

Methoden moderner Röntgenphysik II

Streuung und Abbildung

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- > Methoden moderner Röntgenphysik II:
Streuung und Abbildung
- > Vorlesung zum Haupt/Masterstudiengang Physik
G. Grübel, M. Martins, W. Wurth
- > Location:
Hörs AP, Physik, Jungiusstrasse
Tuesdays 12.45 – 14.15
Thursdays 8:30 – 10.00
- > Übungen: 2 SWS: Dienstag 14:30 – 16:00 (wenn vereinbart)
SemRm 4



Outline I

- > 03.06 : Small-Angle X-ray Scattering (SAXS)
- > 05.06 : Applications &
A short excursion into Polymeric materials
- > 17.06 : Grazing incidence SAXS (GISAXS)
- > 19.06 : In-situ studies of metal layer growth (M. Schwartzkopf)
- > 24.06 : The polymer-metal interface – application of GISAXS
On the route to organic electronics





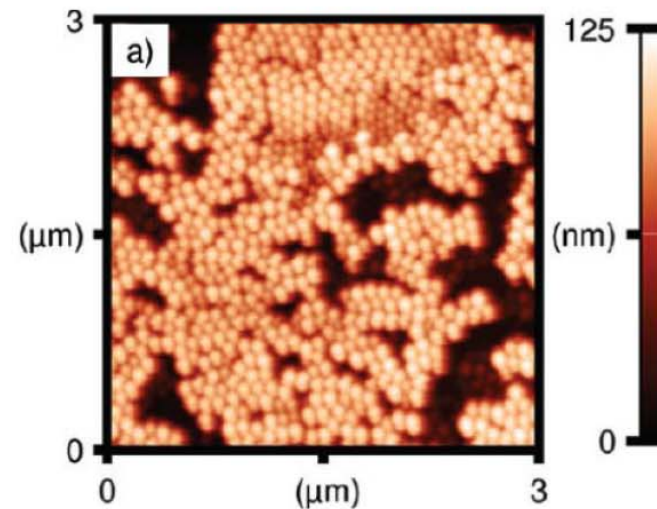
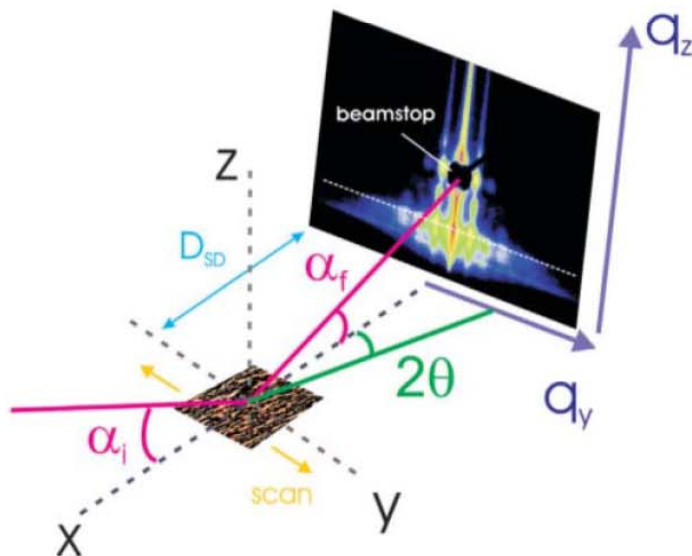
Bachelor-/Masterarbeiten

im Bereich Nanowissenschaften und Materialien für

Wenn Ihr Lust habt, in einem internationalen Team aus Physikern, Chemikern und Informatikern mitzuarbeiten, freuen wir uns auf Euch!

Themenbereiche sind:

- Sputterdeposition von organischen und metallischen Nanostrukturen
- Sprühbeschichtung und Gießtechniken („solution casting“)
- Charakterisierung verschieden hergestellter Nanostrukturen, z.B. mittels Rasterkraftmikroskopie, Ellipsometrie, Kontaktwinkelmessungen und Röntgenstreuung
- Aufbau und Durchführung von Echtzeitexperimenten am Synchrotron
- Simulation und Modellierung von in-situ Streuexperimenten

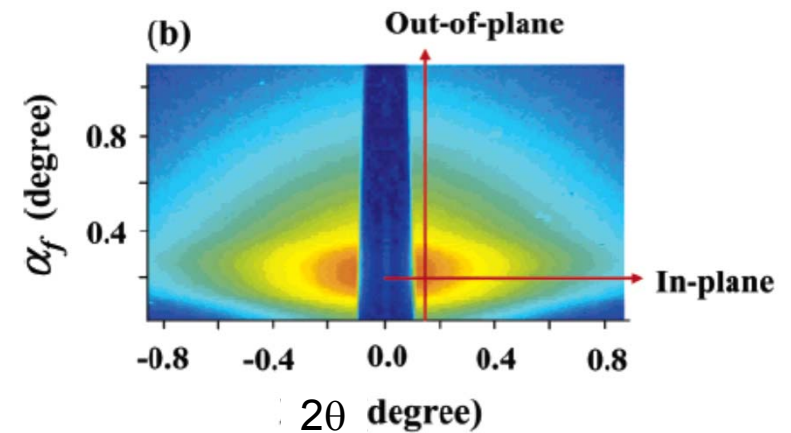
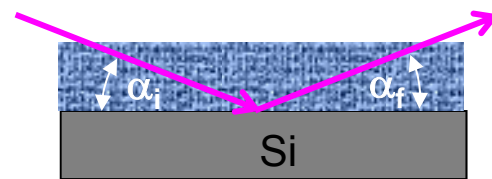
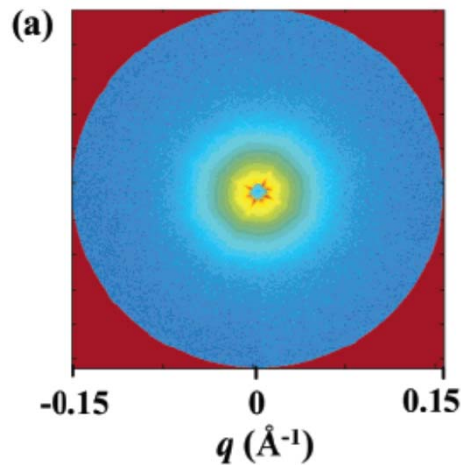
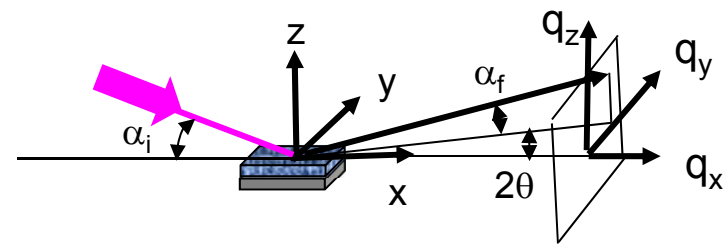
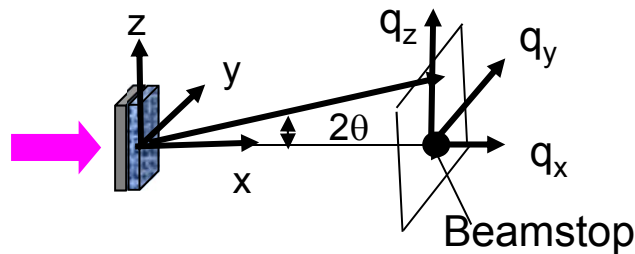


Outline

- ➔ Thin films ➔ Grazing incidence SAXS : A Primer
 - > Nanostructuring by annealing
 - > The highest resolution



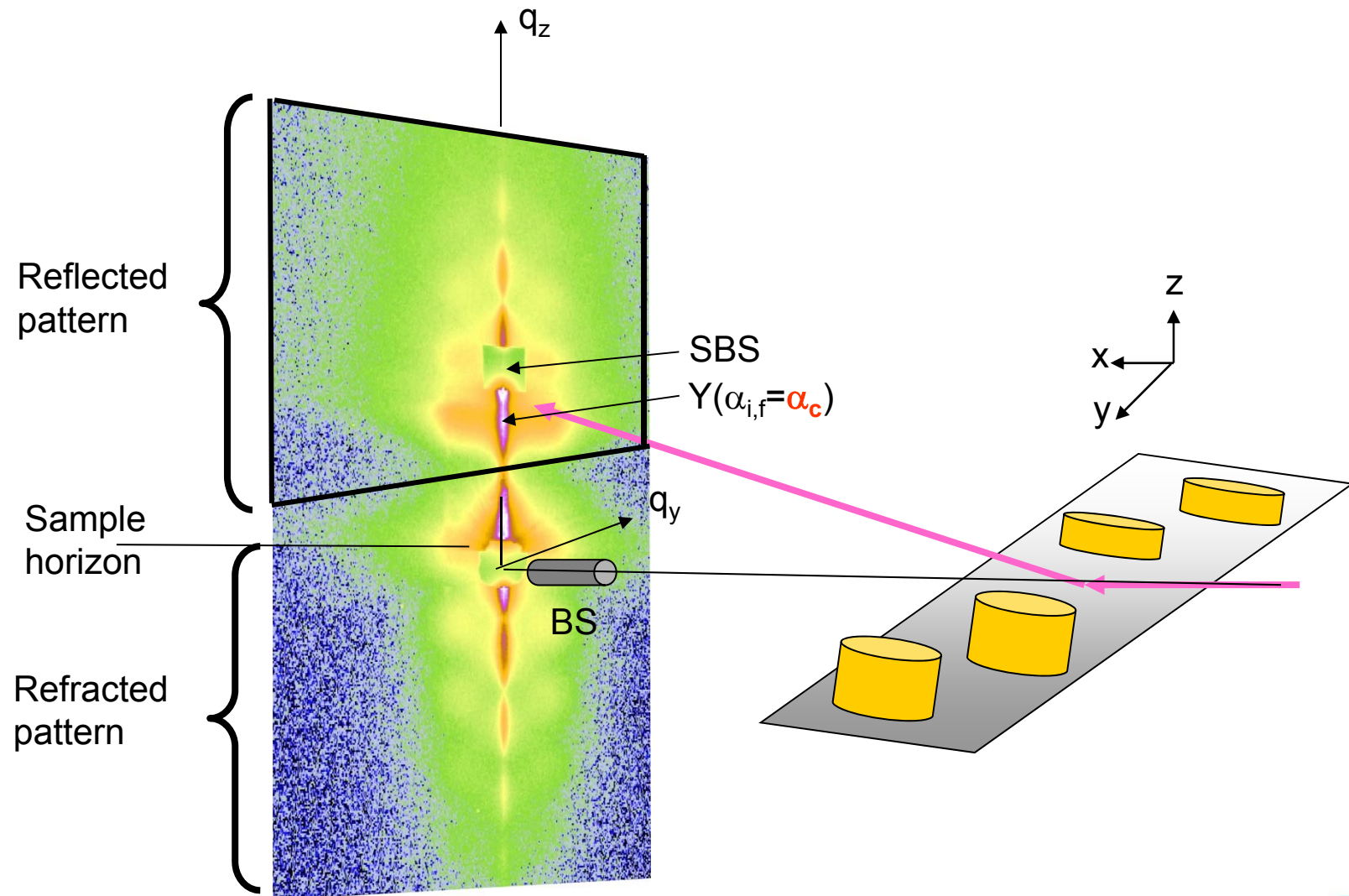
T-SAXS vs. GISAXS



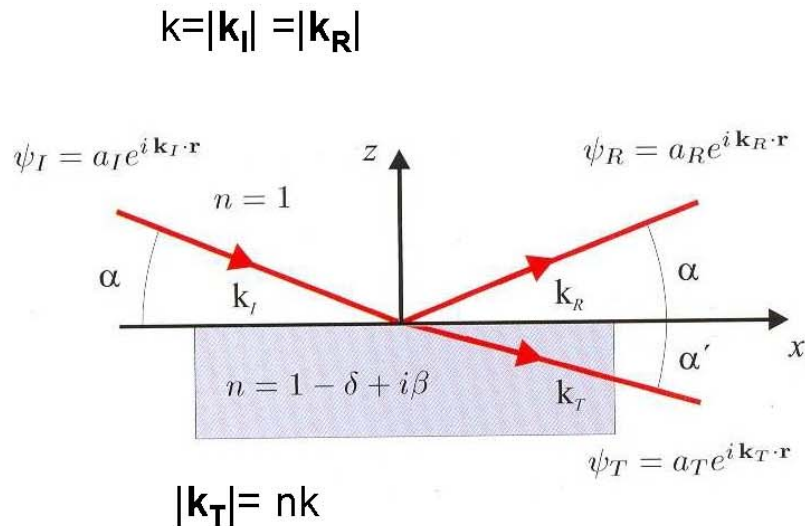
- Easy measurement
- Easy analysis
- In-plane information (q_y, q_z)
- Any possible scattering from substrate
- Transparency of substrate
- High energy

- Strong intensity
- Easy preparation of samples
- Full information (q_x, q_y, q_z)
- Scattering from surface / internal structure
- Scattering from reflected AND transmitted beam
- Refraction effects (DWBA)

Grazing incidence small-angle x-ray scattering



Snell's law and the Fresnel equations (1) (see 10.4.2014)



$$\parallel: a_I k \cos \alpha + a_R k \cos \alpha = a_T (nk) \cos \alpha' \quad (B')$$

$$\perp: -(a_I - a_R) k \sin \alpha = -a_T (nk) \sin \alpha' \quad (B'')$$

$$\cos \alpha = n \cos \alpha' \quad (B' + A)$$

α, α' small: $(\cos z = 1 - z^2/2)$

$$\begin{aligned} \alpha^2 &= \alpha'^2 + 2\delta - 2i\beta \\ &= \alpha'^2 + \alpha_c^2 - 2i\beta \end{aligned} \quad (C)$$

$$a_I - a_R / a_I + a_R = n(\sin \alpha' / \sin \alpha) \approx \alpha' / \alpha \quad (B'' + A)$$

Require that the wave and its derivative is continuous at the interface:

$$a_I + a_R = a_T \quad (A)$$

$$a_I \mathbf{k}_I + a_R \mathbf{k}_R = a_T \mathbf{k}_T \quad (B)$$

Fresnel equations:

$$r = a_R / a_I = (\alpha - \alpha') / (\alpha + \alpha')$$

$$t = a_T / a_I = 2\alpha / (\alpha + \alpha')$$

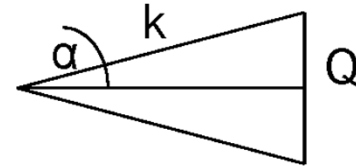
r: reflectivity t: transmittivity

Snell's law and the Fresnel equations (2) (see 10.4.2014)

Note: α' is a complex number

$$\alpha' = \text{Re}(\alpha') + i \text{Im}(\alpha')$$

use wavevector notation:



$$\sin \alpha = (Q/2)/k$$

Consider z-component of transmitted wave:

$$= a_T \exp(iks \sin \alpha' z) \approx a_T \exp(ika' z)$$

$$= a_T \exp(ik \text{Re}(\alpha') z) \cdot \exp(-k \text{Im}(\alpha') z)$$



exponential damping

intensity fall-off: $\exp(-2k \text{Im}(\alpha') z)$

$$Q \equiv 2k \sin \alpha \approx 2ka$$

$$Q_c \equiv 2k \sin \alpha_c \approx 2k\alpha_c$$

use dimensionless units:

$$q \equiv Q/Q_c \approx (2k/Q_c)\alpha$$

$$q' \equiv Q'/Q_c \approx (2k/Q_c)\alpha'$$

1/e penetration depth Λ : $z \ 2k \text{Im}(\alpha') = 1 \quad (z = \Lambda)$

$$q^2 = q'^2 + 1 - 2i b_u$$

(D)

$$\Lambda = 1 / 2k \text{Im}(\alpha')$$

$$b_u = (2k/Q_c)\beta = (4k^2/Q_c^2)\mu/2k = 2k\mu/Q_c^2$$

$$Q_c = 2k\alpha_c = 2k \sqrt{2\delta}$$

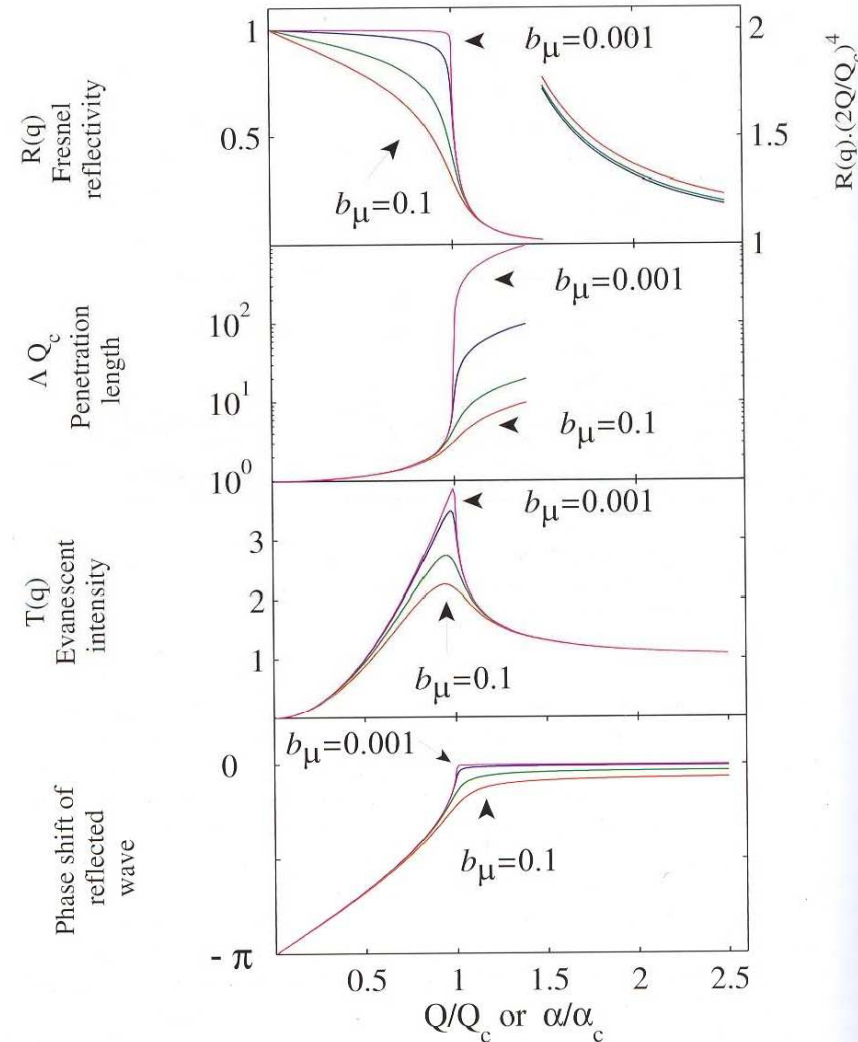
Snell's law and the Fresnel equations (4) (see 10.4.2014)

Fresnel equations:

$q \gg 1$: $R(Q) \sim 1/q^4$,
 $\Lambda \approx \mu^{-1}$,
 $T \approx 1$,
 no phase shift

$q \ll 1$: $R \approx 1$,
 $\Lambda \approx 1/q_c$ small,
 T very small,
 $-\pi$ phase shift

$q=1$: $T(q=1) \approx 4 a_1$



Total reflection – Yoneda peak

> Refractive Index for X-rays $n = 1 - \delta + i\beta$

- Real part: $1 - \delta = 1 - \frac{\lambda^2}{2\pi} r_0 \rho_e$; $\rho_e = NZ$
N = Number density of atoms, Z = Atomic number
- Imaginary Part: $\beta = \frac{\lambda}{4\pi} \mu$

> Snell's Law / Total reflection: $\alpha_c = \sqrt{2\delta} \sim \sqrt{\rho}$

> Maximum of the Fresnel transmission function

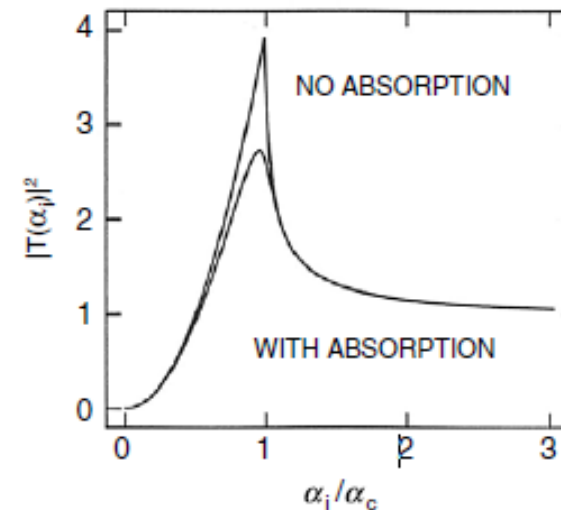
> Electrical field on surface: $2xE_i$

> Increased scattering at surface

> Yoneda peak [Yoneda, 1963]

- Occurs when $\alpha_{i,f} = \alpha_c$

> Material sensitive



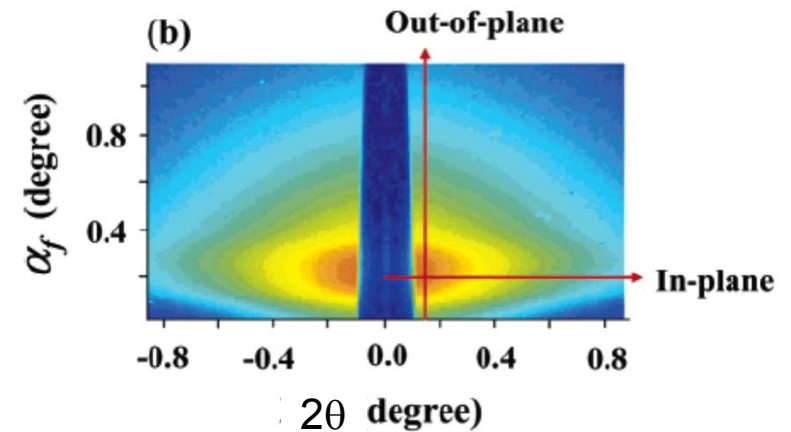
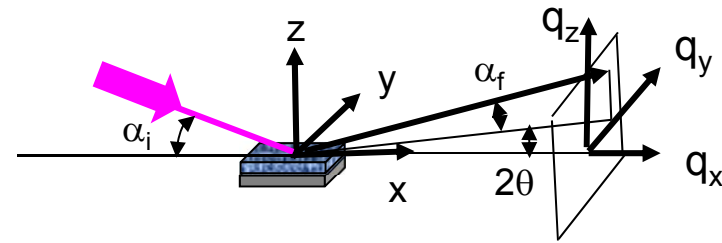
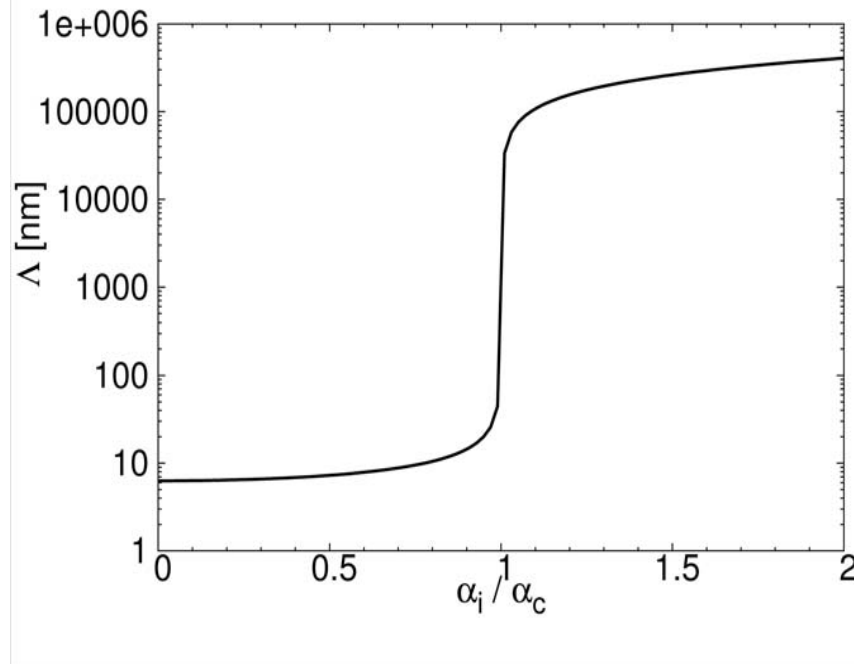
GISAXS: Tuning of penetration depth

> Scattering depth:

$$\Lambda = \frac{\lambda}{\sqrt{2\pi}} * \frac{1}{\sqrt{\sqrt{(\alpha_i^2 - \alpha_c^2)^2 + 4\beta^2} - (\alpha_i^2 - \alpha_c^2)}}$$

> Tune depth sensitivity

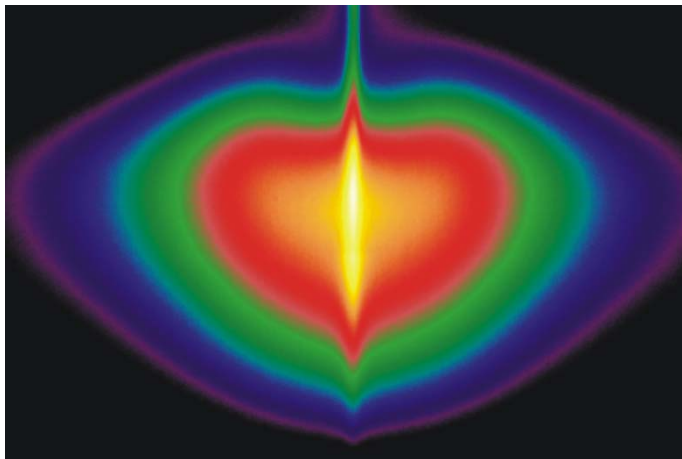
> Exercise: energy variation



- Strong intensity
- Easy preparation of samples
- Full information (q_x, q_y, q_z)
- Scattering from surface / internal structure
- Scattering from reflected AND transmitted beam
- Refraction effects (DWBA)

History

- | | | |
|--------------|--------------------------|--|
| > 1963 | Yoneda | Anomalous Surface Reflection of X-Rays |
| > 1988 | Sinha et al. | surface roughness |
| > 1989 | Levine et. al. | simple qualitative analysis |
| > 1995 | Lairson et. al. | GISAXS with a 1D-Detector |
| > 1995 | Rauscher et. al. | Theory of GISAXS in DWBA |
| > 1996 | Müller-Buschbaum et. al. | GIUSAXS on soft matter: DESY |
| > 1999 | Kegel et. al. | GISAXS on semiconductors quantum dots |
| > 2002 | Lazzari | IsGISAXS |
| > Since 2003 | Müller-B., Roth et. al. | Micro-/nanoGISAXS: ESRF / DESY |



BW4, CCD
Au
d=5nm
t=3h
T=300°C

History

> 1963 Yoneda – anomalous Scattering below α_i

PHYSICAL REVIEW

VOLUME 131, NUMBER 5

1 SEPTEMBER 1963

Anomalous Surface Reflection of X Rays

Y. YONEDA

Department of Applied Physics, Faculty of Engineering, Kyushu University, Fukuoka, Japan

(Received 9 January 1963; revised manuscript received 2 May 1963)

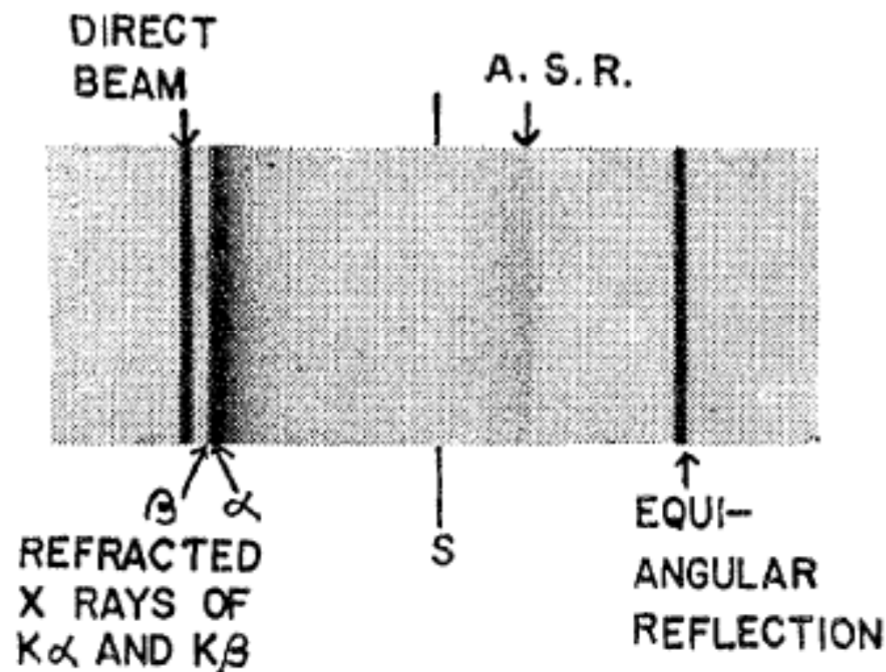


FIG. 2. Photograph of A.S.R. by a glass sample, $\times 2$.

The first successful experiment

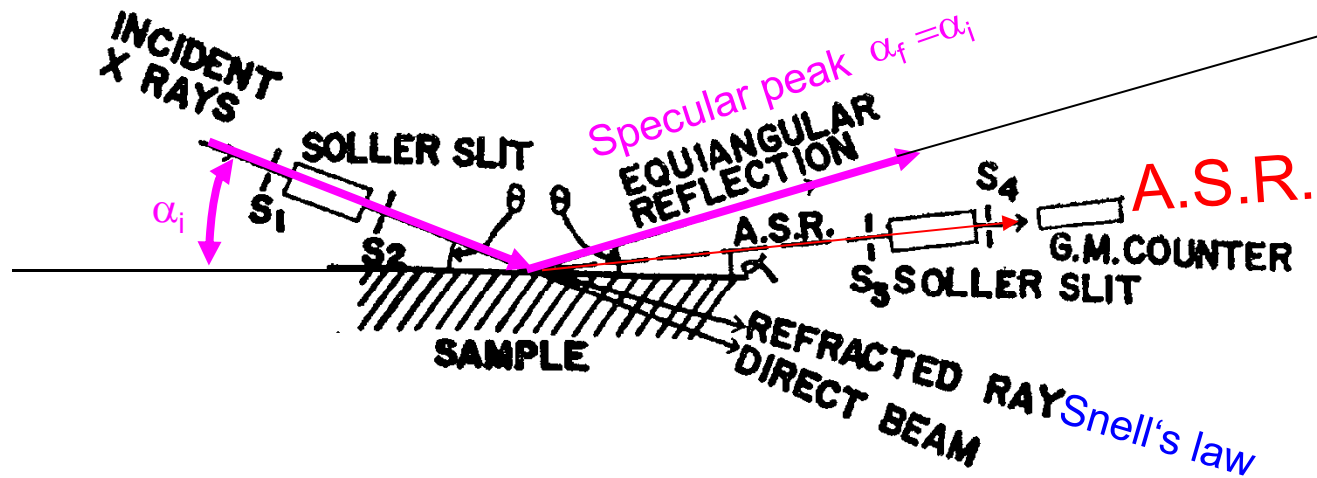


FIG. 1. Schematic view of the experimental arrangement in the incident plane.

Anomalous Surface Reflection
(diffuse scattering)

Au, 20nm-200nm

Si

Intensity between $\alpha_f=0^\circ$ and $\alpha_f=\alpha_i$!!!

Why ?

Refractive index for x-rays

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

real part

$$\delta = \frac{\lambda^2}{2\pi} r_0 \underbrace{NZ}_{\rho_e}$$

Number density of atoms

Atomic number

imaginary part

$$\beta = \frac{\lambda}{4\pi} \mu$$

wavelength

Absorption coefficient

$$e^{-\mu x}$$

(Lambert-Beers law)

	$r_0\rho_e [10^{10}\text{cm}^{-2}]$	$\mu_x [\text{cm}^{-1}]$
Vacuum	0	0
PS (C8H8)n	9.5	4
Si	19.7	85
Au	131.5	4170

$$\alpha_c = \sqrt{2\delta}$$

Critical angle

$$\alpha_c(\text{Si})=0.2^\circ$$

$$\alpha_c(\text{Au})=0.5^\circ$$

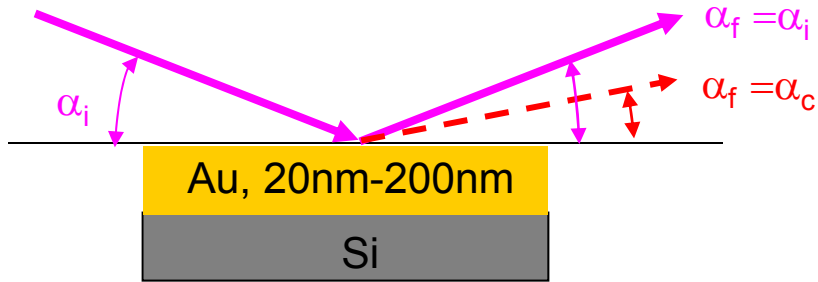
$$\lambda \approx 1\text{\AA} \Rightarrow \delta \sim 10^{-7} \dots 10^{-6}$$

Very small!

Matter: $|n(\text{X-rays})| < 1$ optically less dense than vacuum (remember Bragg's law)

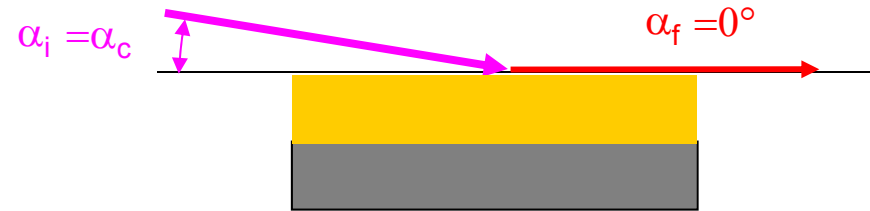


Origin of intensity at α_c

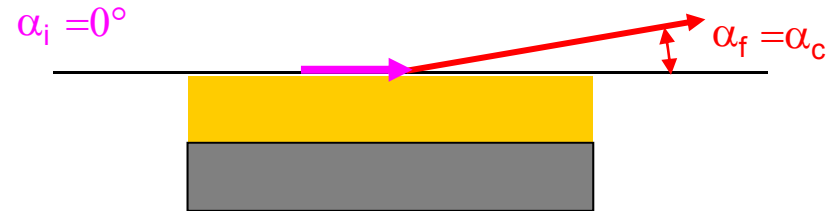


$\alpha_f(\text{Au}) = 0.56^\circ = \alpha_c(\text{Au}, 1.8\text{\AA})$

Total external reflection

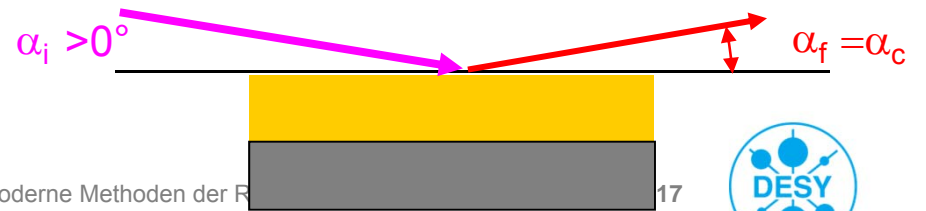


Reciprocity theorem & critical angle



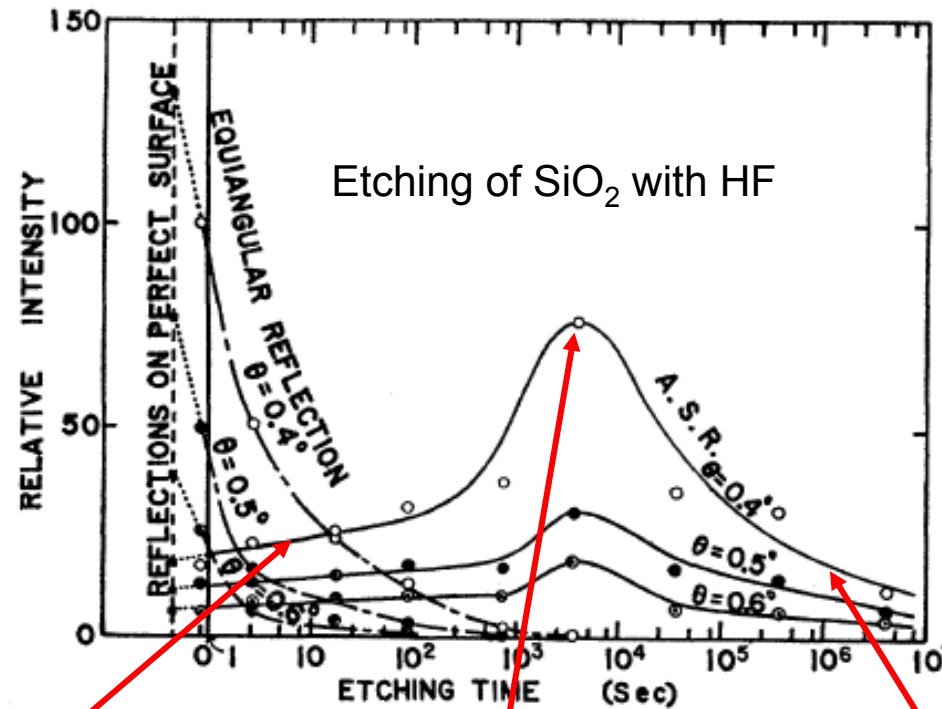
must stem from wave parallel to surface

Yoneda



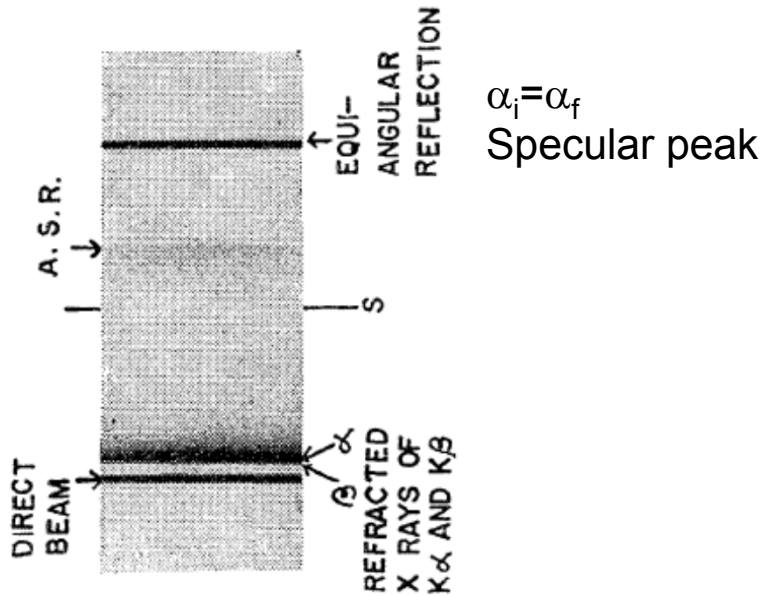
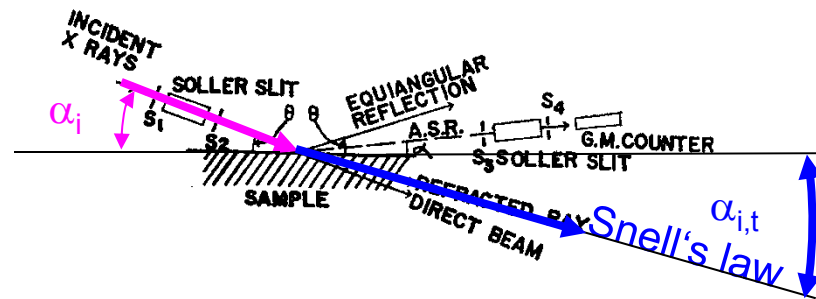
Hint: Roughness of the sample

Yoneda peak = Scattering effect!

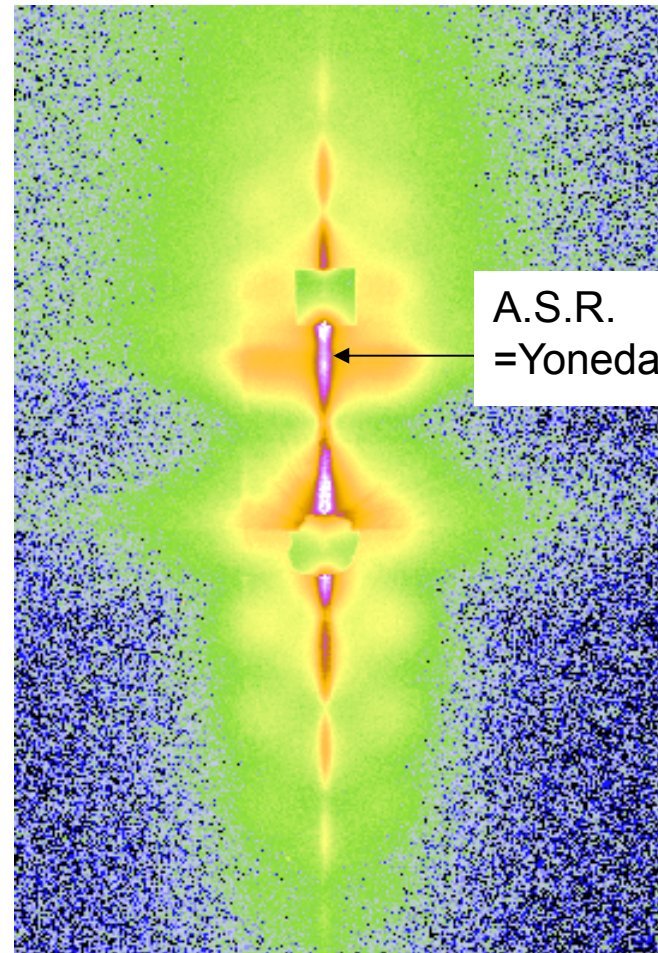


Basically the same

1963



today



Theory

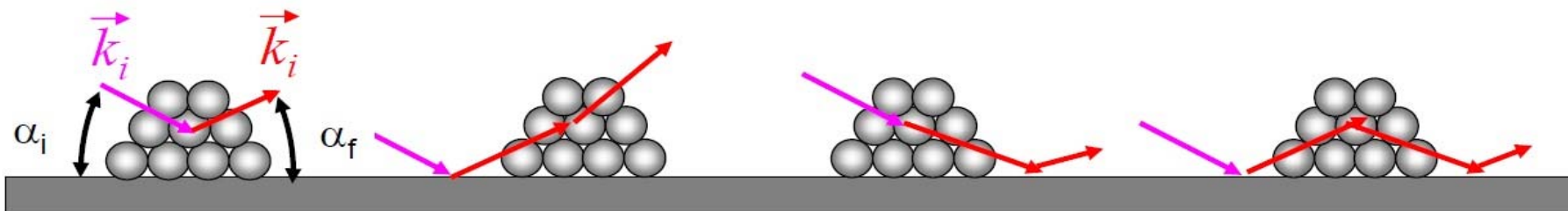
➤ Distorted-wave Born approximation

Term 1

Term 2

Term 3

Term 4



$$\frac{d\sigma}{d\Omega} \propto \left| \underbrace{P(q_y, k_{fz} - k_{iz})}_{\text{Born term}} + R(\alpha_i)P(q_y, k_{fz} + k_{iz}) + R(\alpha_f)P(q_y, -k_{fz} - k_{iz}) + R(\alpha_i)R(\alpha_f)P(q_y, -k_{fz} + k_{iz}) \right|^2$$

Born term

with $P(\vec{q}) = \int_V \exp(i\vec{q}\vec{r}) d^3r$

- coherent interference between four waves along α_f
- each term weighted with the Fresnel coefficients
- cross section just depends on q_y and q_z

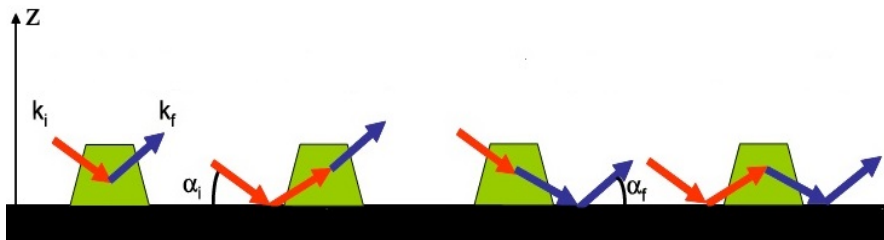


Theory - Simulation

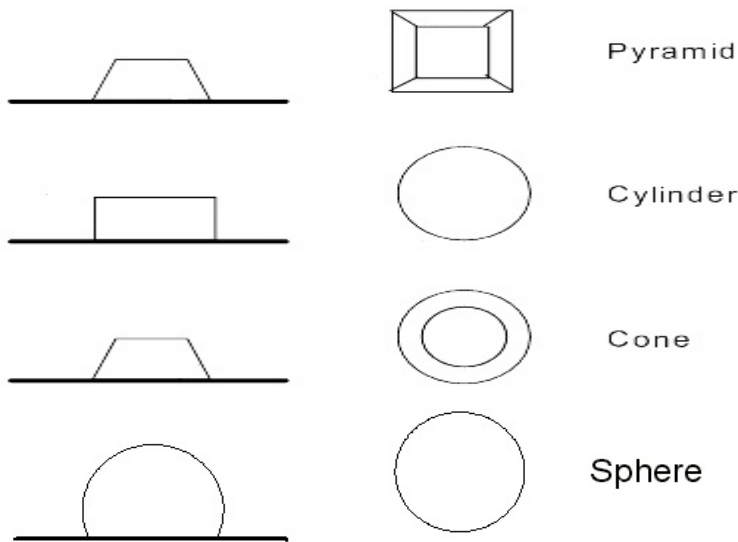
> Cross section (particle form factor * interference function)

> $I(q_y, q_z) = c * P(q_y, q_z) * S(q_y)$

Particle form factor: multiple scattering



- Shape, Size, Orientation, Distribution

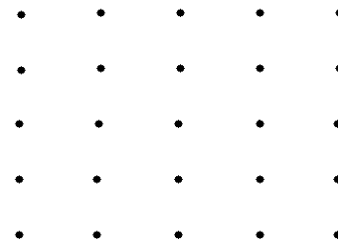


Interference function

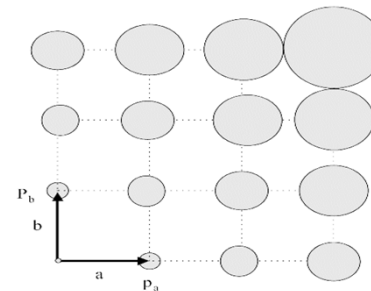
Three main cases

- 1) Disordered lattice
- pair correlation function

- 2) Regular bidimensional lattice

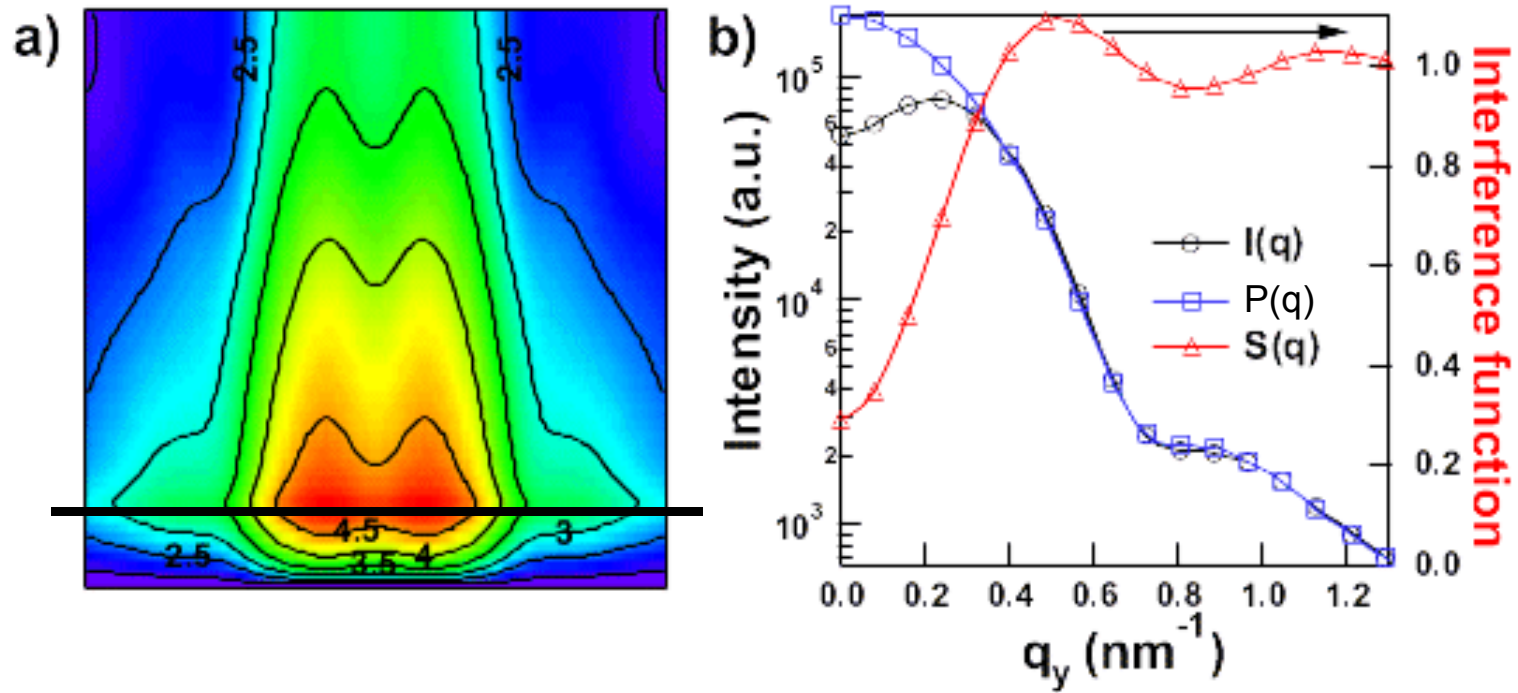


- 3) Bidimensional paracrystal

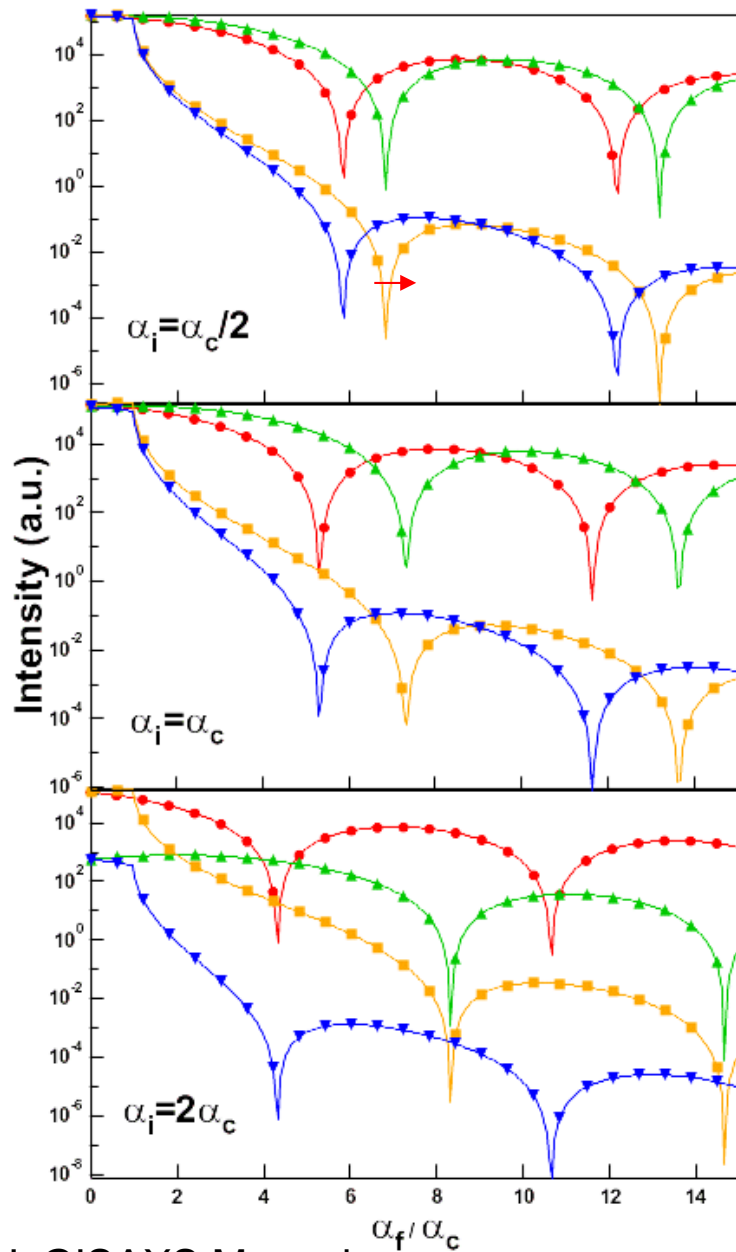


Simulations: IsGISAXS (R. Lazzari)

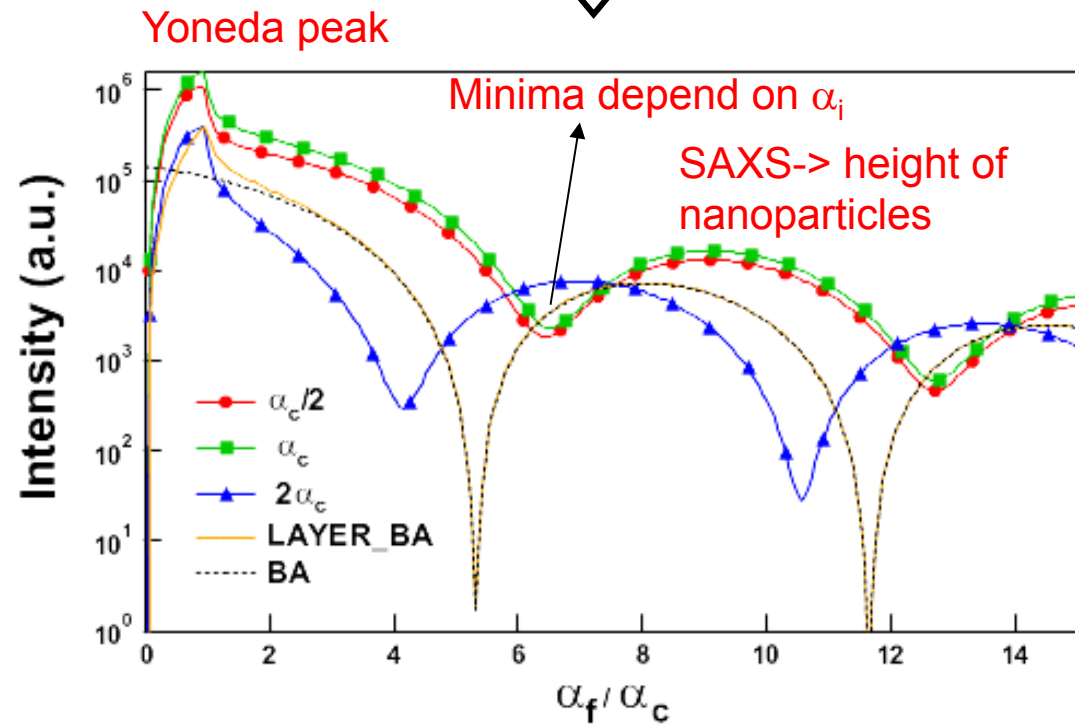
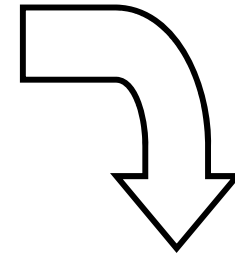
$$I(q_y, q_z) = c P(q_y, q_z) \times S(q_y)$$



DWBA – results

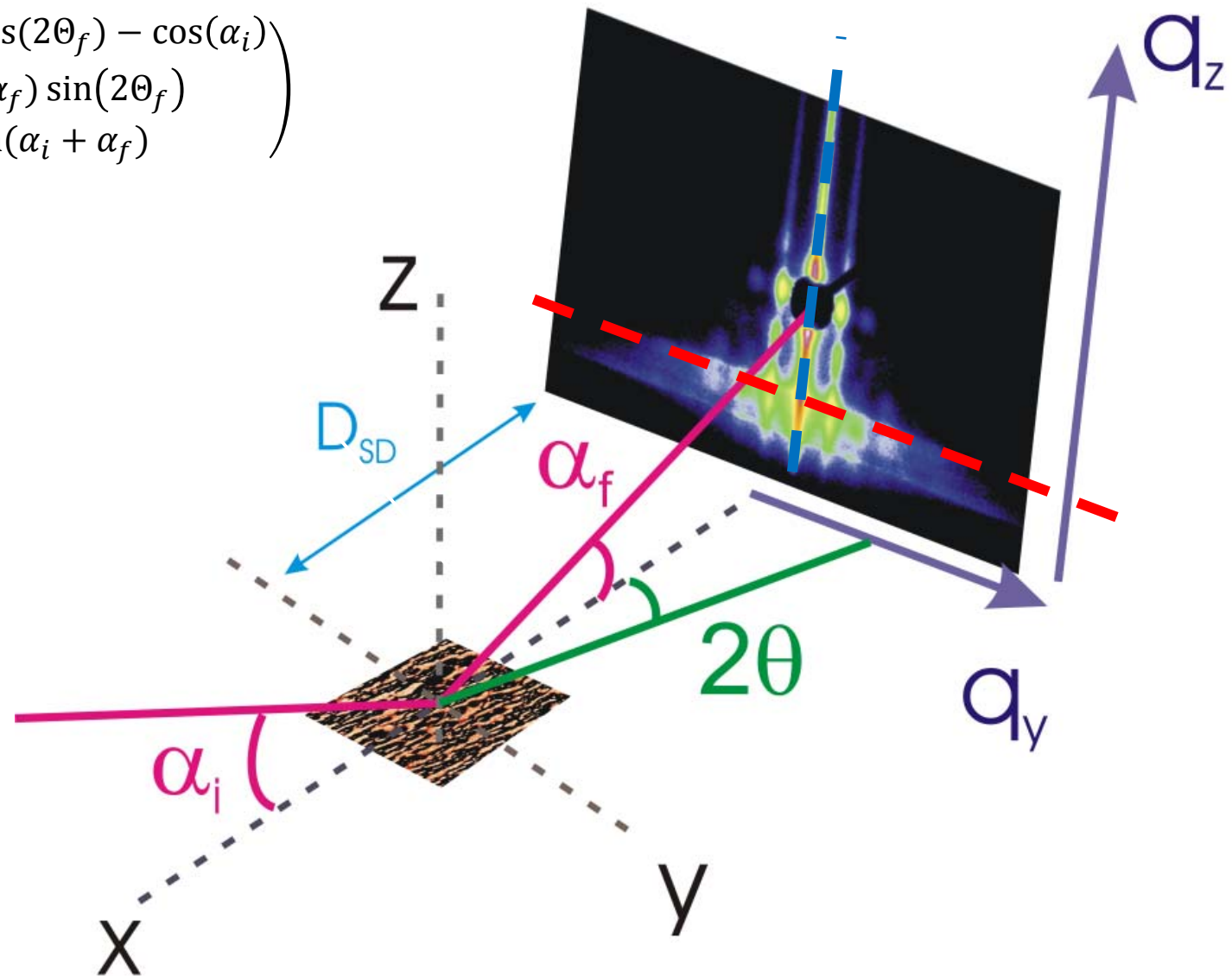


- Term 1
- Term 2
- Term 3
- Term 4

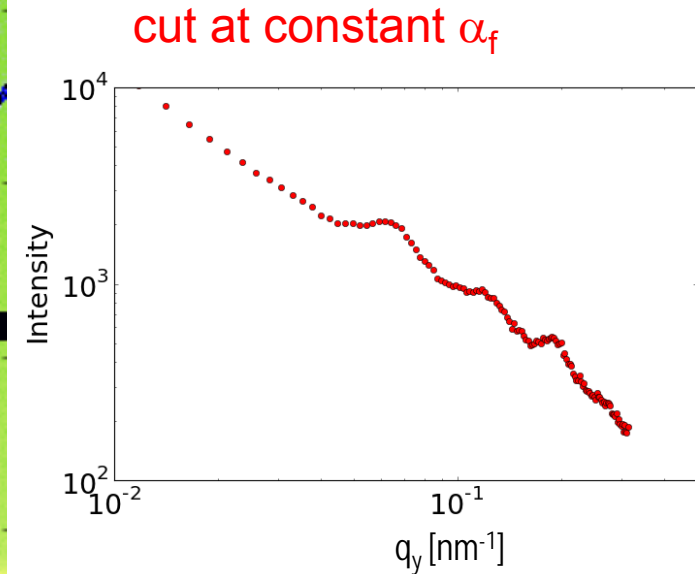
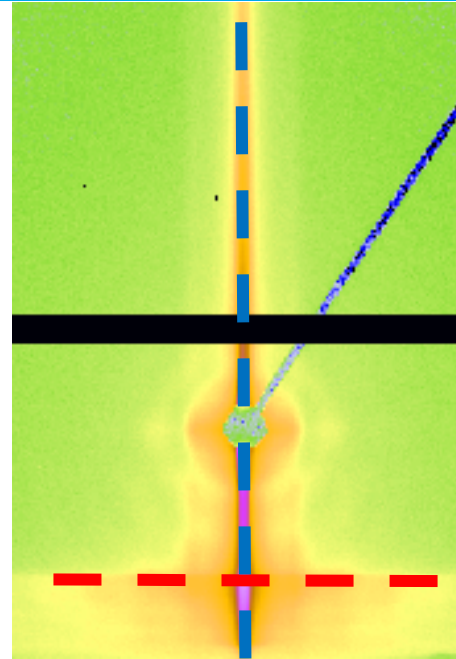
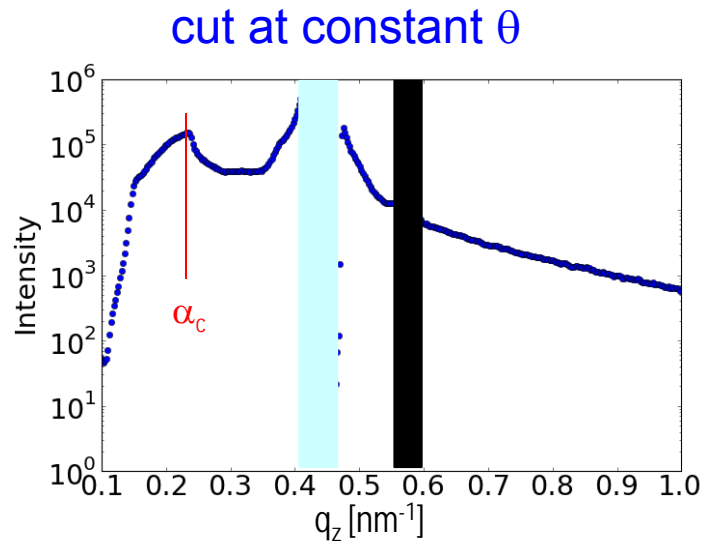


Grazing incidence small-angle x-ray scattering

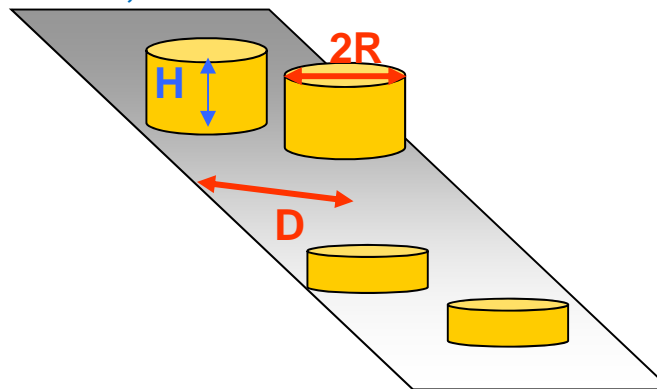
$$\vec{q} = \frac{2\pi}{\lambda} \begin{pmatrix} \cos(\alpha_f) \cos(2\theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f) \sin(2\theta_f) \\ \sin(\alpha_i + \alpha_f) \end{pmatrix}$$



GISAXS – A Primer



Correlation perpendicular to surface,
e.g. height of clusters, roughness,
layer thickness



In-plane structures, e.g.
distances D , Radius R

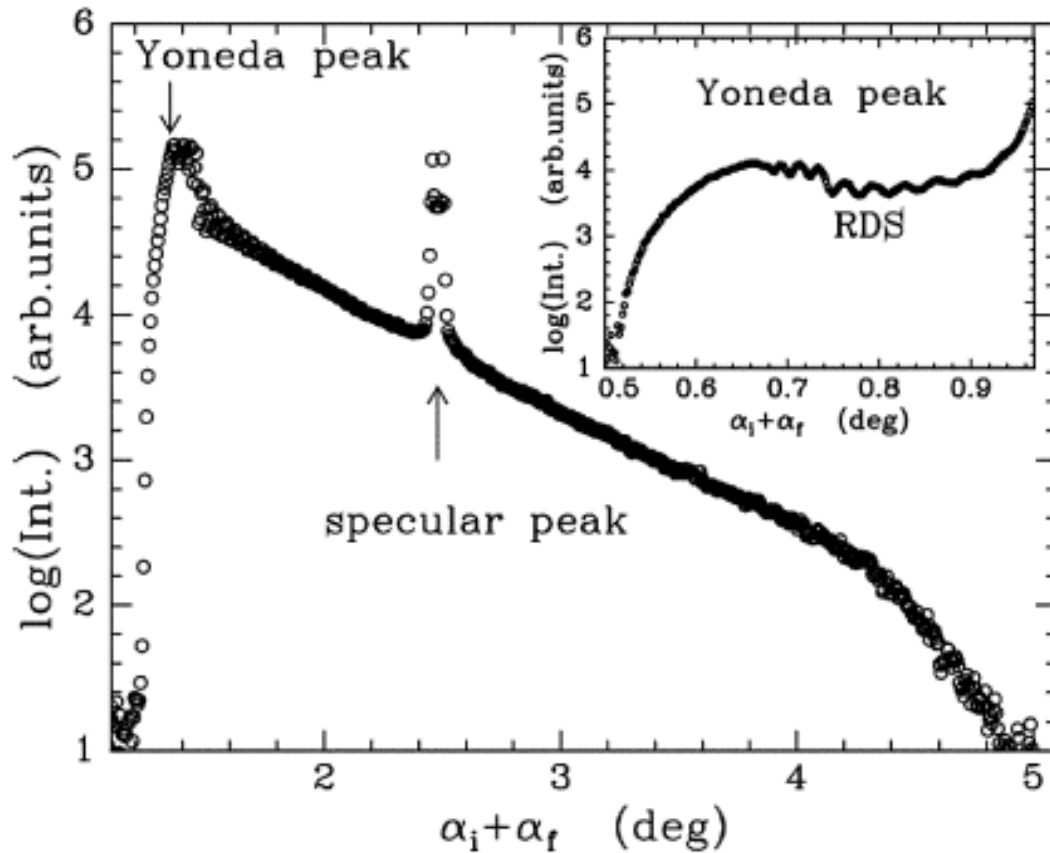
$$q_z = 2\pi/\lambda \sin(\alpha_i + \alpha_f)$$

$$q_y = 2\pi/\lambda \sin(2\theta)\cos(\alpha_f)$$

Salditt et al.; Phys.Rev.B **51**, 5617 (1995)
Naudon et al.; Physica B, **283**, 69 (2000)
Renaud et al.; Science, **300**, 1416 (2003)

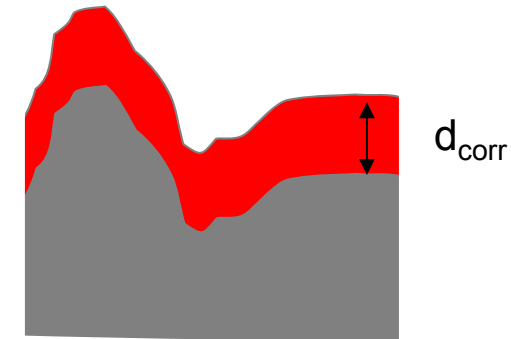


Resonant diffuse scattering (RDS)

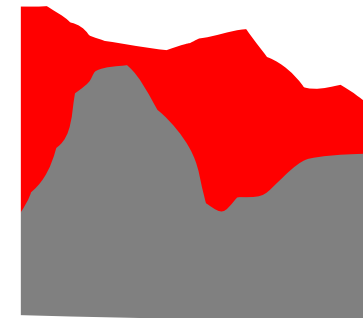


Correlated roughness

$$\Delta q_z = 2\pi / d_{\text{corr}}$$

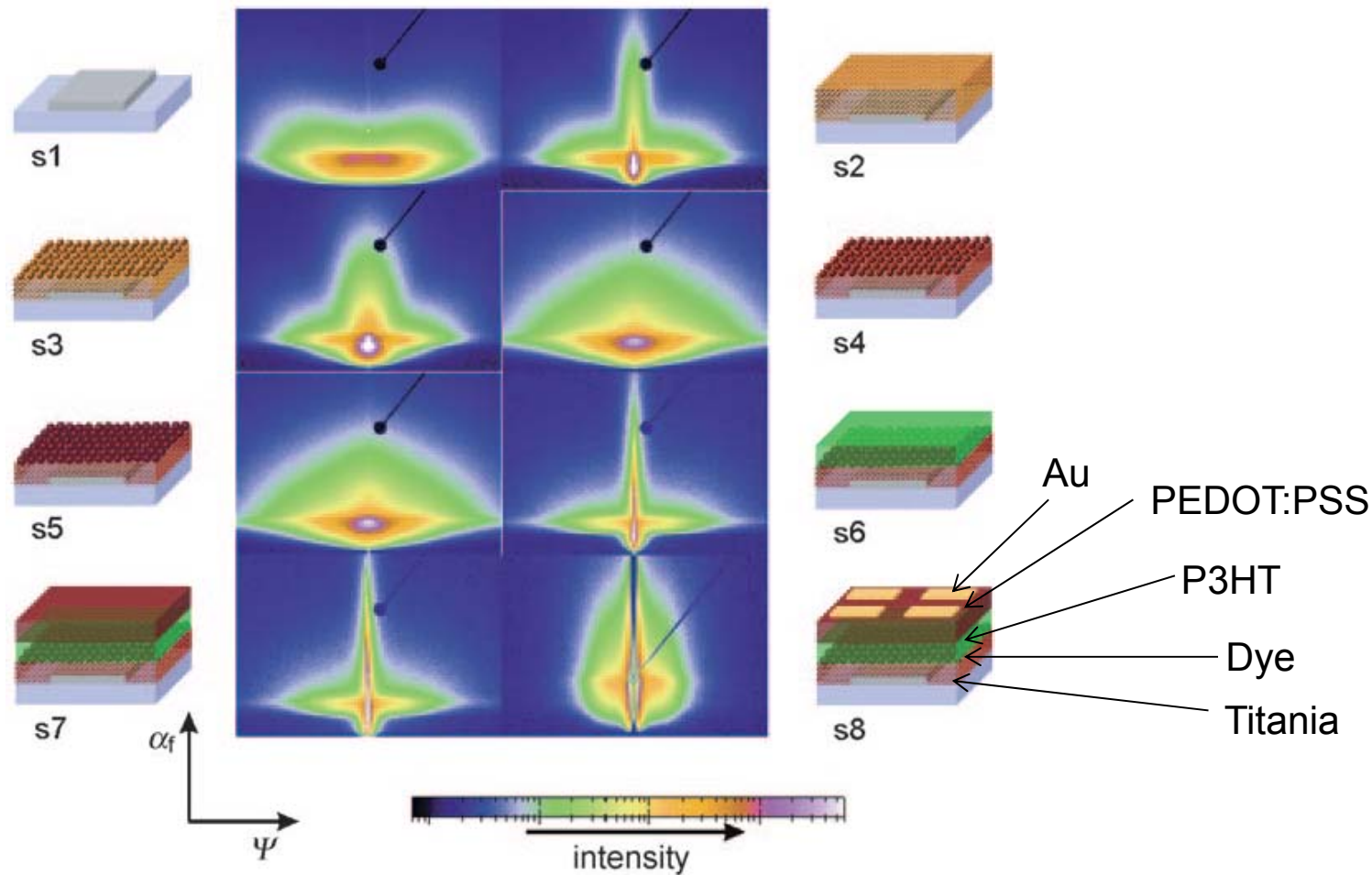


Uncorrelated interfaces



Application of penetration depth

- > Preservation of morphology of a self-encapsulated thin titania film



- > Self-assembly, dip-, spin-, sputter-, spray-coating, fluidic, vacuum deposition



Outline

> Thin films → Grazing incidence SAXS : A Primer

 Nanostructuring by annealing

> The highest resolution

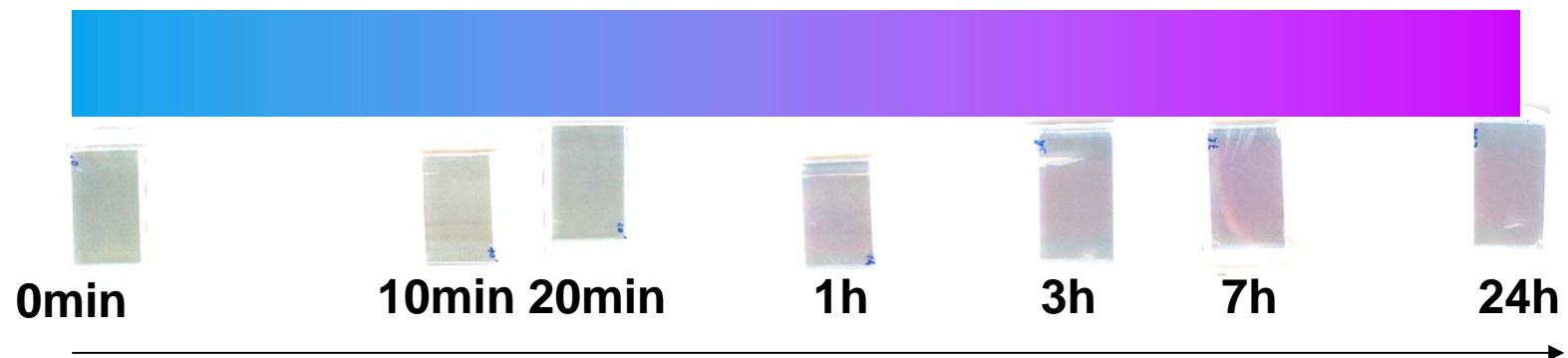
Annealing

> Au on glass

> Parameters:

- Au layer mass thickness: 3nm , 5nm , 8nm
- Annealing time

approaching critical coalescence thickness
(cluster -> metal character)

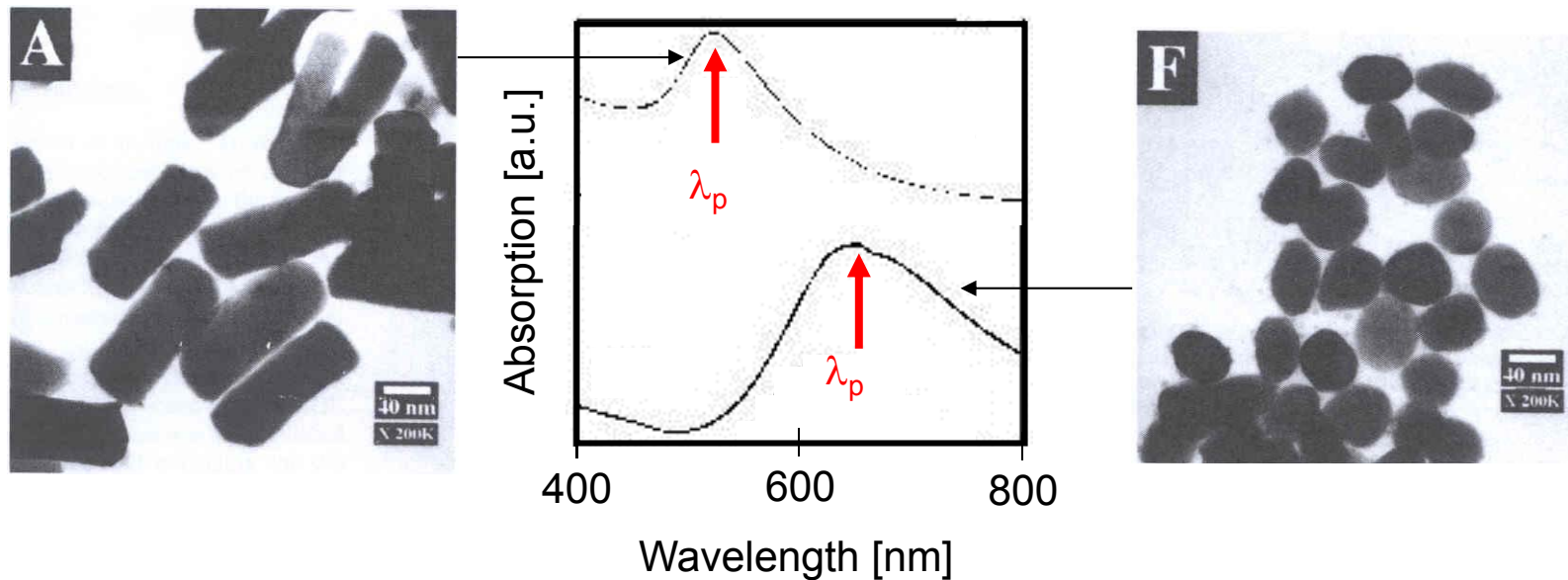


Log (Annealing time)

@ $T_{\text{anneal}} = 300^\circ\text{C} < 1064^\circ\text{C}$ (bulk melting point)

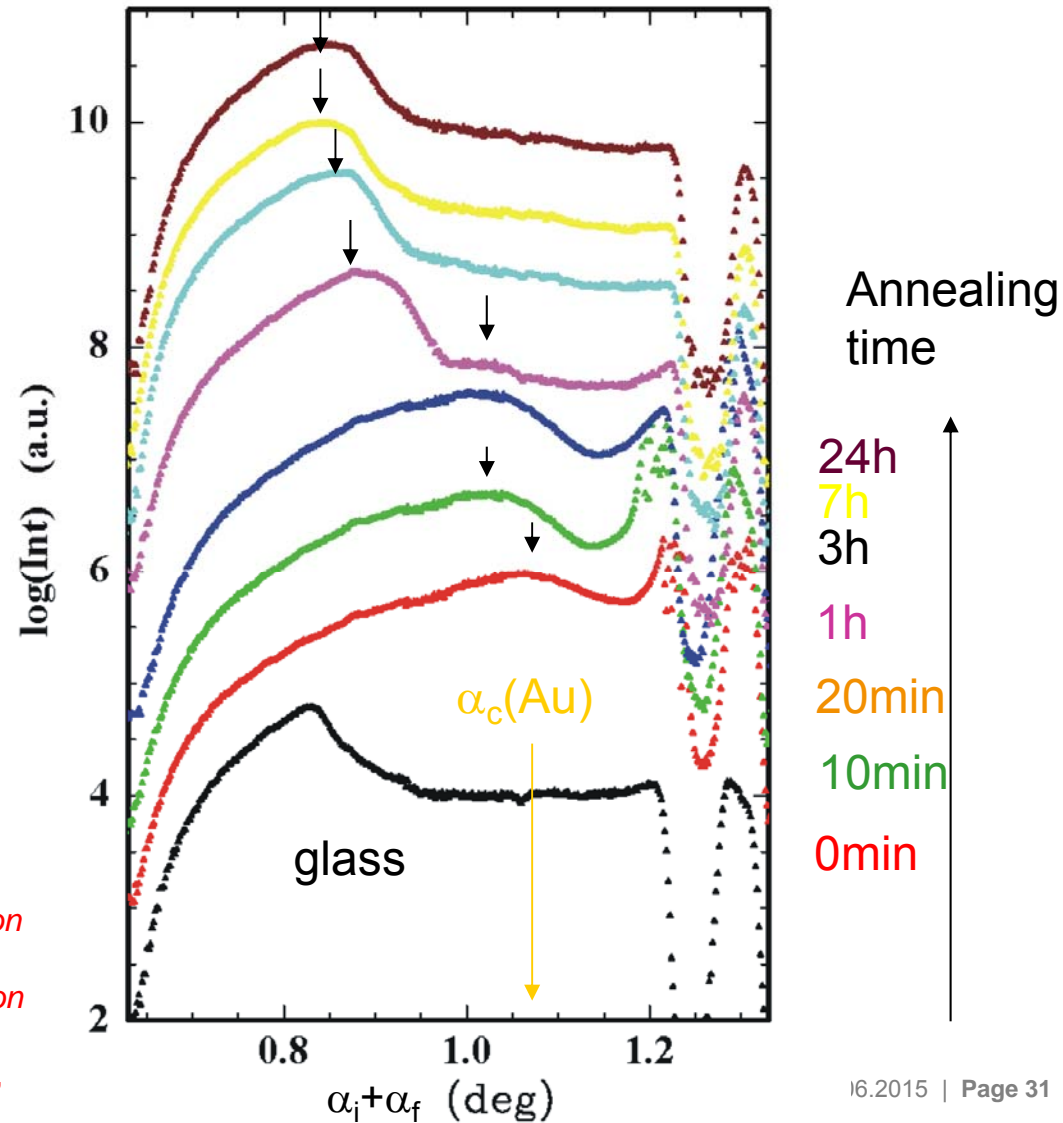
Plasmon resonance

Optical properties: sharp resonances \leftrightarrow plasmon resonances
(visible light) cluster arrangement & shape



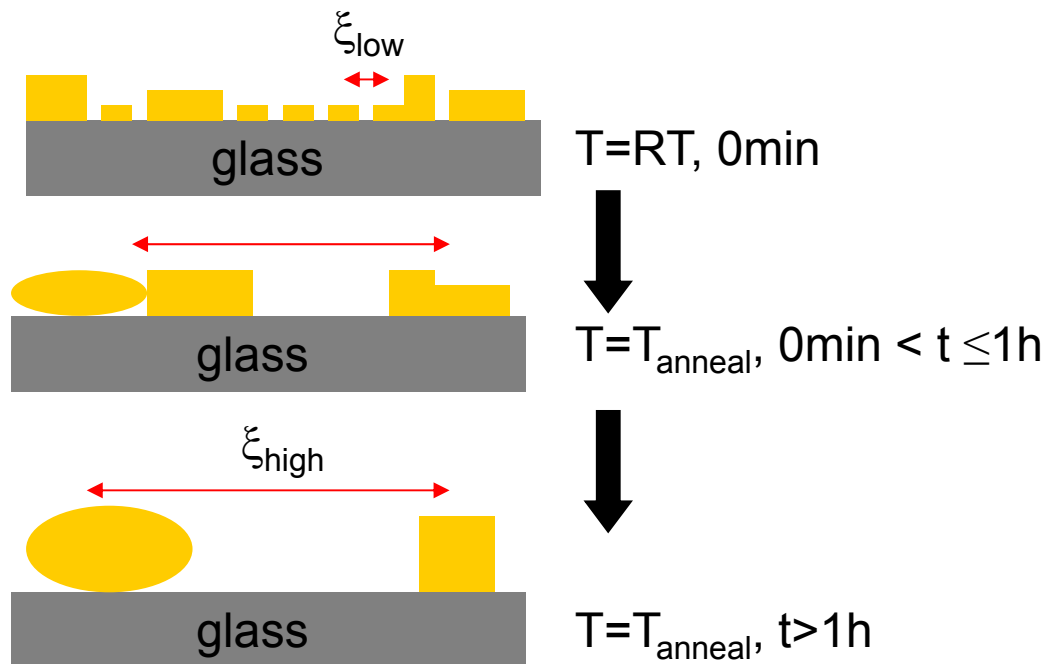
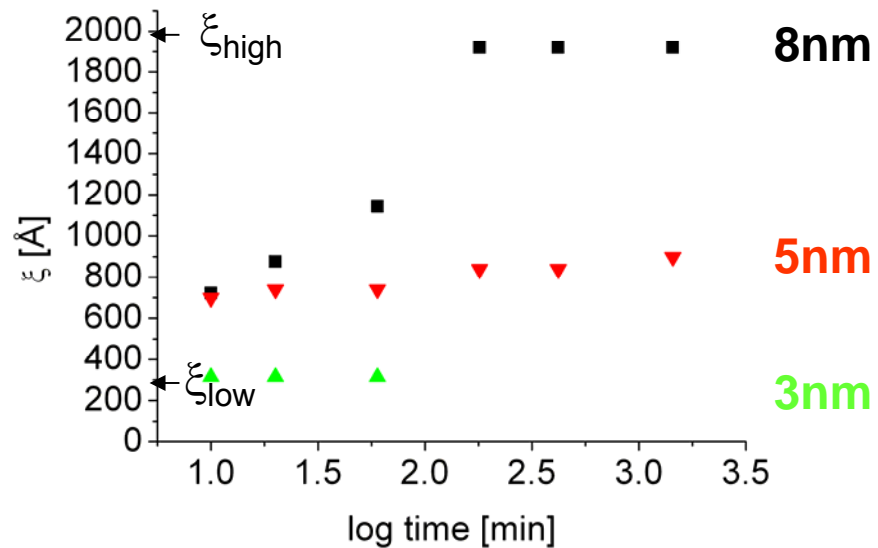
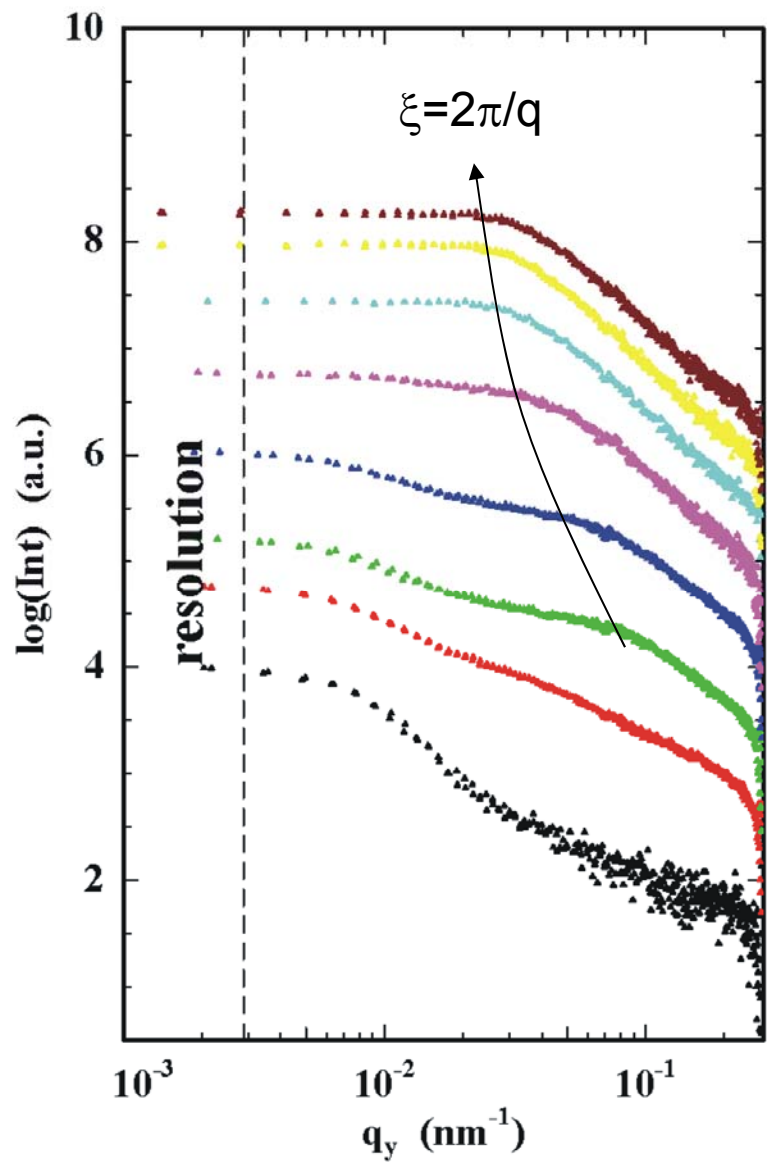
Surface coverage

> Thickness Au 8nm



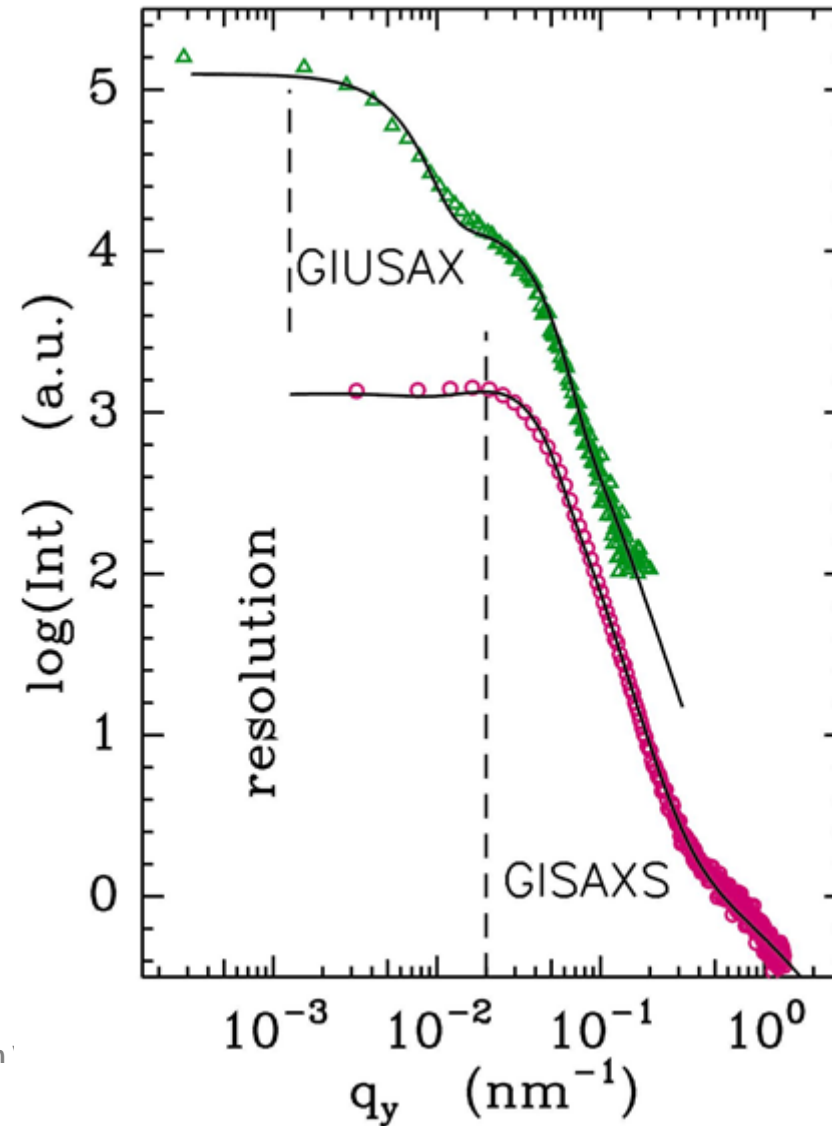
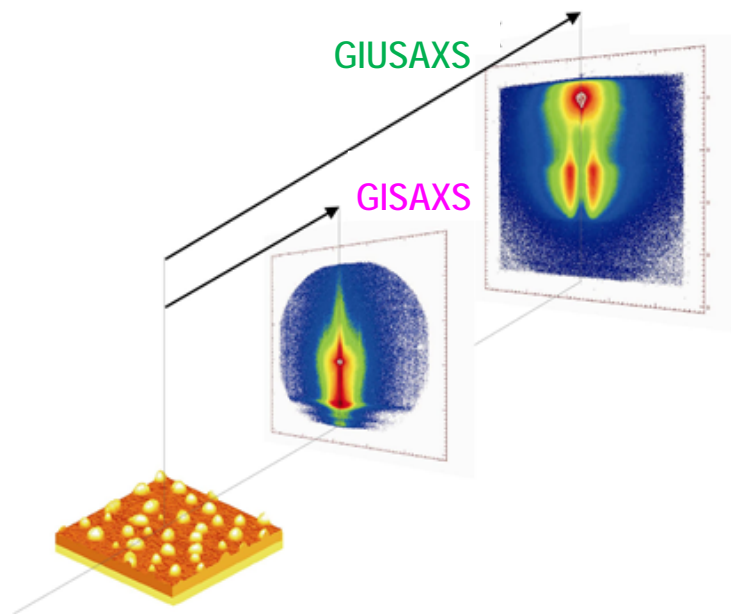
Roth et al., "Gold nanoparticle thin films on glass: Influence of film thickness and annealing time", in: "Synchrotron Radiation and Structural Proteomics", Pan Stanford Series on Nanobiotechnology - Volume 2, Eds.: E. Pechkova and C. Riekell (2010)

Cluster distance



GISAXS and GIUSAXS

- > Combination of GIUSAXS and GISAXS experiment at same ai
- > GIUSAXS SDD = 12.8m
- > GSAXS SDD=1.9m



Stephan

Data: Courtesy by P. Müller-Buschbaum, TUM



Outline

> Thin films → Grazing incidence SAXS : A Primer

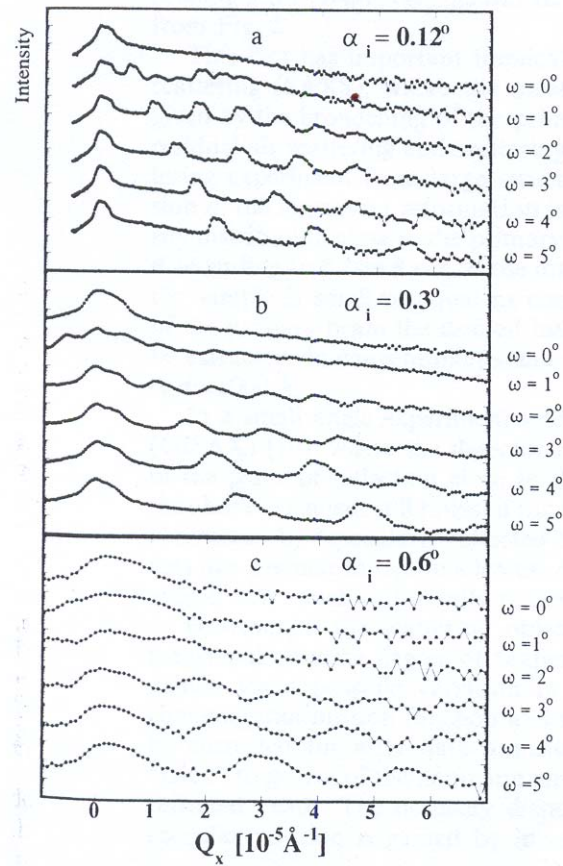
> Nanostructuring by annealing

 The highest resolution

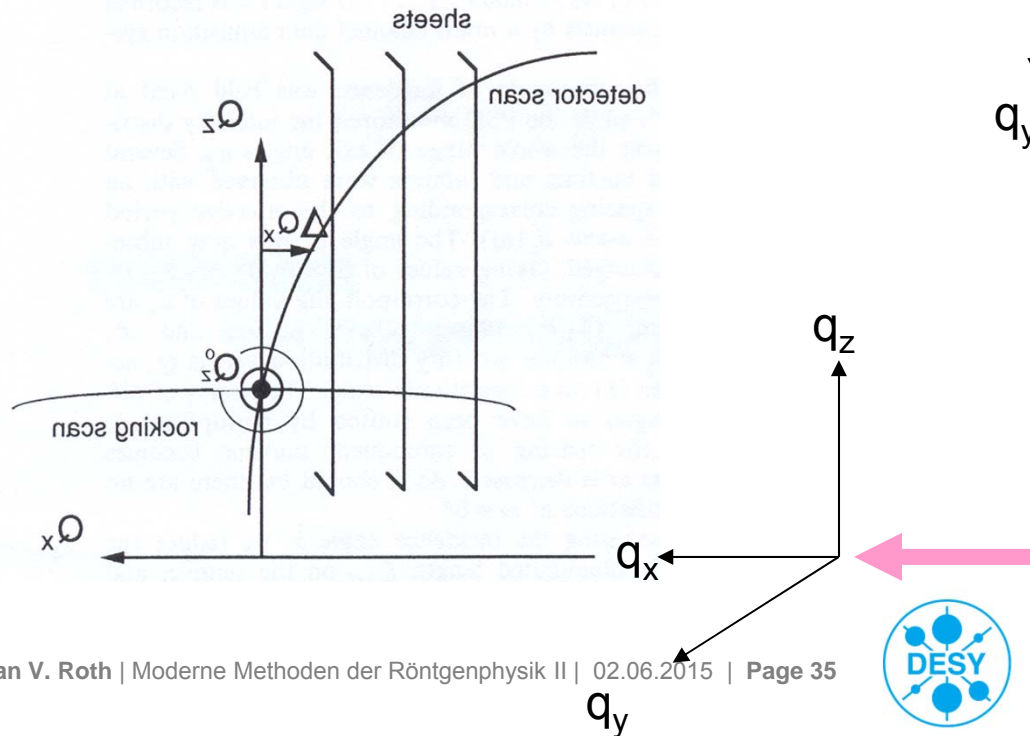
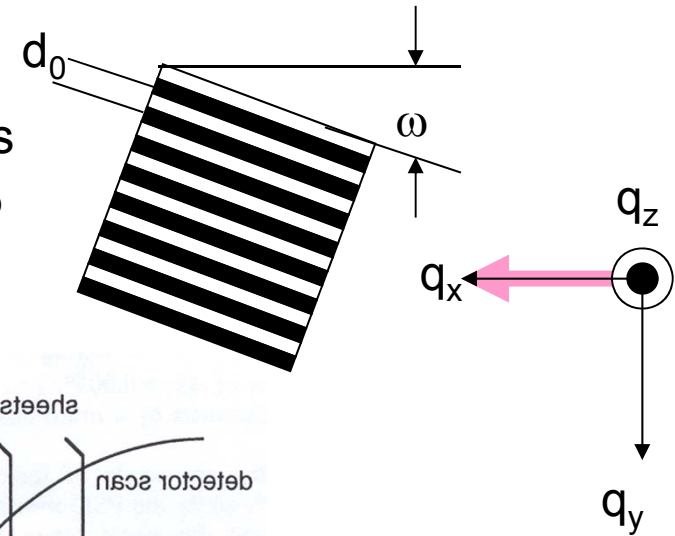


The highest resolution...

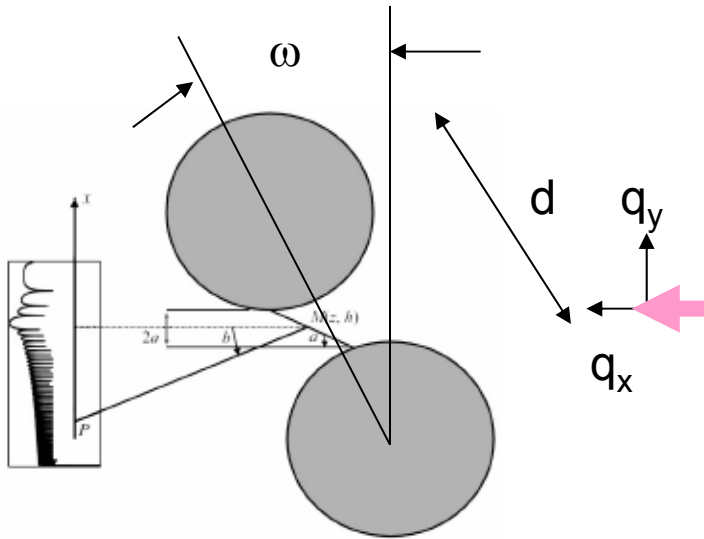
Following Salditt et al., Z. Phys. B **96** (1994) 227: Use grids!



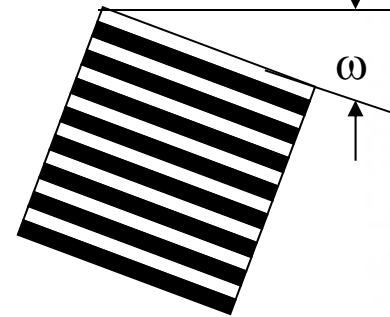
Adjacent orders
 $2\pi/d = \Delta(q_x) / \omega$
 $d = d_0 / \omega$



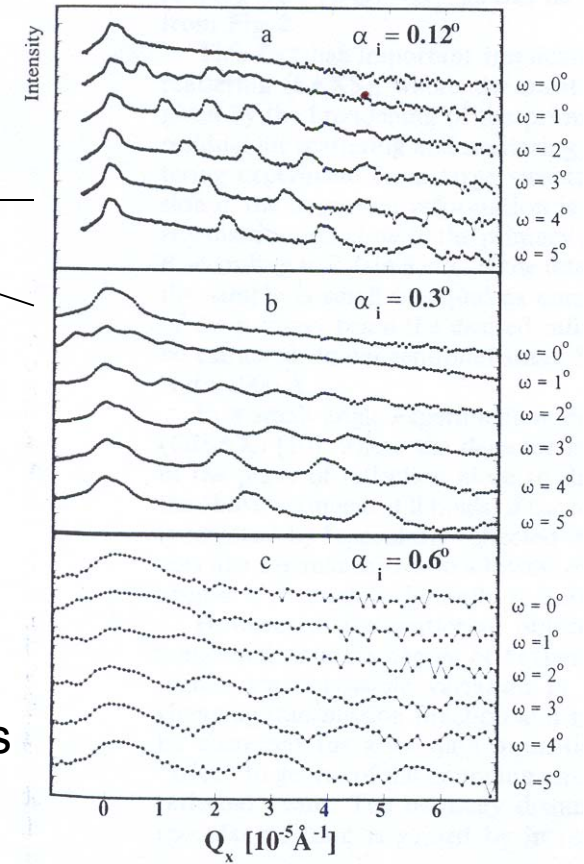
...some analogons...



Zero order
 $q_y + 2\pi/\lambda \sin(\alpha_f) = 0$
 $q_x = 2\pi/\lambda (\cos(\alpha_f) - \cos(\alpha_i))$



Adjacent orders
 $2\pi/d = \Delta(q_x) / \omega$



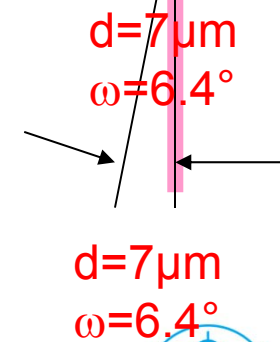
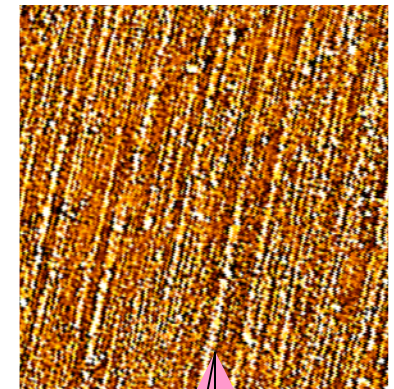
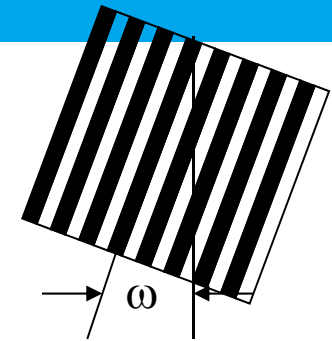
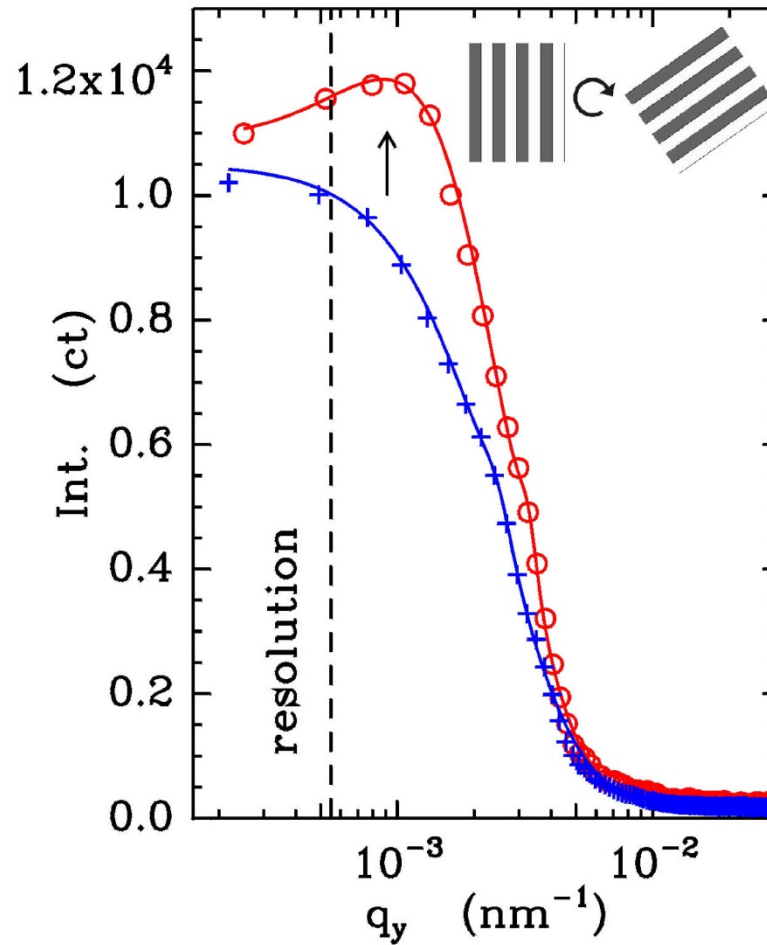
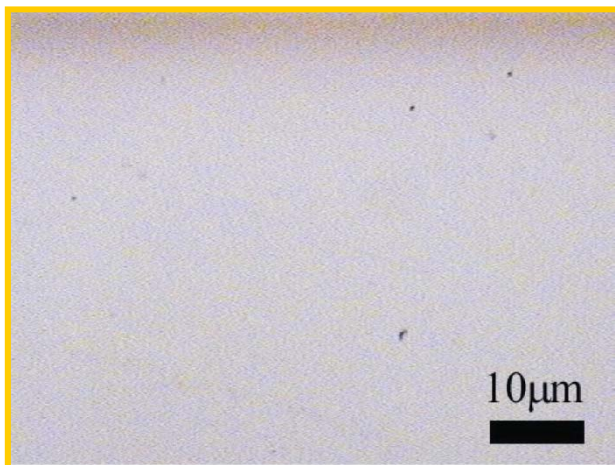
$-q_y + q_x / \tan \omega = 0$



...and at BW4: Polymeric nanochannels

Müller-Buschbaum et al., Appl. Phys. Lett. **88**, 083114 (2006)
 HASYLAB – highlight, www.hASYlab.desy.de (2006/2007)

Beam size:
 $B=400 \times 400 \mu\text{m}^2$
 $\lambda=1.38 \text{ \AA}$
 $L_{SD}=13 \text{ m}$
 $\alpha_i=0^\circ$





Theory

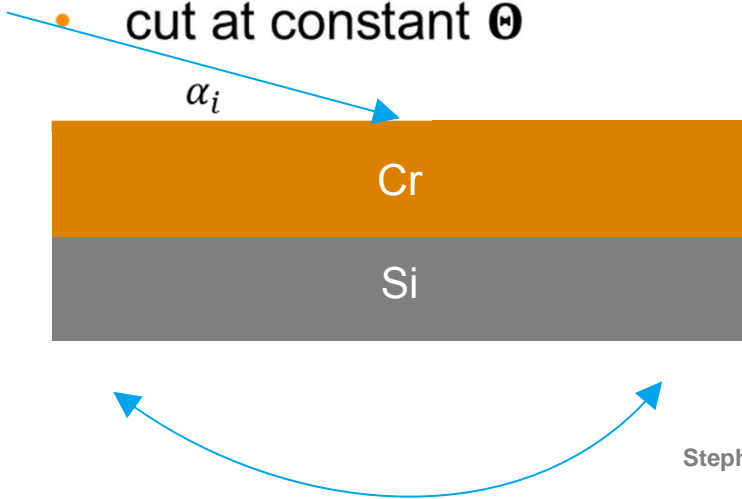
	$r_0\rho_e [10^{10}cm^{-2}]$	$\mu_x [cm^{-1}]$	$\alpha_c [^\circ]$
vacuum	0	0	---
Si	19,9	93	0,2
Cr	56,3	1208	0,32

> $\alpha_c = \sqrt{2\delta}$

$\delta = \frac{\lambda^2}{2\pi} r_0\rho_e$ $\lambda = 1,34 \text{ \AA}$

>

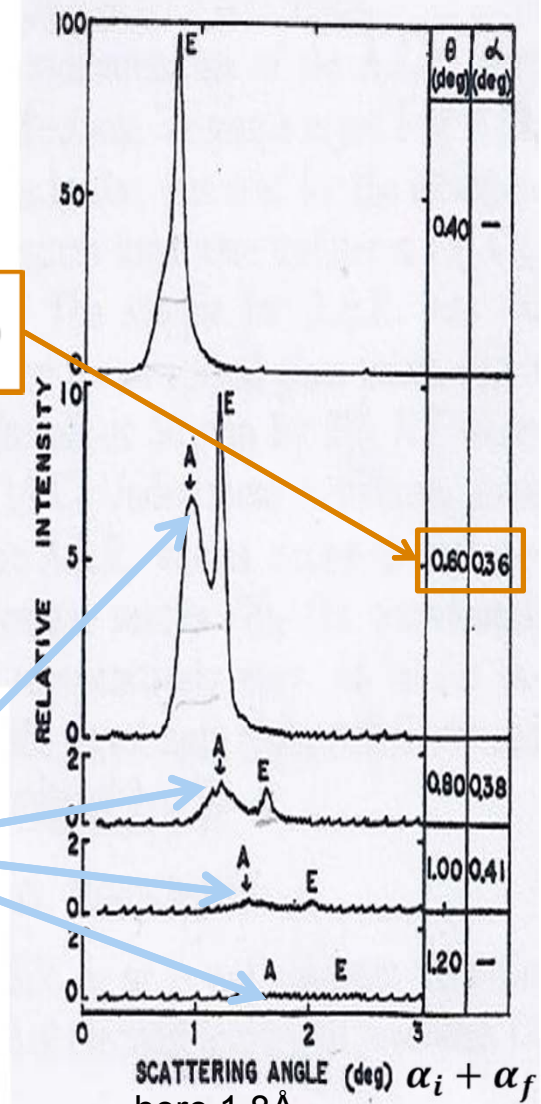
- dependent on material and wavelength
- reflection under α_c called Yoneda-Peak
- cut at constant Θ



$\alpha_i + \alpha_f = 0,6 + \alpha_f = 0,96^\circ$
 $\Rightarrow \alpha_f = 0,36^\circ = \alpha_c (\text{Cr}, 1,8\text{\AA})$

FIG. 5. A.S.R. and equiangular reflection by a Cr sample. X-ray source: Mo radiation, no filter, 35 kV, 13 mA.

YONEDA-Peak



here 1,8Å



Snell's law and the Fresnel equations (3) (see 10.4.2014)

use table to extract μ , ρ , f' yielding Q_c

and calculate b_u ($b_u \ll 1$):

$$b_u = 2k\mu/Q_c^2$$

use (D): $q^2 = q'^2 + 1 - 2ib_u$

	Z	Molar density (g/mole)	Mass density (g/cm ³)	ρ (e/Å ³)	Q_c (1/Å)	$\mu \times 10^6$ (1/Å)	b_μ
C	6	12.01	2.26	0.680	0.031	0.104	0.0009
Si	14	28.09	2.33	0.699	0.032	1.399	0.0115
Ge	32	72.59	5.32	1.412	0.045	3.752	0.0153
Ag	47	107.87	10.50	2.755	0.063	22.128	0.0462
W	74	183.85	19.30	4.678	0.081	33.235	0.0409
Au	79	196.97	19.32	4.666	0.081	40.108	0.0495

get:

$$r(q) = (q - q') / (q + q')$$

$$t(q) = 2q / (q + q')$$

$$\Lambda(q) = 1 / Q_c \operatorname{Im}(q')$$