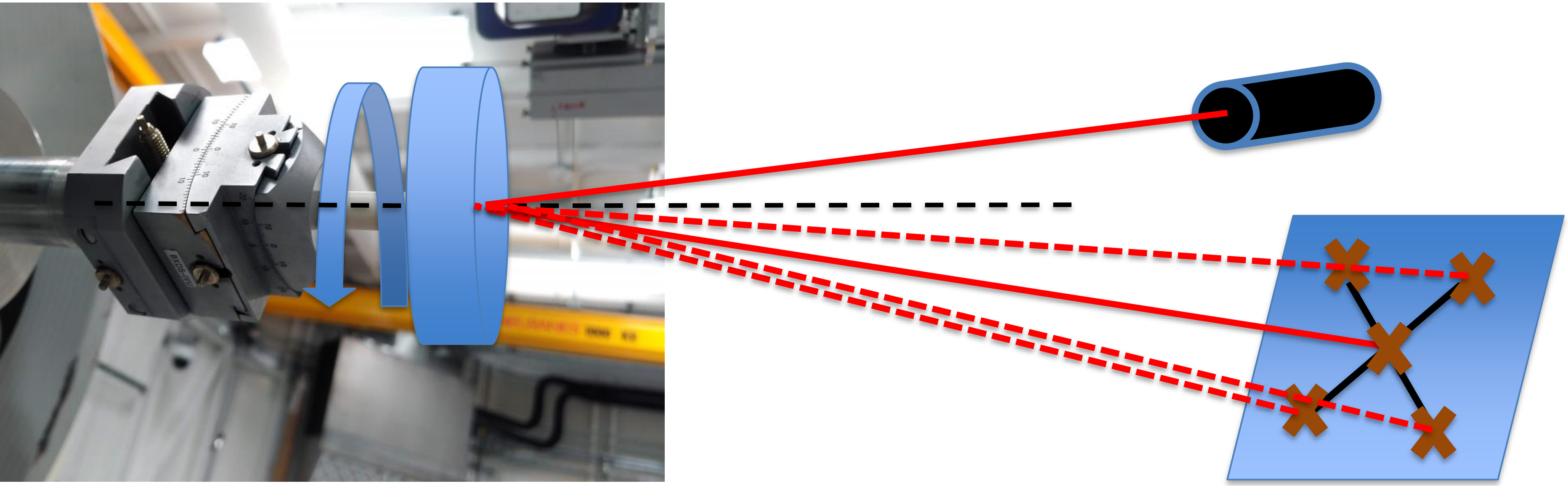
Sample alignment



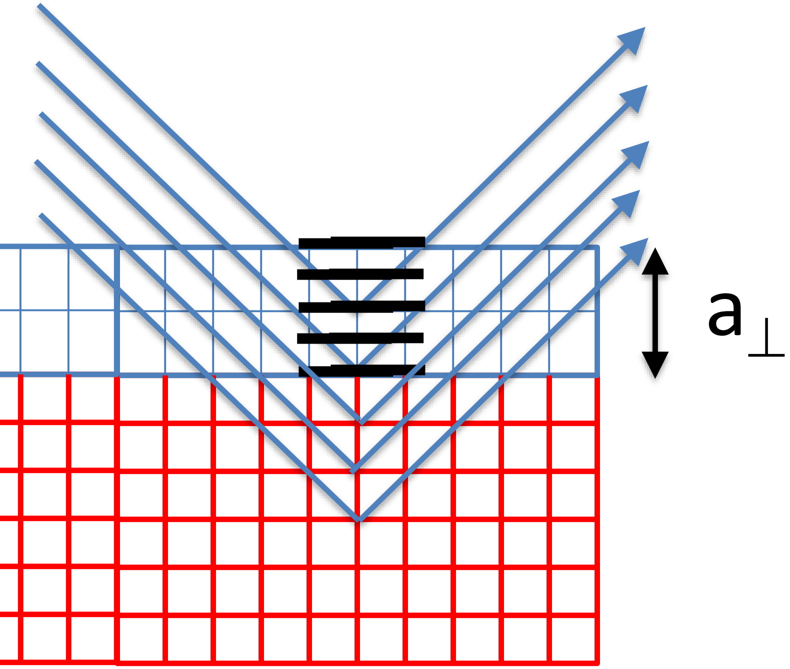
BEAM

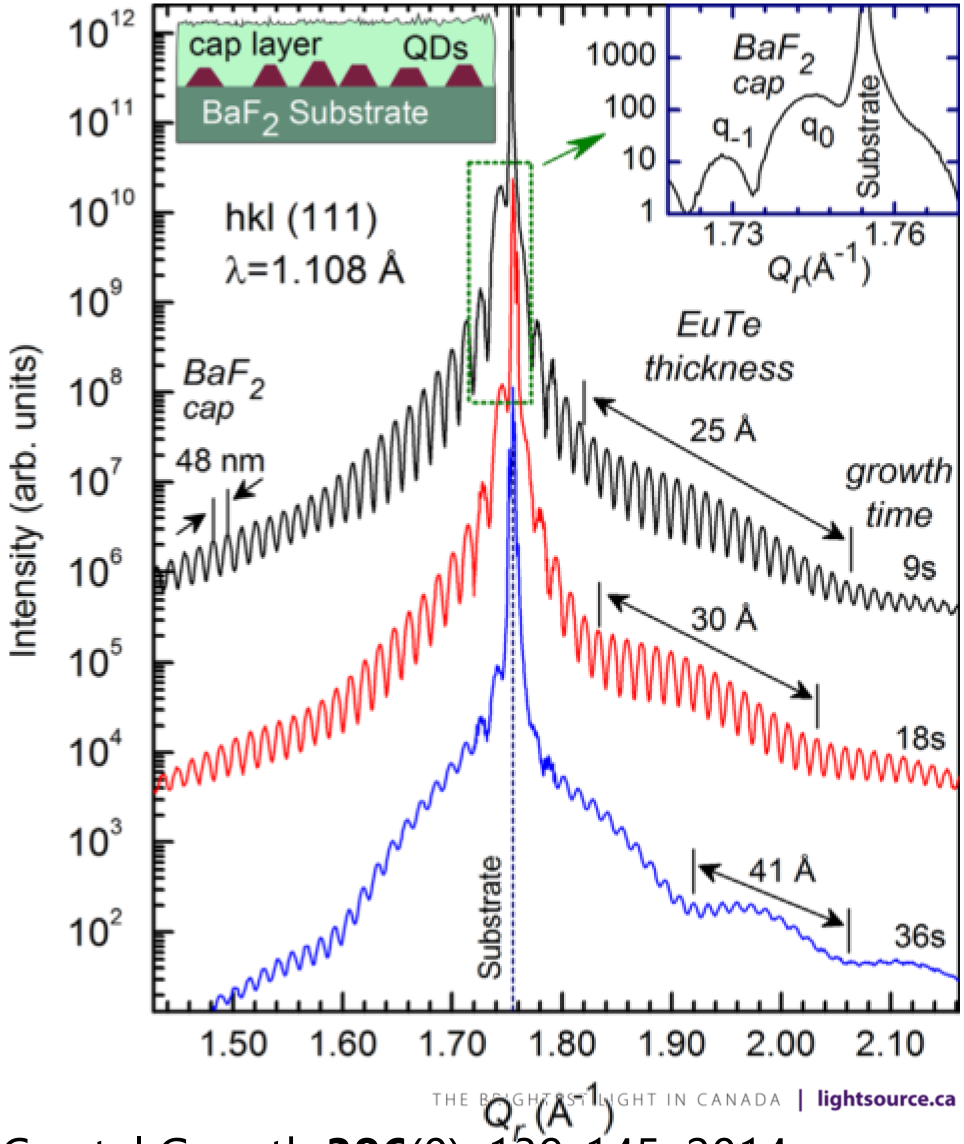
SAMPLE





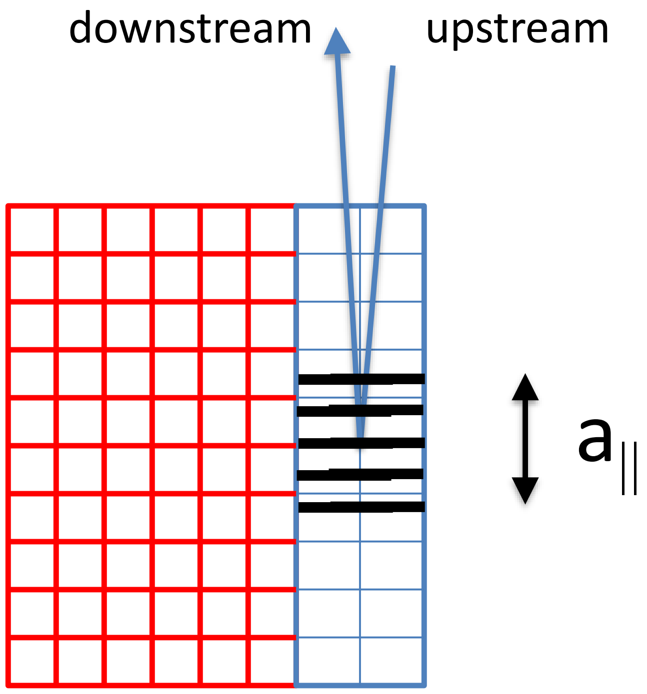
Not-Grazing incidence diffraction

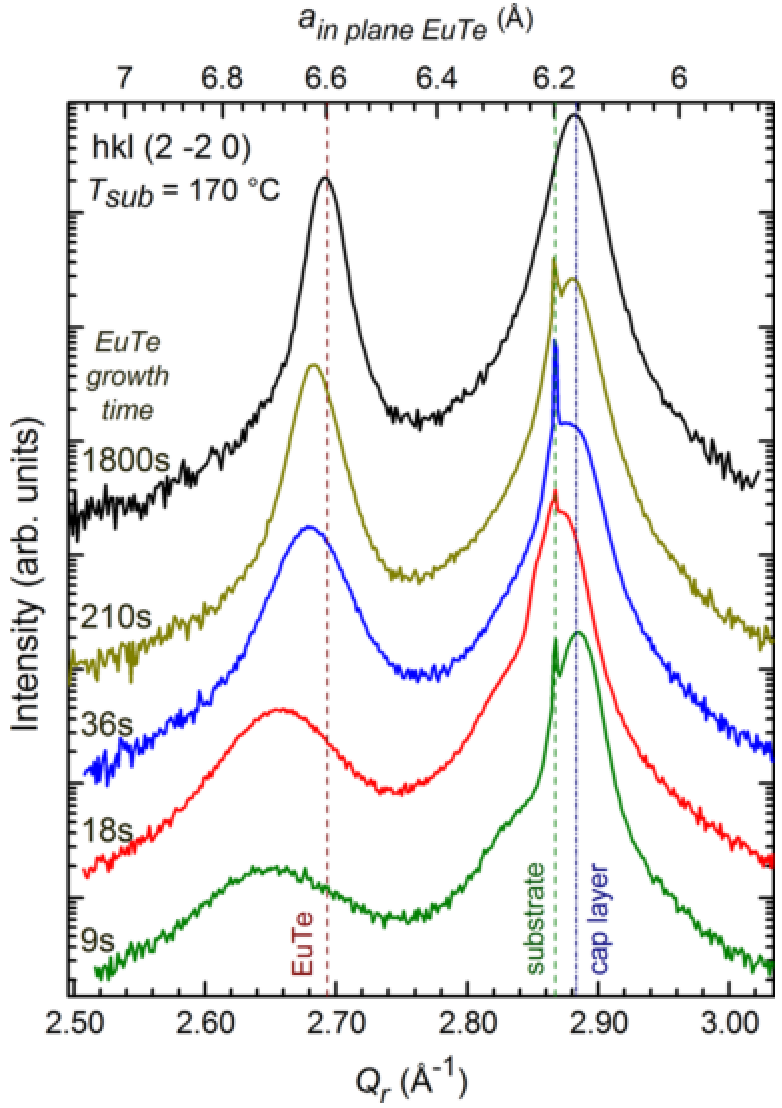




Journal of Crystal Growth **386**(0): 139-145, 2014

Grazing incidence diffraction





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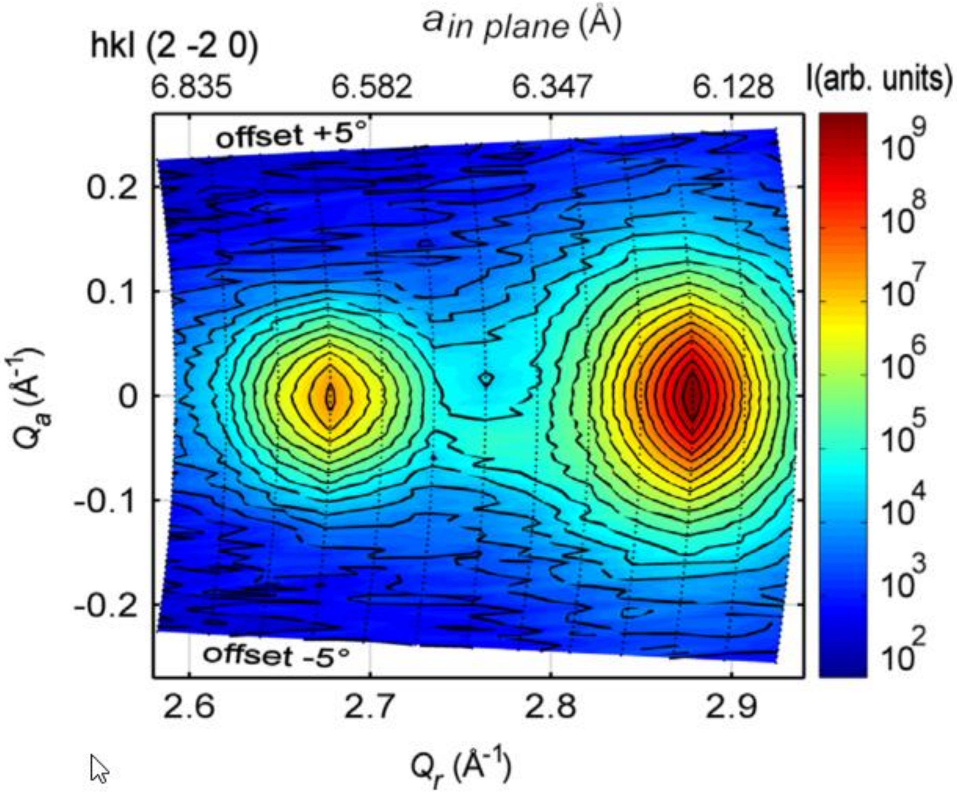
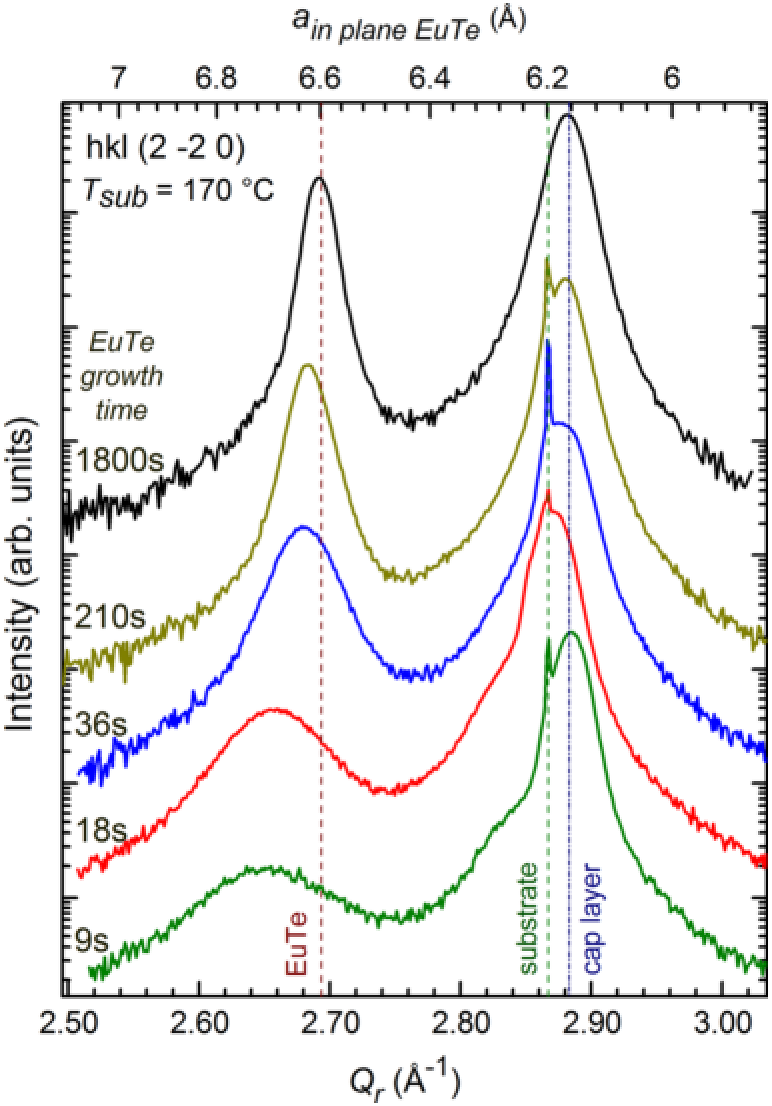
Grazing incidence diffraction





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

Grazing incidence ~~diffraction~~

Small angle x-ray reflectivity

Single crystal films

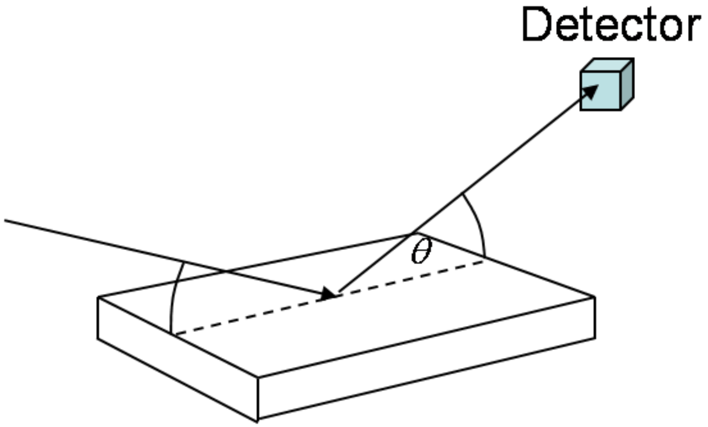
Polycrystalline films

Amorphous films

Small angle X-Ray reflectivity

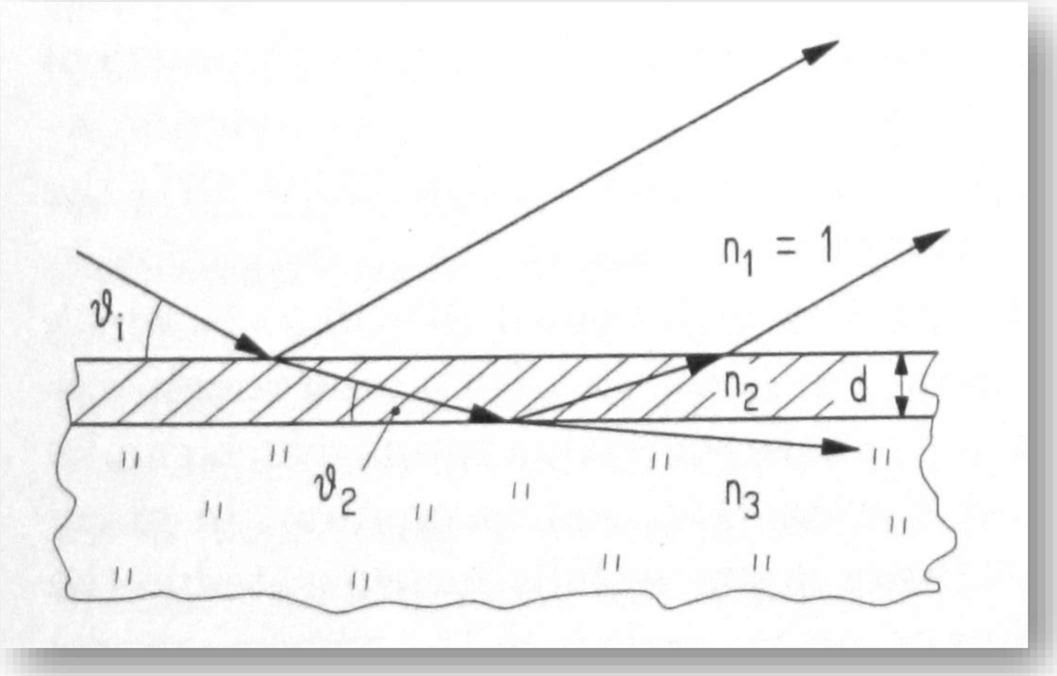
- Reflectivity yields information about the
  - ➢ Thicknesses
  - ➢ Density / porosity
  - ➢ Roughness of the interfaces

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



No diffraction!

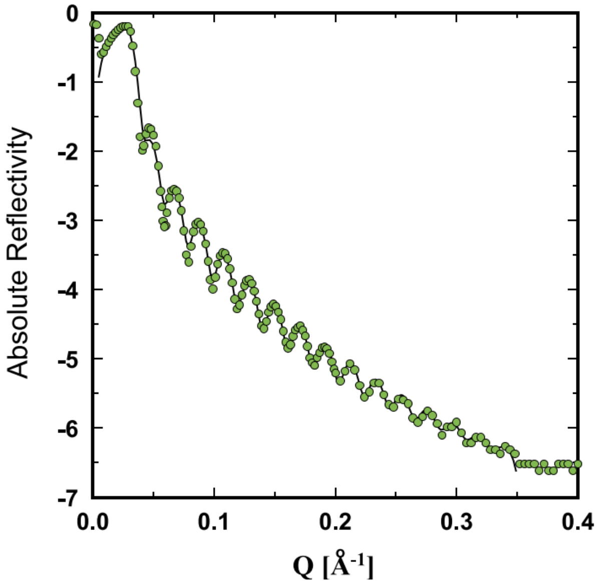
Small angle X-Ray reflectivity



Snell's law

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

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



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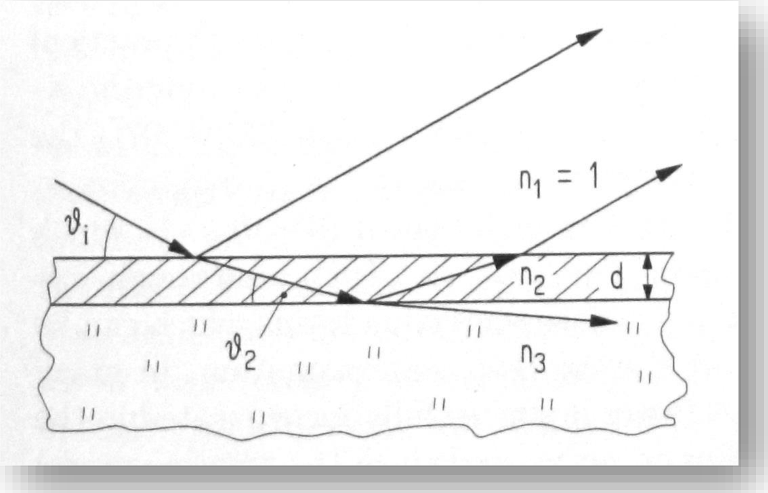
Gibaud 2013 – X-ray reflectivity chapter

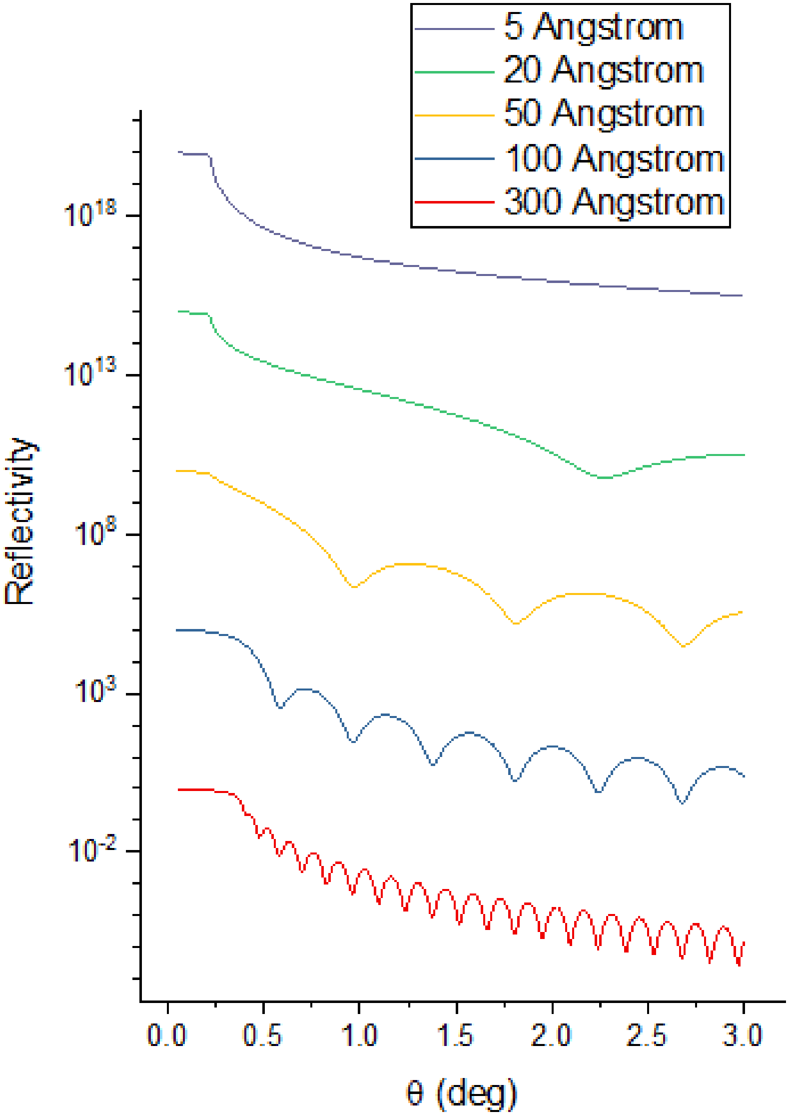
Small angle X-Ray reflectivity

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

Kiessig fringes

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





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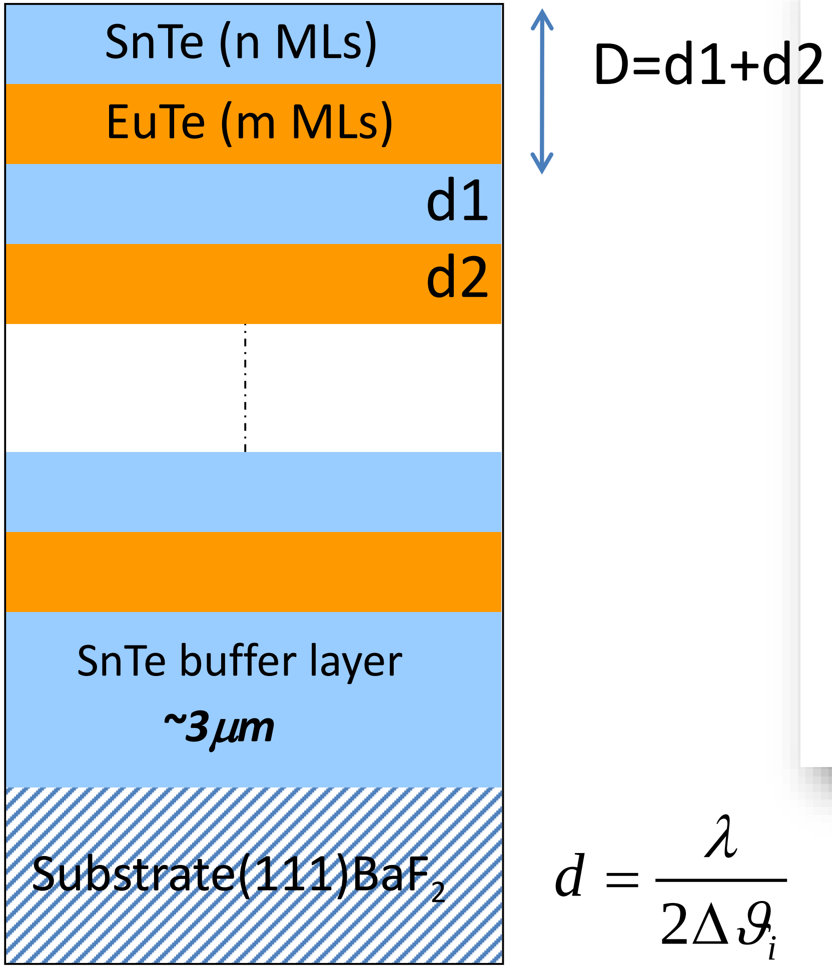
Small angle X-Ray reflectivity



SnTe (n MLs)

EuTe (m MLs)

d1

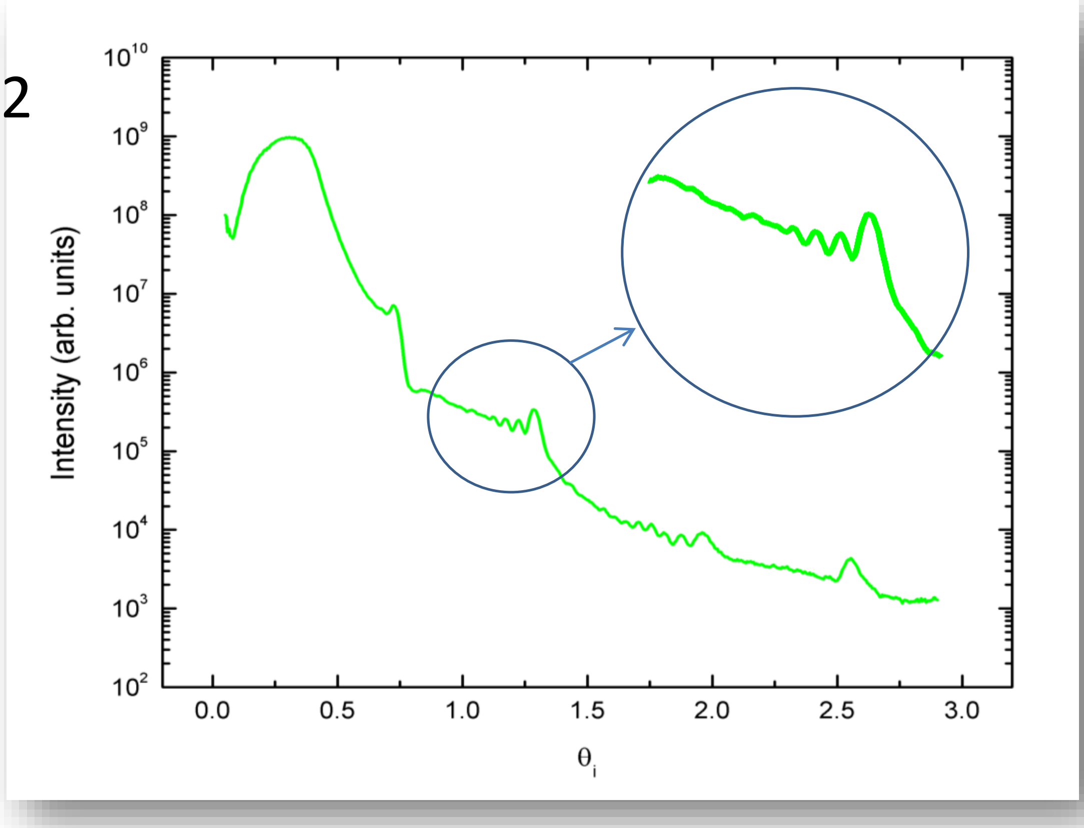
d2

D=d1+d2

SnTe buffer layer

~3 μm

Substrate(111)BaF_2



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

Kiessig fringes spacing:

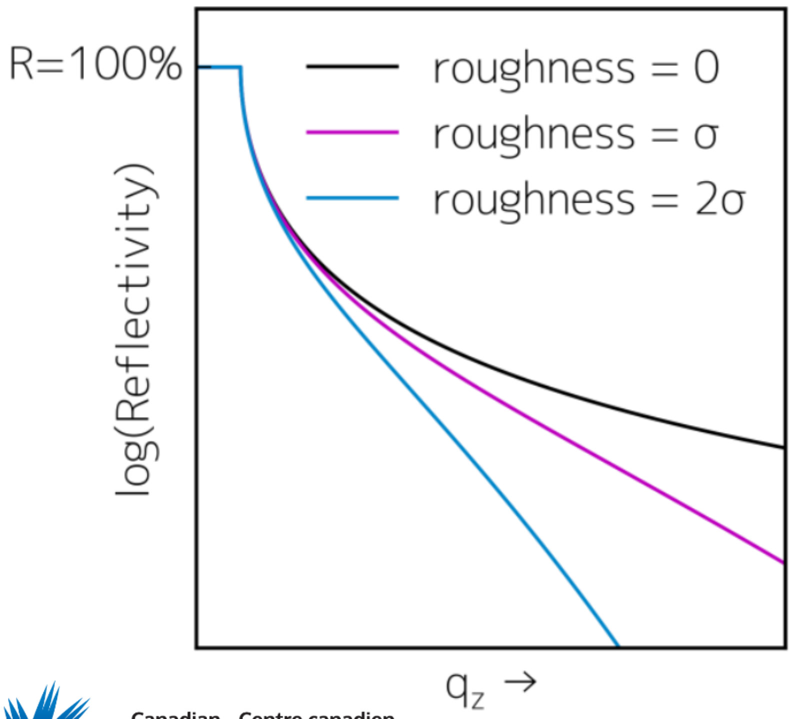
0.61 deg ~ 83 Å (SL period)

0.05 deg ~ 994.9 Å (Stack thickness)

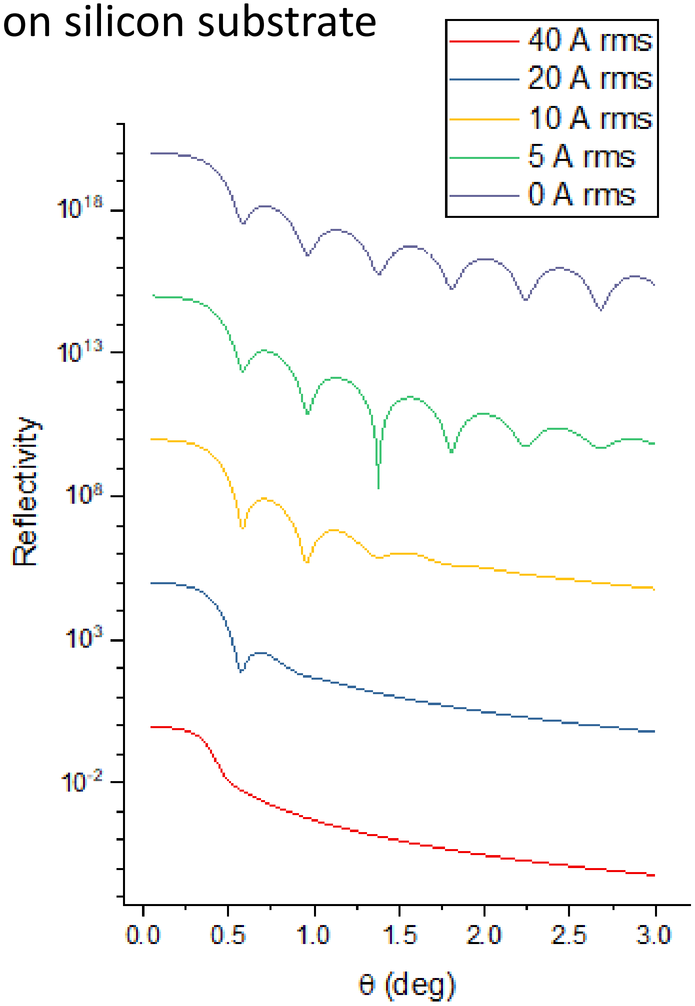
Small angle X-Ray reflectivity

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

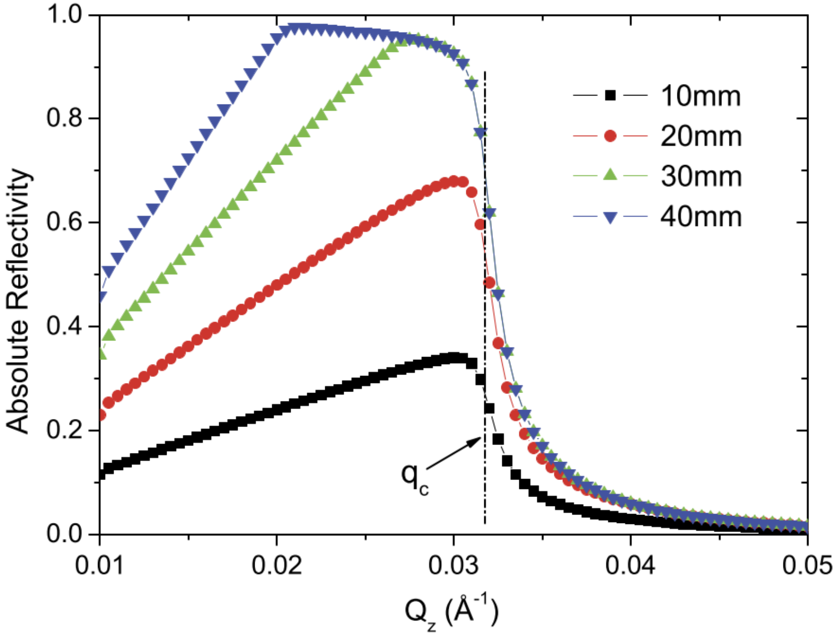
Critical angle

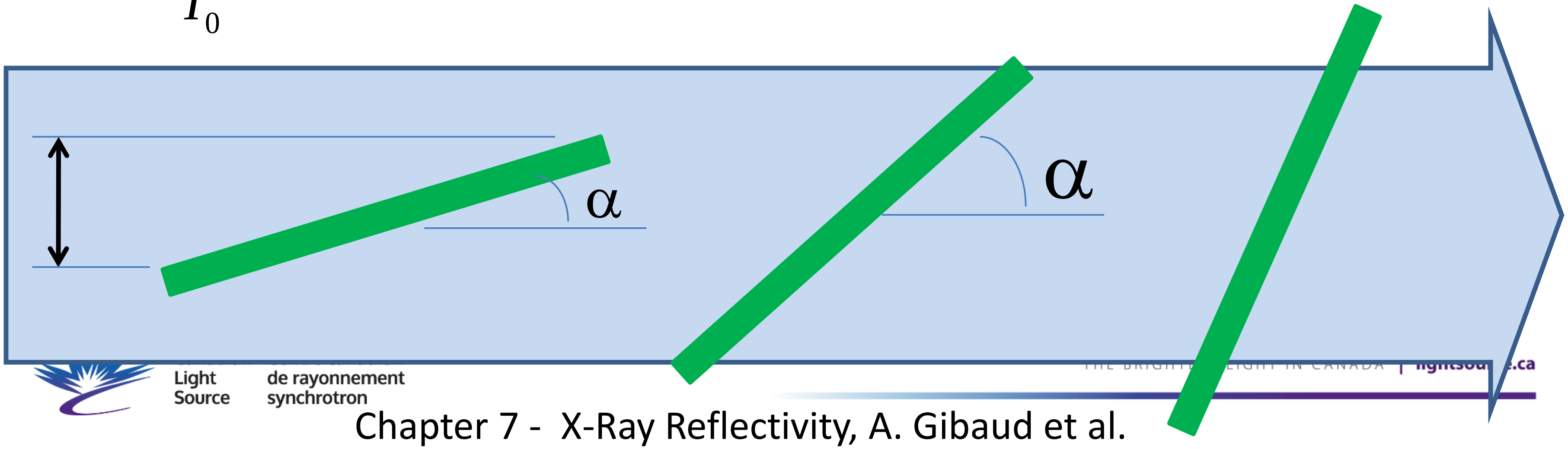
$$\theta_c \sim \lambda\sqrt{\rho}$$

Beam footprint length

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

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

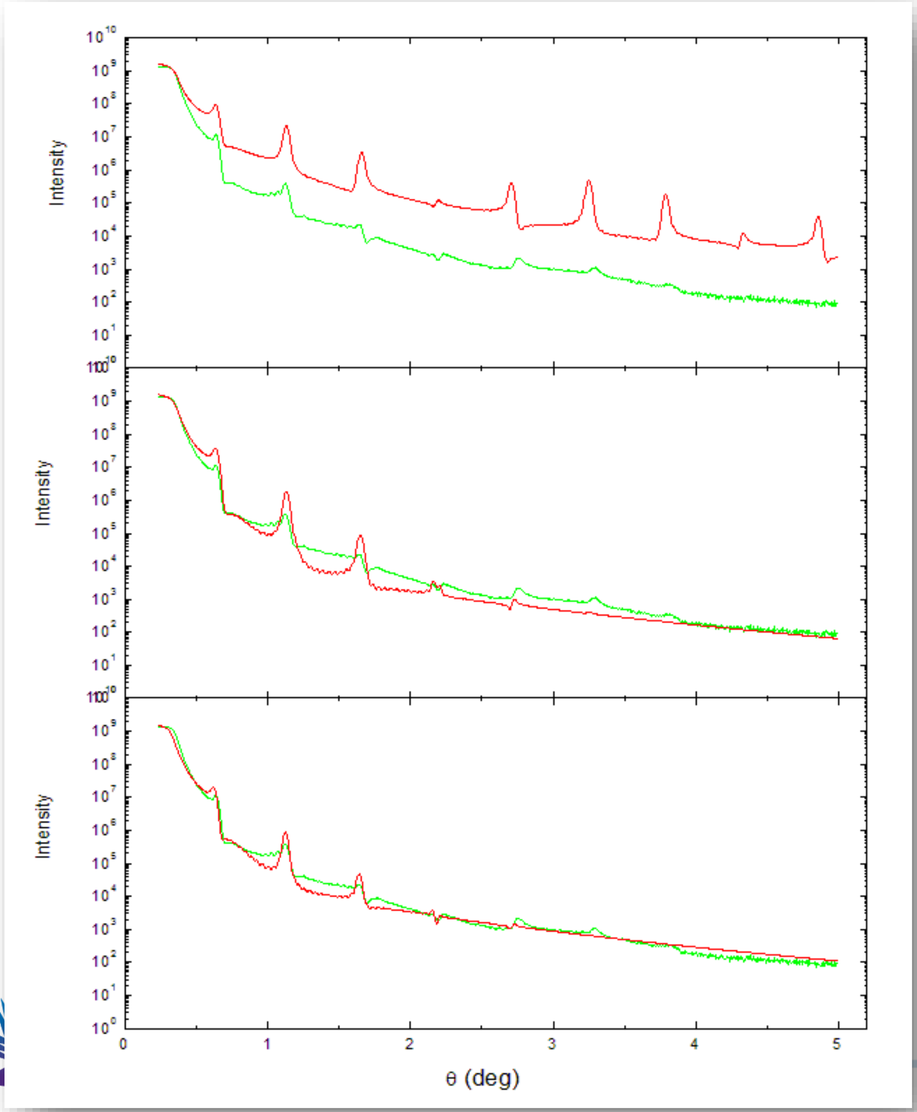




Chapter 7 - X-Ray Reflectivity, A. Gibaud et al.

Small angle X-Ray reflectivity

Fits to the measurement



Smooth interfaces

Rough interfaces

Lower densities
(porous sample?)

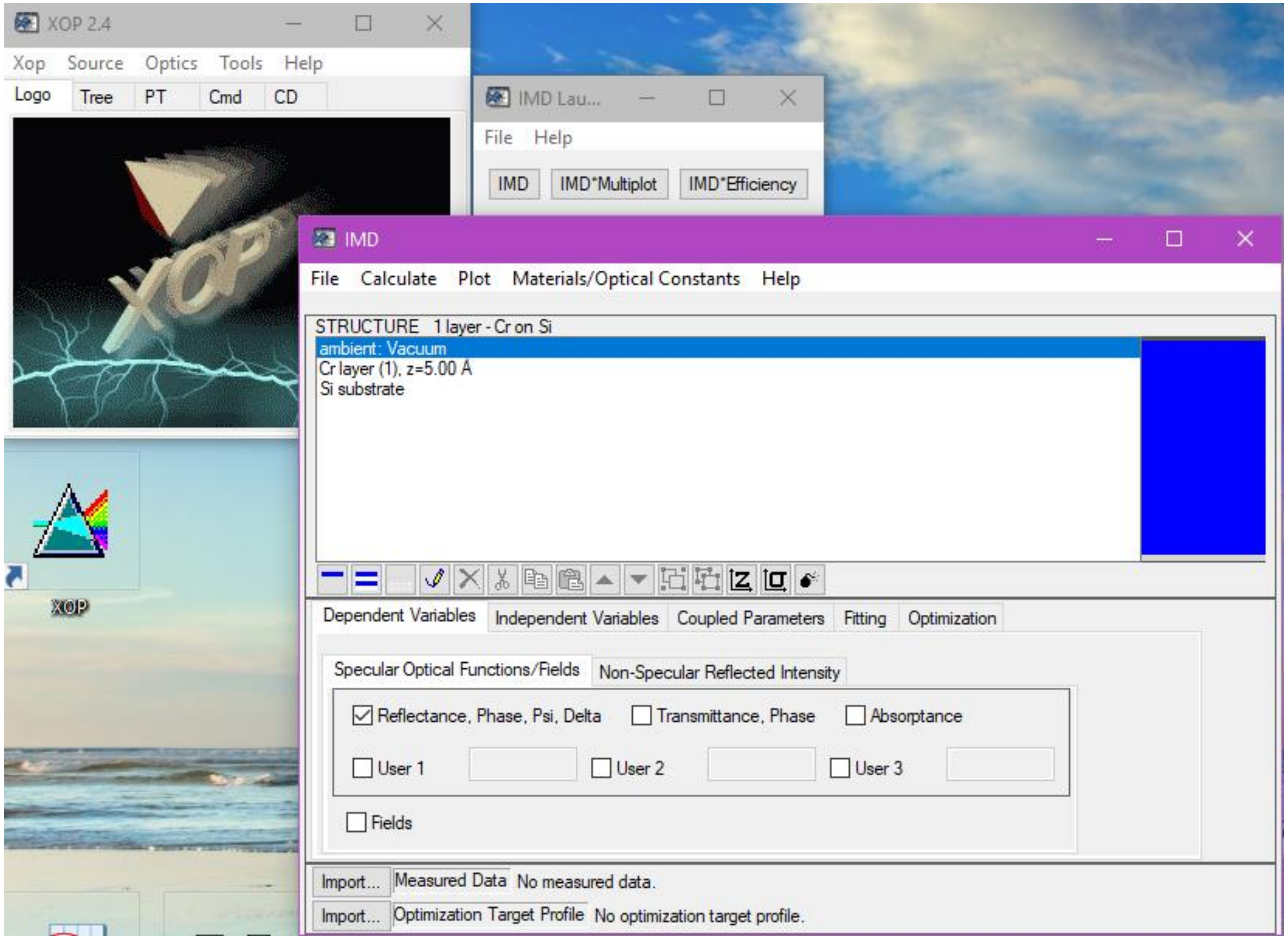
Oxide layer cap!

Programs for simulating and fitting reflectivity

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

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

IMD/XOP to simulate x-ray reflectivity



STRUCTURE 1 layer - Cr on Si
ambient: Vacuum
Cr layer (1), z=5.00 Å
Si substrate

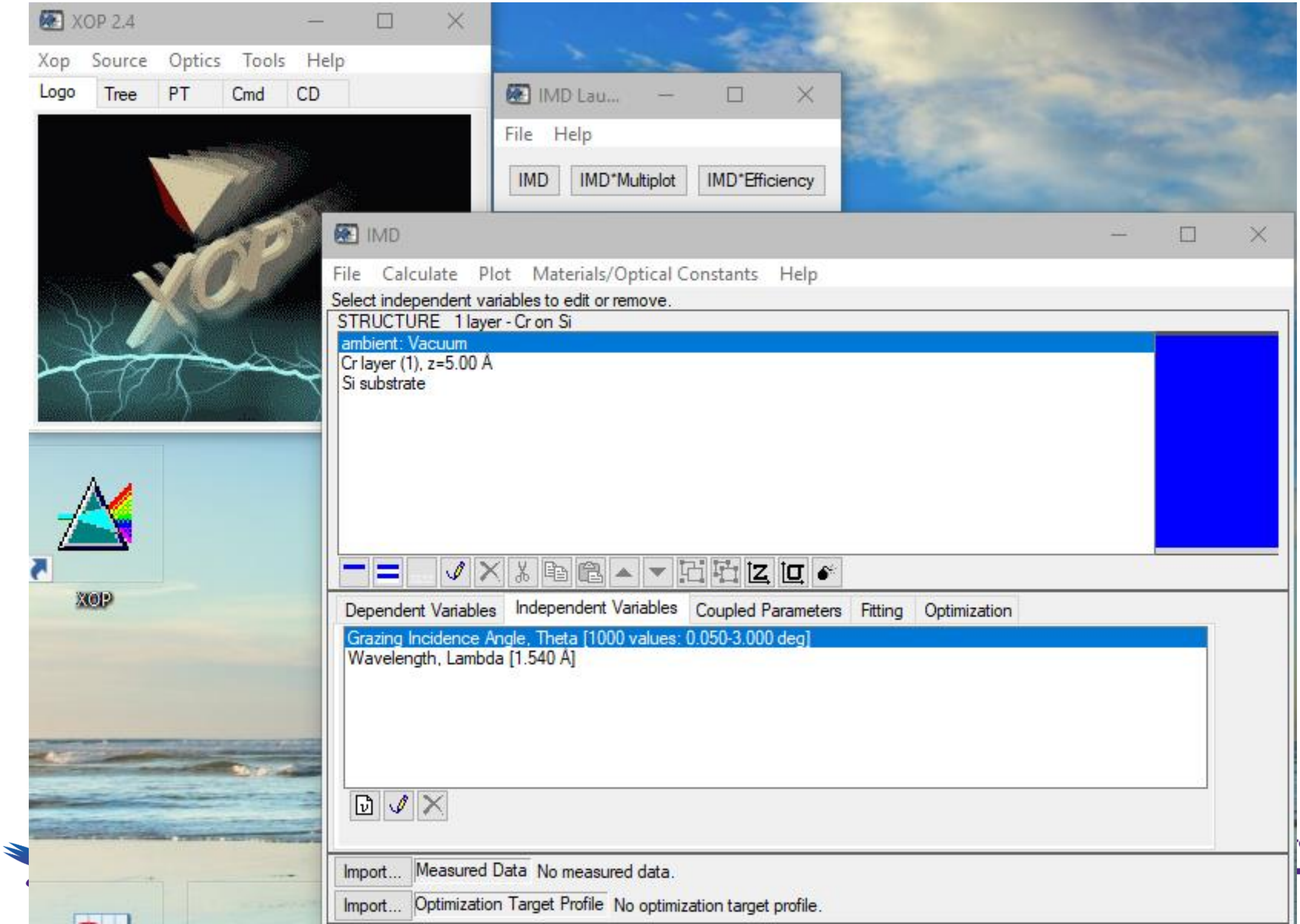
☑ Reflectance, Phase, Psi, Delta ☐ Transmittance, Phase ☐ Absorptance
☐ User 1 ☐ User 2 ☐ User 3
☐ Fields

Measured Data No measured data.
Optimization Target Profile No optimization target profile.

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

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

IMD/XOP to simulate x-ray reflectivity



Select independent variables to edit or remove.

STRUCTURE 1 layer - Cr on Si

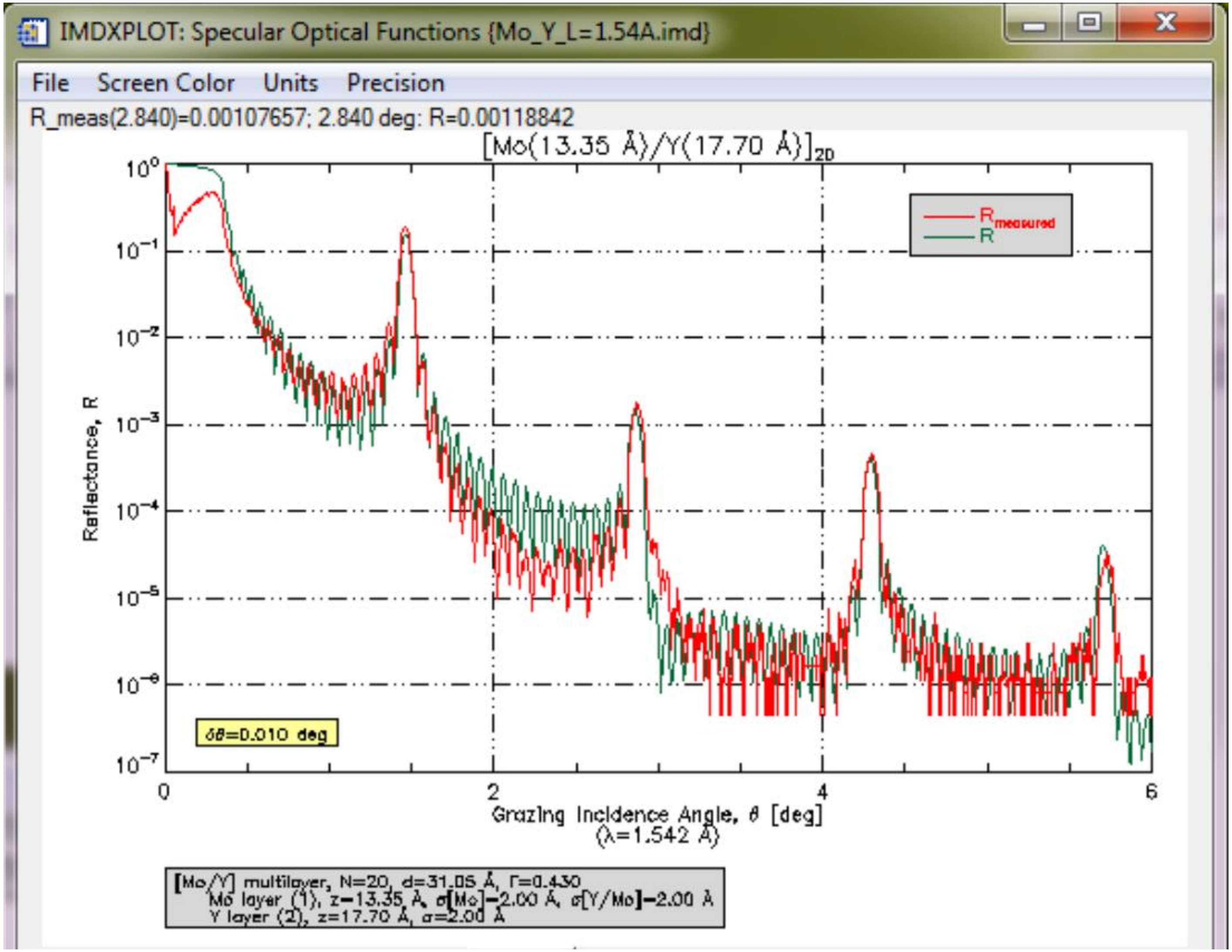
ambient: Vacuum
Cr layer (1), z=5.00 Å
Si substrate

Grazing Incidence Angle, Theta [1000 values: 0.050-3.000 deg]
Wavelength, Lambda [1.540 Å]

Measured Data No measured data.

Optimization Target Profile No optimization target profile.

IMD/XOP to simulate x-ray reflectivity



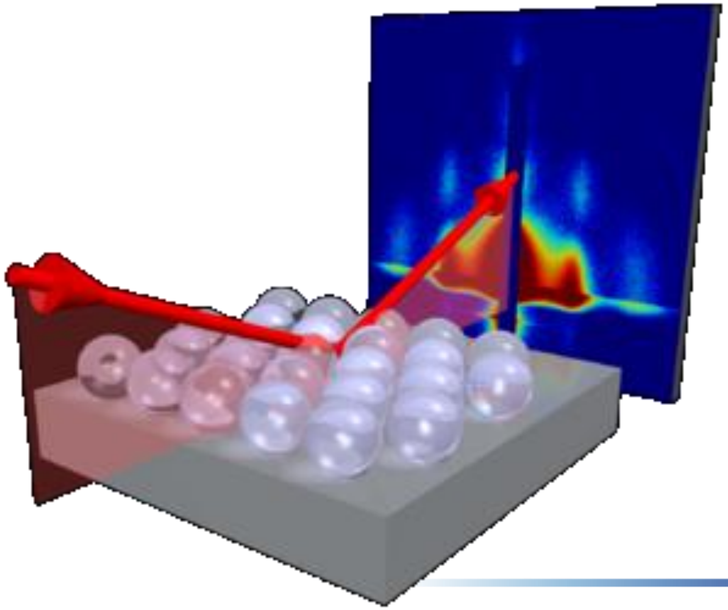
R_meas(2.840)=0.00107657; 2.840 deg: R=0.00118842

[Mo/Y] multilayer, N=20, d=31.05 Å, Γ=0.430
Mo layer (1), z=13.35 Å, σ[Mo]=2.00 Å, σ[Y/Mo]=2.00 Å
Y layer (2), z=17.70 Å, σ=2.00 Å

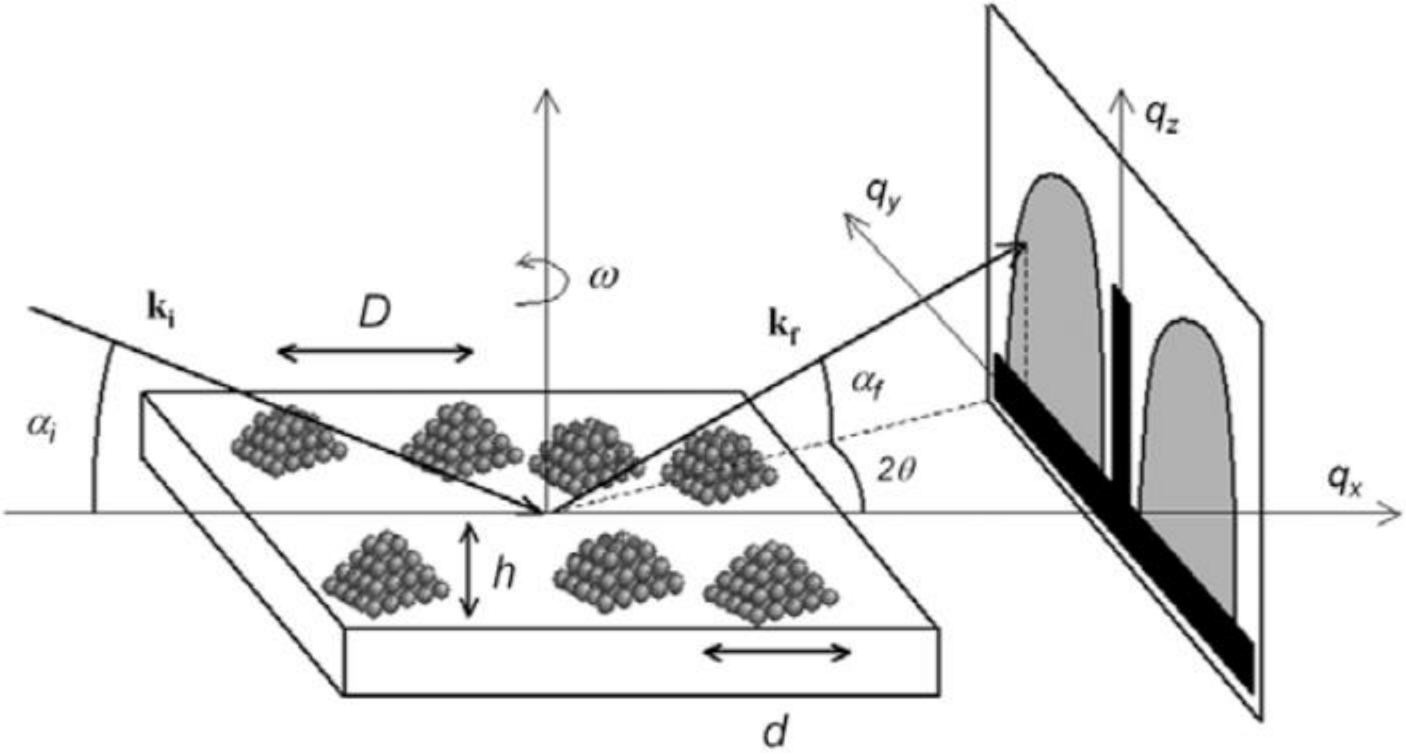
Grazing incidence

Small angle X-ray scattering

GISAXS

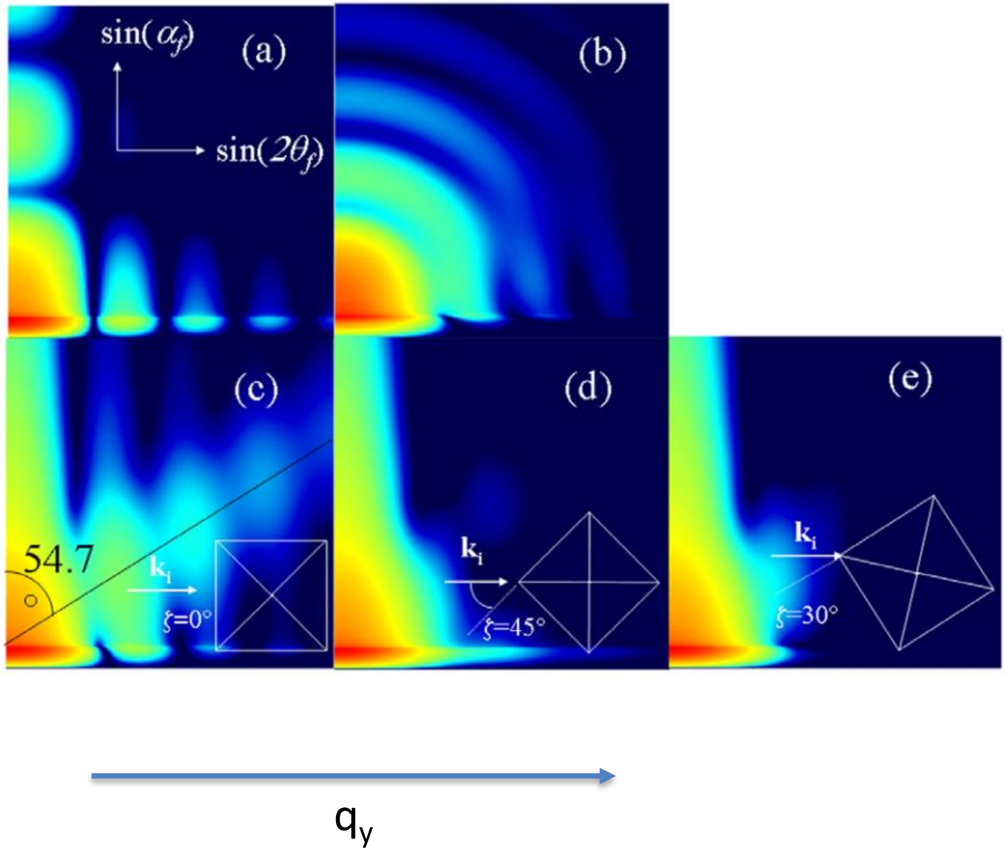


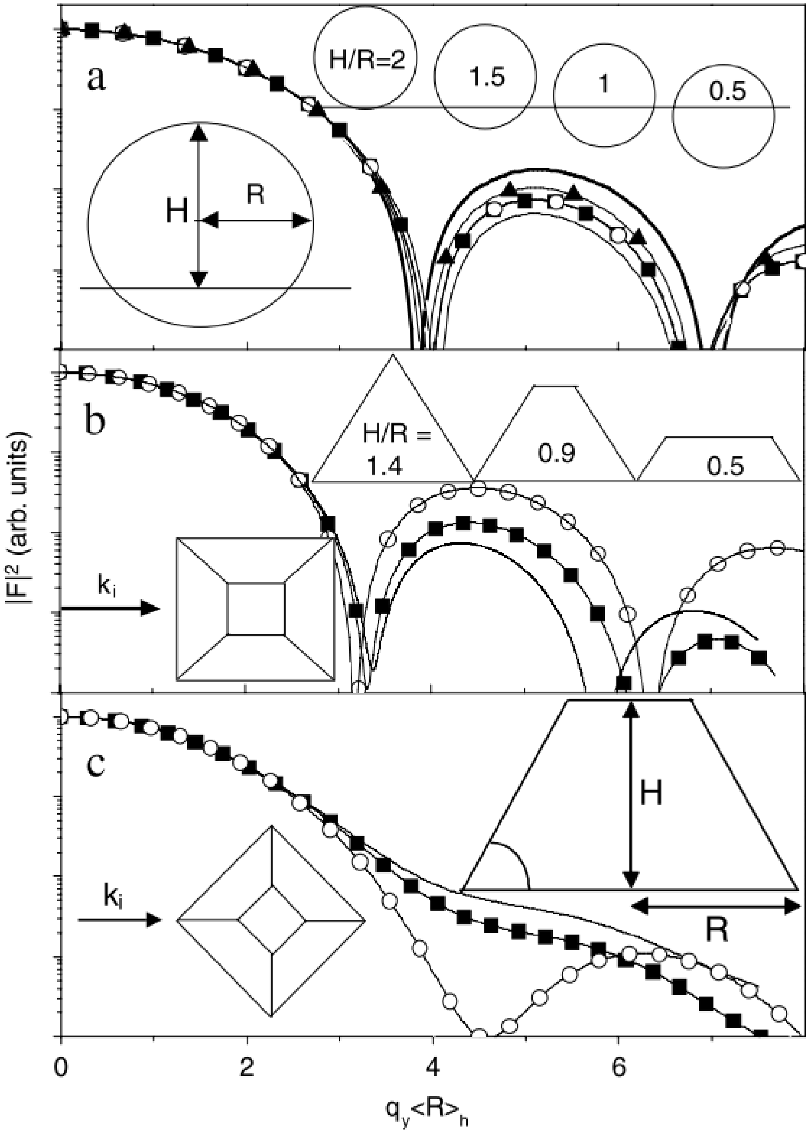
GISAXS



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

GISAXS





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

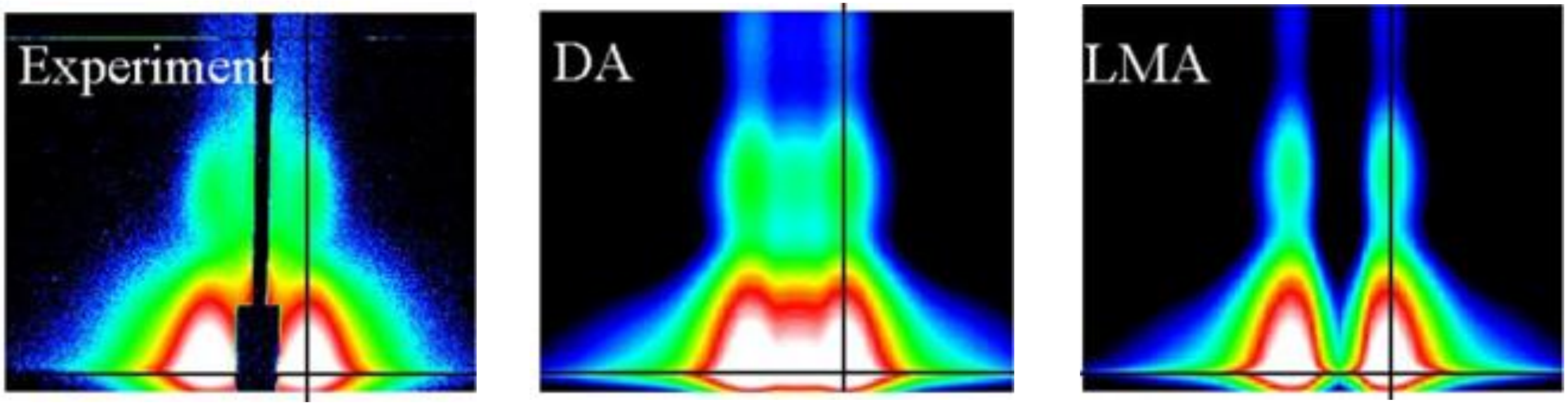
Modelling software

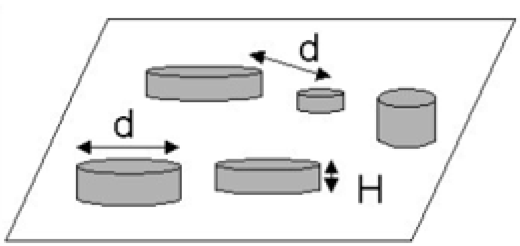
- R. Lazzari, IsGISAXS: A program for grazing-incidence small-angle X-ray scattering analysis of supported islands, J. Appl. Crystallogr. 35 (2002) 406–421.
- http://www.insp.jussieu.fr/oxydes/IsGISAXS/isgisaxs.htm

- 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

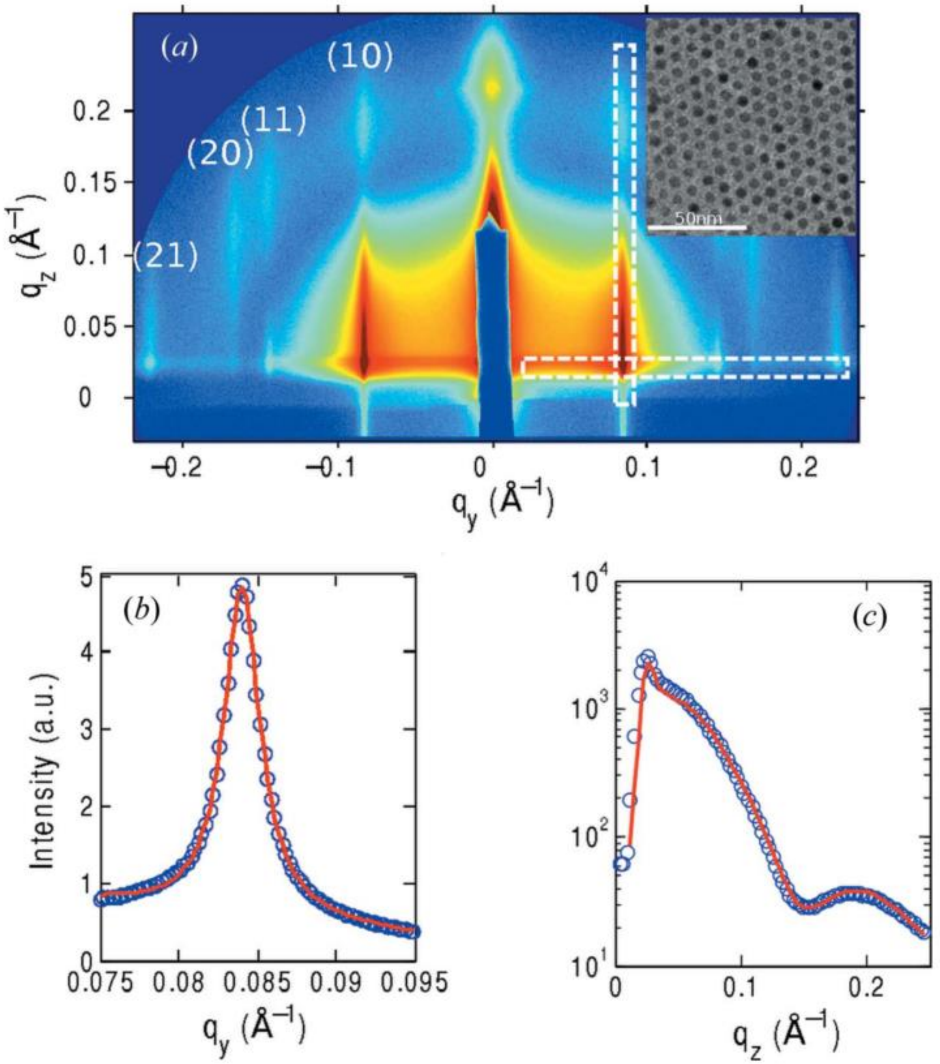




PARAMETERS :
cylinder
D = 20.7 nm
d = 10.2 nm
H = 6.6 nm
σ_R = 1.3
σ_H = 1.1

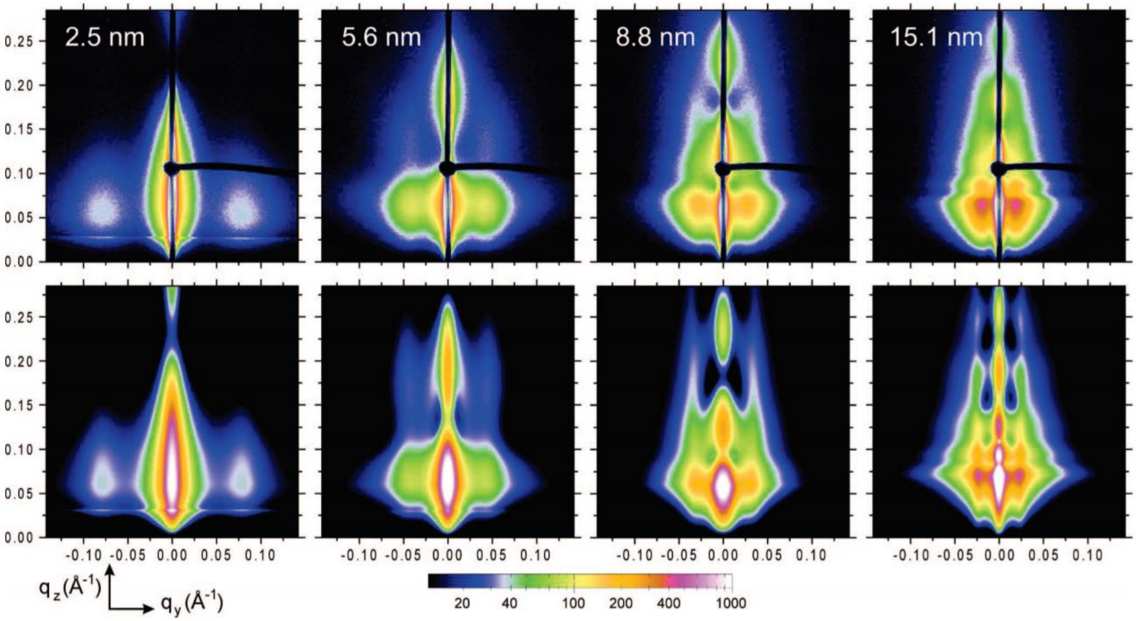
http://www.insp.jussieu.fr/oxydes/IsGISAXS/isgisaxs.htm#Introduction

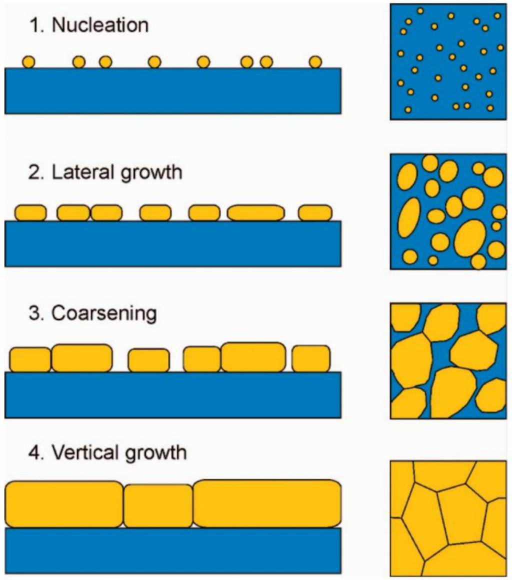
GISAXS

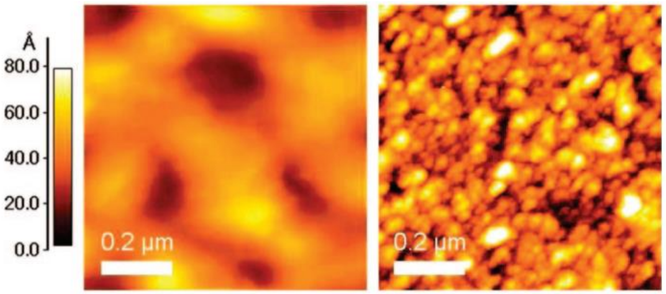


Journal of Applied Crystallography **48**(3): 917-926, 2015

In Situ GISAXS Study of Gold Film Growth on Conducting Polymer Films







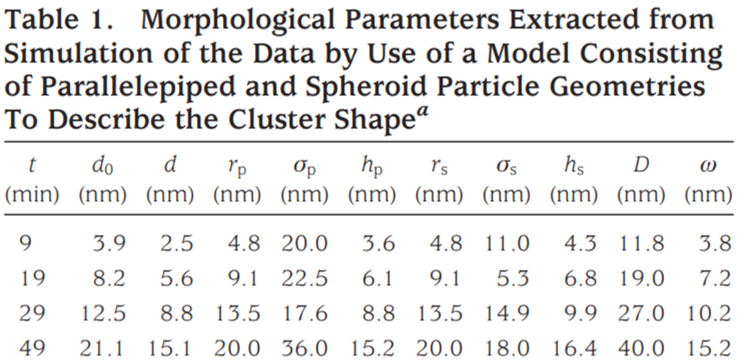
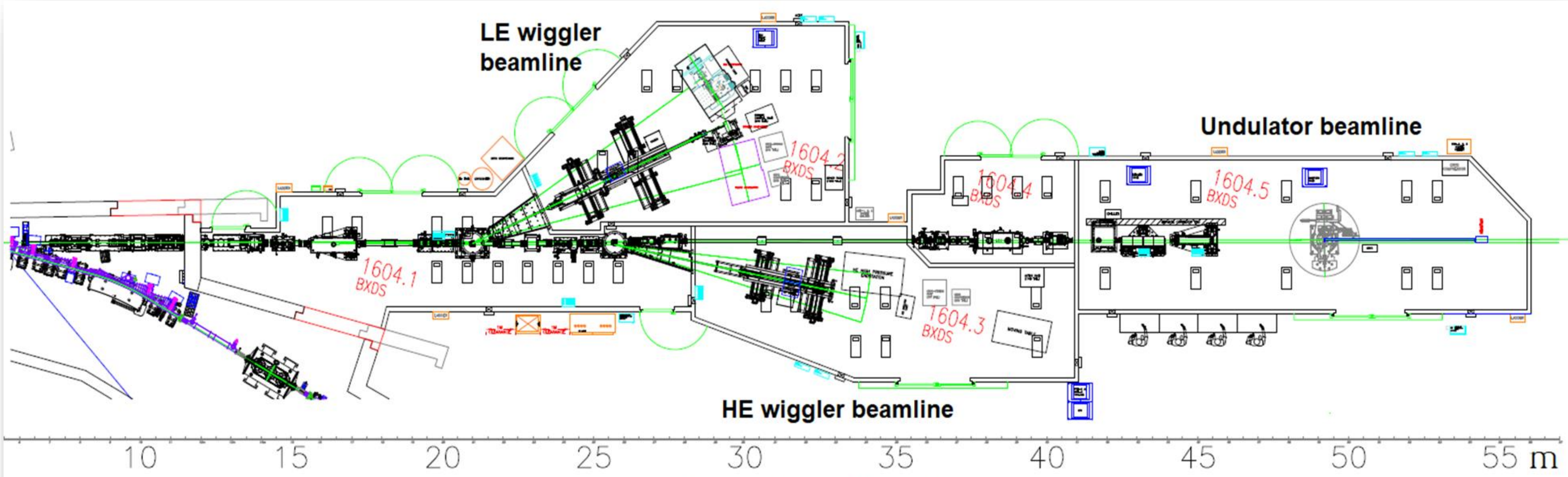


Table 1. Morphological Parameters Extracted from Simulation of the Data by Use of a Model Consisting of Parallelepiped and Spheroid Particle Geometries To Describe the Cluster Shape[a]

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

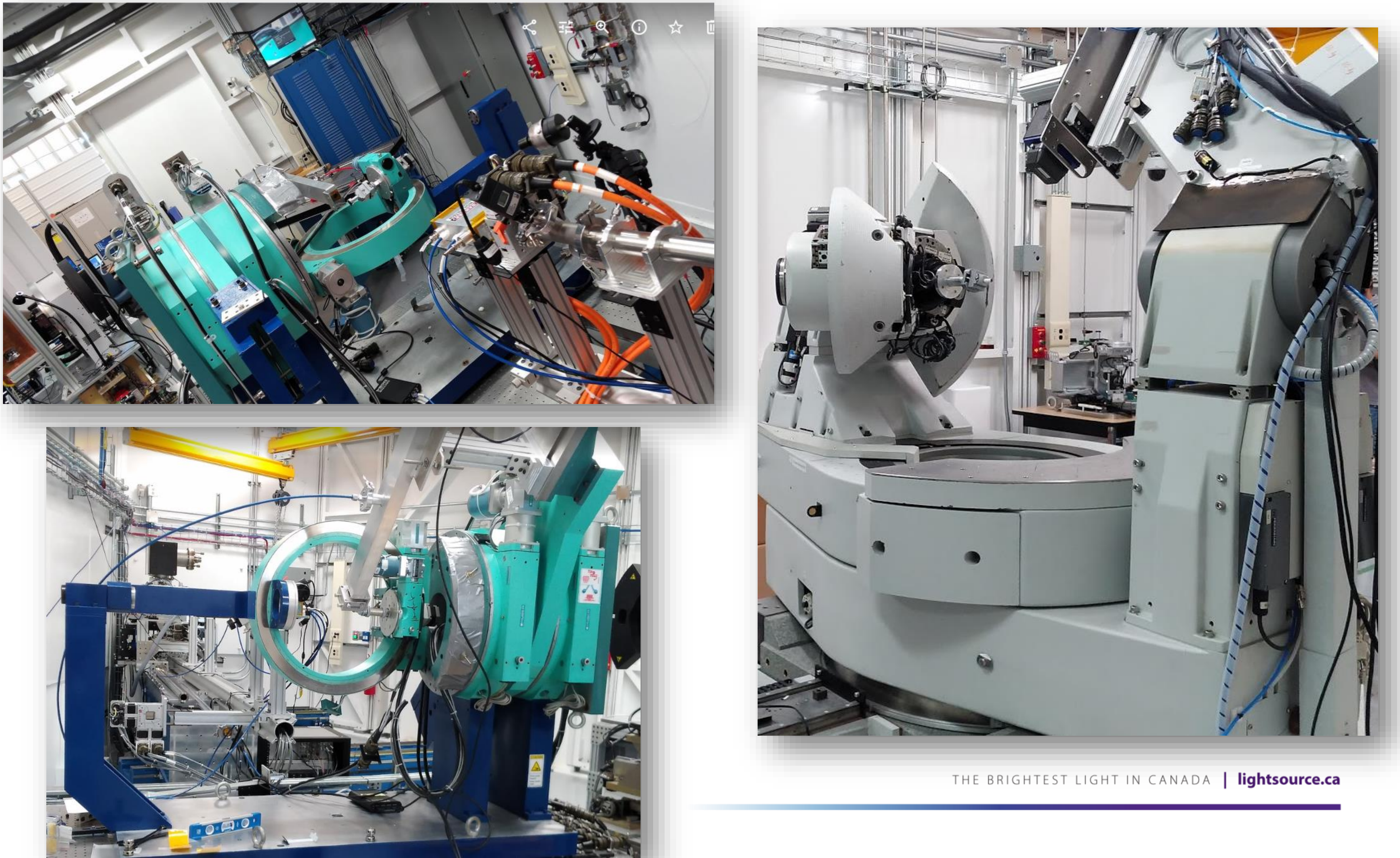
Thin film characterization at the Brockhouse sector



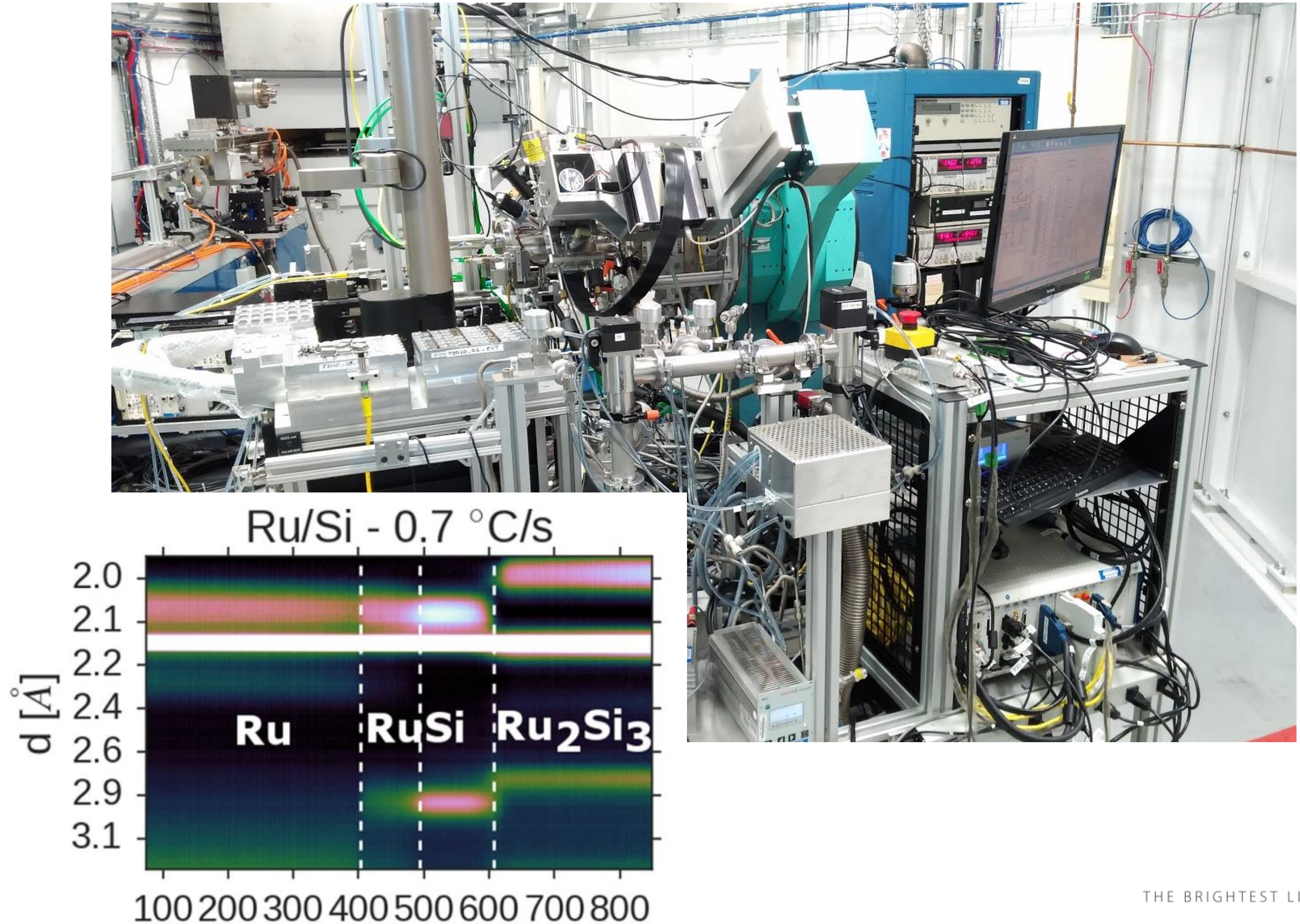
Brockhouse beamlines layout

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

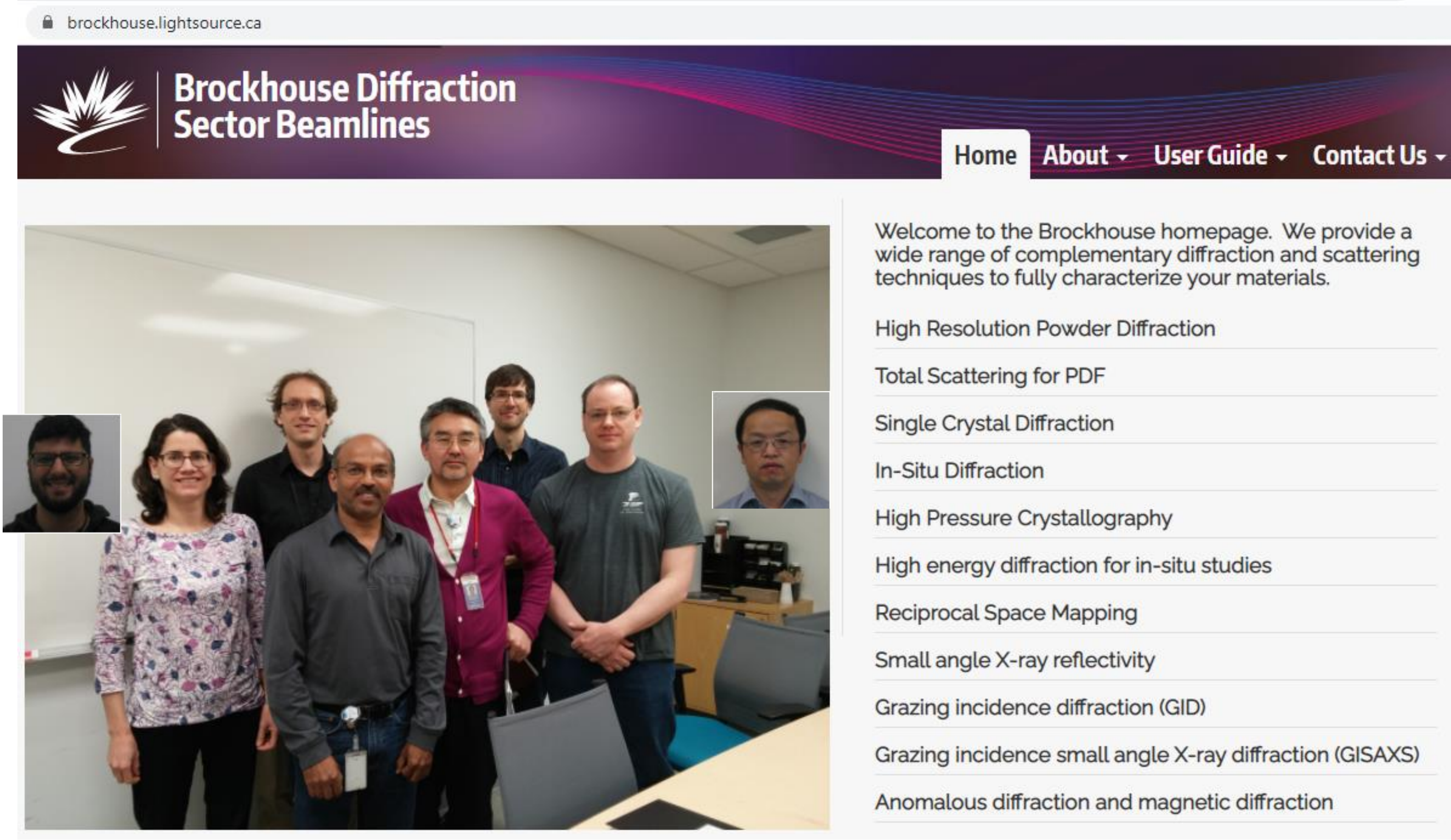
XRD

RTA up to 1000 °C

H_2 or N_2 ultrahigh purity atmosphere

Resistance probe

Roughness probe



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
- Total Scattering for PDF
- Single Crystal Diffraction
- In-Situ Diffraction
- High Pressure Crystallography
- High energy diffraction for in-situ studies
- Reciprocal Space Mapping
- Small angle X-ray reflectivity
- Grazing incidence diffraction (GID)
- Grazing incidence small angle X-ray diffraction (GISAXS)
- 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

Canadian Light Source Centre canadien de rayonnement synchrotron

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