



*The Abdus Salam
International Centre for Theoretical Physics*



1936-45

**Advanced School on Synchrotron and Free Electron Laser Sources
and their Multidisciplinary Applications**

7 - 25 April 2008

Grazing Incidence Small Angle X-ray Scattering (GISAXS)

Sigrid Bernstorff
Sincrotrone Trieste

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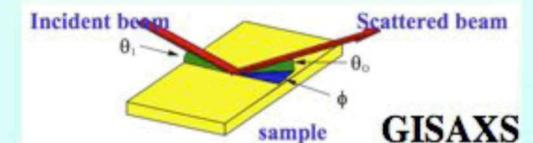
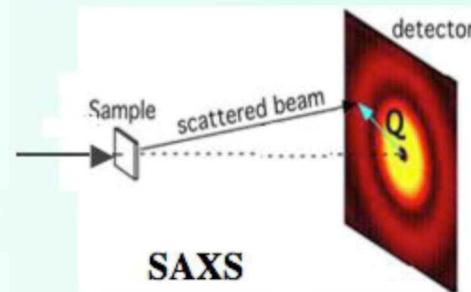
Sincrotrone Trieste

S.S.14 km 163,5 in Area Science Park, 34012 Basovizza (TS), Italy

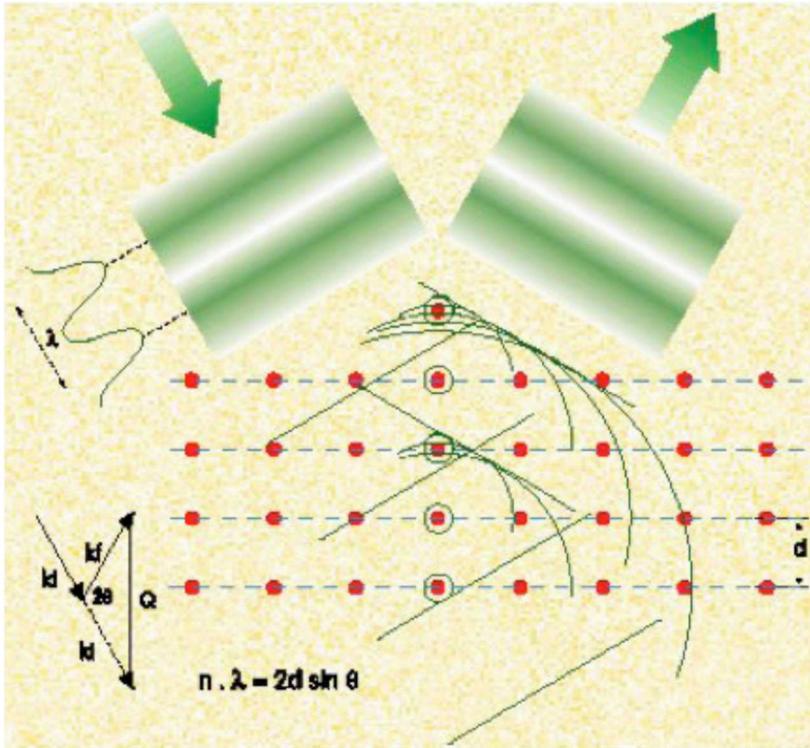
bernstorff@elettra.trieste.it

Introduction:

- Scattering with incidence at high angle --> grazing angle: what changes ?
- When is grazing incidence scattering useful ?
- Other grazing incidence techniques:
 - GI X-ray Diffraction
 - X-ray Reflectivity
- Some hints for a good set-up



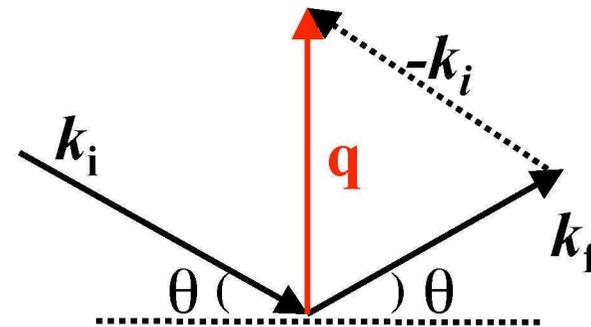
The SAXS technique



Bragg's Law

$$\lambda = 2d \sin\theta$$

Scattering Vector q

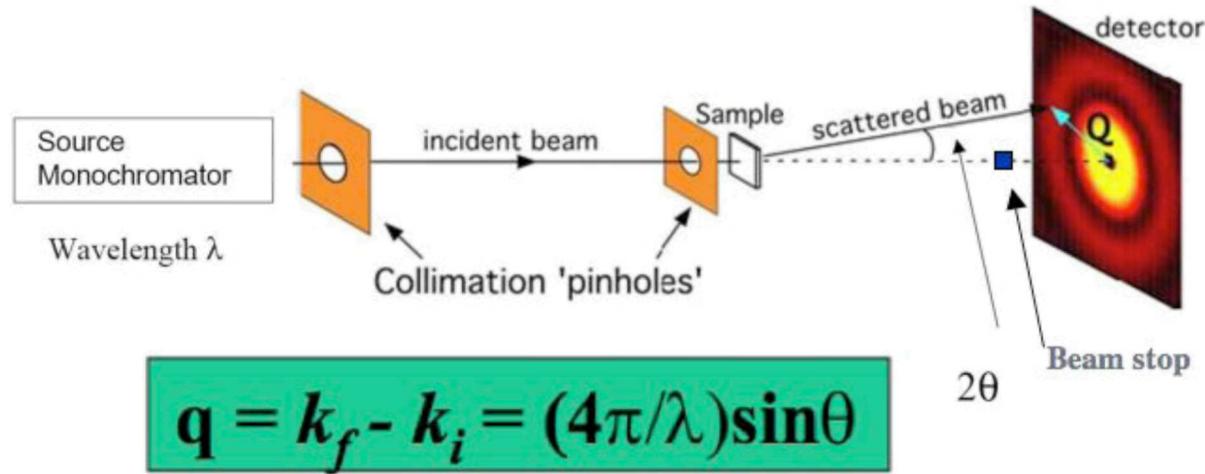


$$q = k_f - k_i = (4\pi/\lambda)\sin\theta$$

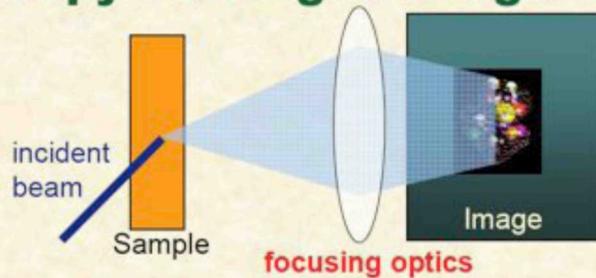
$$|q| = 2k \sin\theta$$

$$q = 2\pi/d \quad \text{inverse distance}$$

Method of Small Angle X-Ray Scattering SAXS



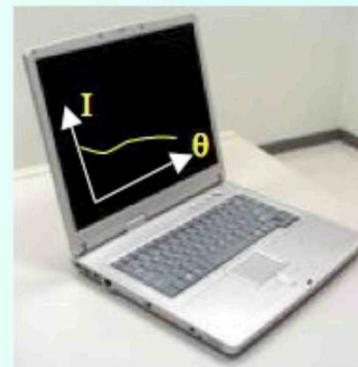
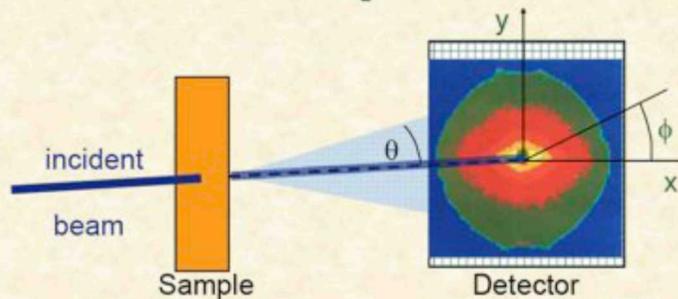
Microscopy : enlarged image



SAXS intensity

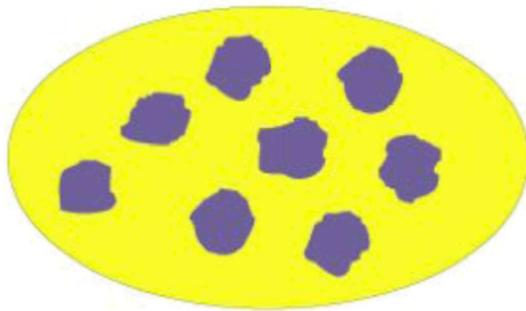
$$I(\mathbf{q}) = \frac{1}{V} \left| \int \rho(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{r} \right|^2 \quad \rho(\mathbf{r}) = \text{electron density}$$

SAS : interference pattern



SAXS technique

$$I(\mathbf{q}) = \frac{1}{V} \left| \int \rho(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} d^3\mathbf{r} \right|^2 \quad \rho(\mathbf{r}) = \text{electron density}$$



$\rho_{1(2)}$ = electron density
in phase 1(2)

$$I(\mathbf{q}) = \frac{N}{V} (\rho_2 - \rho_1)^2 |F(\mathbf{q})|^2 S(\mathbf{q})$$

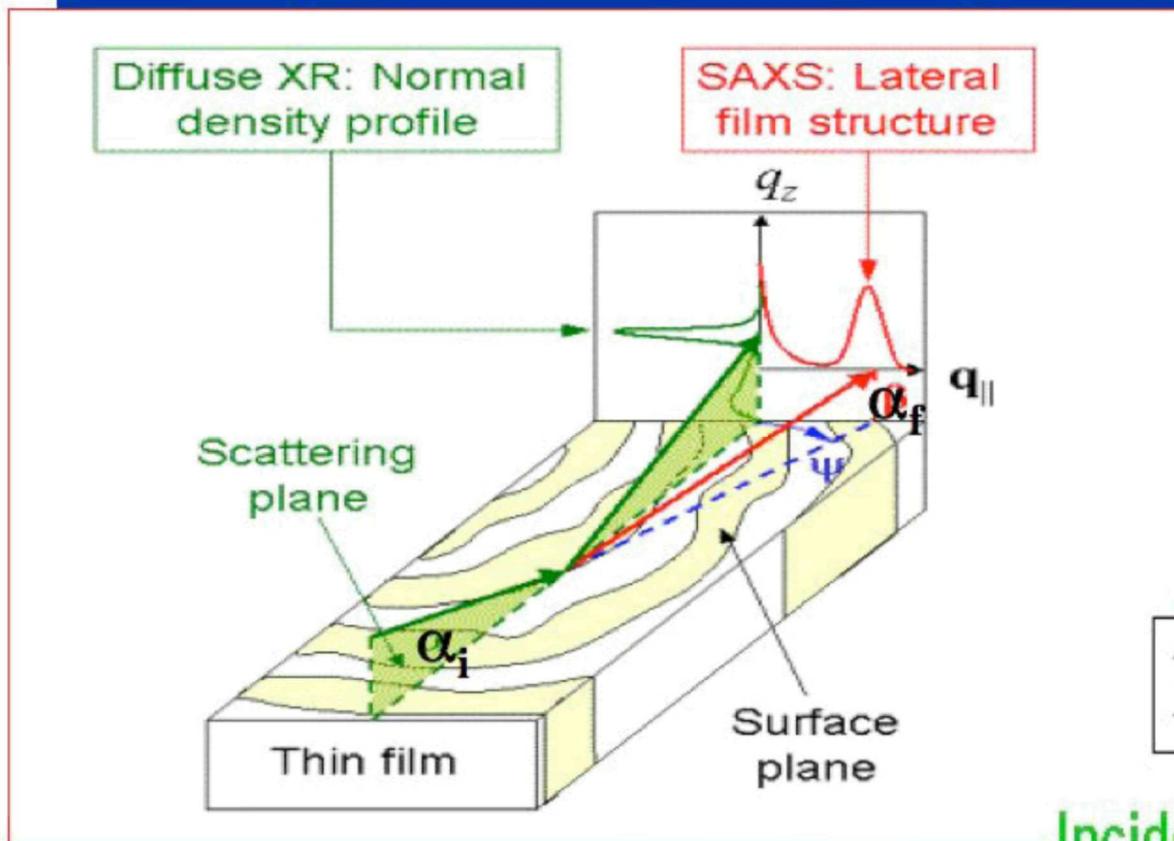
single particle
SAXS

inter particle
scattering

Principle of Babinet :
pores = particles

$$\int_{V_1} e^{i\mathbf{q} \cdot \mathbf{r}} d^3\mathbf{r}$$

Grazing Incidence Small Angle X-Ray Scattering (GISAXS)

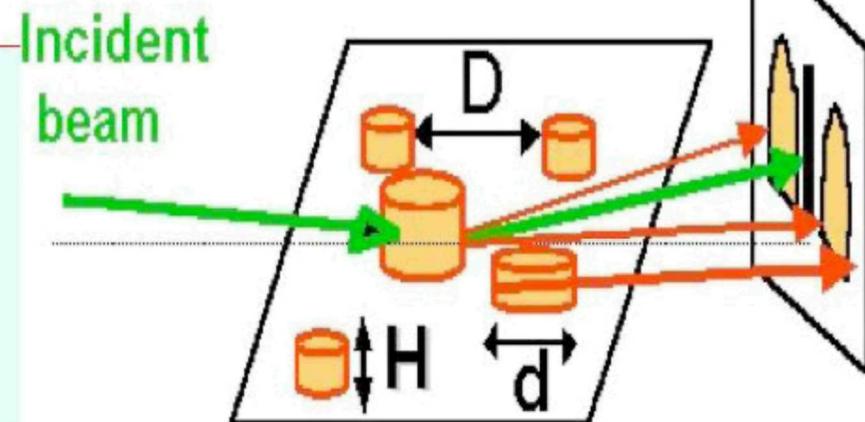


GISAXS

- combines features from SAXS and diffuse X-ray Reflectivity
- Allows to choose a limited penetration depth -> enhance surface signal (typ. 10^{-6} times < substrate scattering)
- is a versatile tool for characterizing average size, shape and particle distance of nano-particles on surfaces, or in thin films

Principle

Detector plane



- X-rays are totally reflected under very small grazing angles
- The X-ray grazing angle α_i is chosen between about half the critical angle, α_C , and several critical angles

GISAXS: refraction effects of X-rays

α_i is small -> effects of refraction at the surface needs to be considered:

Refractive index n of matter for x-rays is:

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

with:

$$\delta = \frac{1}{2\pi} \times \frac{e^2}{mc^2} \times \frac{N_a \sum_i (Z_i - f_i')}{\sum_i A_i} \times \rho \lambda^2$$

$$\beta = \frac{1}{2\pi} \times \frac{e^2}{mc^2} \times \frac{N_a \sum_i f_i''}{\sum_i A_i} \times \rho \lambda^2 = \mu \frac{\lambda}{4\pi}$$

$$= 2.701 \times 10^{-6} \times \frac{\sum_i (Z_i - f_i') \text{ [el. units]}}{\sum_i A_i \text{ [g / mol]}} \times \rho \text{ [g/cm}^3\text{]} \lambda^2 \text{ [Å}^2\text{]}$$

summation over all atomic species i :

$(Z_i - f_i')$ scattering factor

f_i'' anomalous dispersion factor

A_i atomic weight

N_a Avogadro's number

ρ density

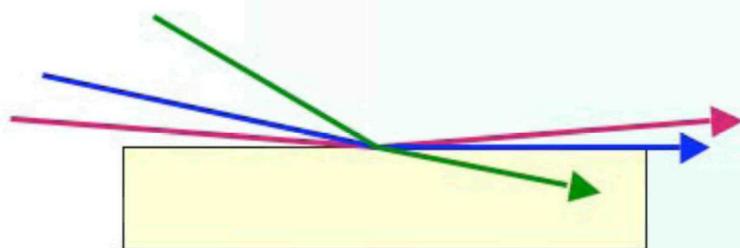
λ wave length

μ photo electric absorption coefficient

GISAXS: refraction effects of X-rays

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

critical angle of total reflection $\alpha_c \propto \sqrt{2\delta}$



Typical orders of magnitude:

$$\delta \approx 10^{-5} \quad (10 \text{ keV})$$

$$\beta \approx 10^{-6}$$

$$\alpha \approx 0.1^\circ - 0.5^\circ$$

Note:

- Real part of $n = 1 - \delta + i\beta$ is always slightly < 1
- Because of refraction, a beam passing from vacuum into a sample comes closer to the sample surface
- For $\alpha_i < \alpha_c$, the beam is totally reflected, and only an evanescent wave, which decays over some nm, is present below the surface
- For $\alpha_i > \alpha_c$ the transmitted wave propagates

Scattering Depth

The perpendicular components of the incident and emergent wave vectors are modified upon crossing the surface, and become complex due to refraction and absorption:

$$k'_{i,f\perp} = \frac{2\pi}{\lambda} (A_{i,f} - iB_{i,f})$$

For small incidence and emergence angles:

$$A_{i,f} = \frac{1}{\sqrt{2}} (\sqrt{(\alpha_{i,f}^2 - \alpha_c^2)^2 + 4\beta^2} + \alpha_{i,f}^2 - \alpha_c^2)^{0.5}$$

$$B_{i,f} = \frac{1}{\sqrt{2}} (\sqrt{(\alpha_{i,f}^2 - \alpha_c^2)^2 + 4\beta^2} + \alpha_c^2 - \alpha_{i,f}^2)^{0.5}$$

-> the perpendicular momentum transfer $Q'_{\perp} = k'_{f\perp} - k'_{i\perp}$ inside the sample becomes complex

The scattering depth $\Lambda = \frac{1}{\text{Im}(Q'_{\perp})} = \frac{\lambda}{4\pi(B_i + B_f)}$ is thus strongly affected by refraction when α_i and / or α_f are close to α_c

Refraction effects

Scattering depth $\Lambda = \frac{1}{\text{Im}(Q'_{\perp})} = \frac{\lambda}{4\pi(B_i + B_f)}$

The reflection and transmission coefficients are also strongly affected by refraction when α_i and / or α_f are close to α_c :

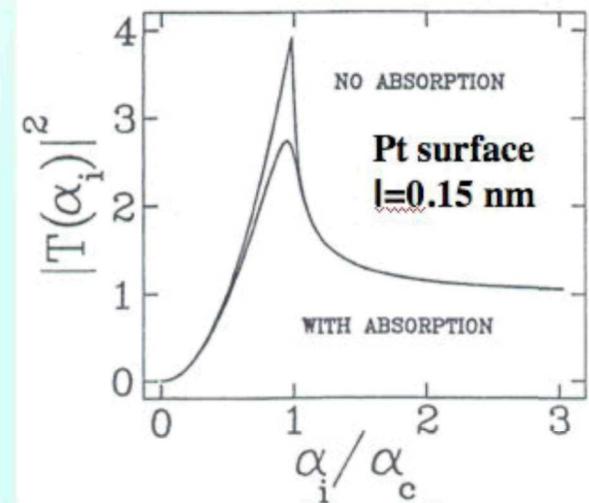
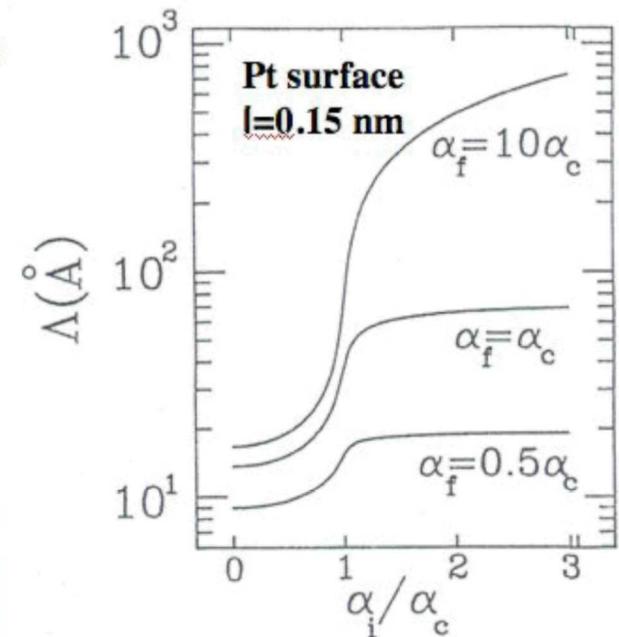
$$R_{i,f} = \frac{\alpha_{i,f}^2 - 2\alpha_{i,f} A_{i,f} + A_{i,f}^2 + B_{i,f}^2}{\alpha_{i,f}^2 + 2\alpha_{i,f} A_{i,f} + A_{i,f}^2 + B_{i,f}^2}$$

$$T_{i,f} = \frac{4\alpha_{i,f}^2}{\alpha_{i,f}^2 + 2\alpha_{i,f} A_{i,f} + A_{i,f}^2 + B_{i,f}^2}$$

$R_{i,f} = 1$ for $\alpha_{i,f} < \alpha_c$ (regime of total reflection)

$T = 4$ (max value) at α_c

-> use α_i and / or α_f close to α_c to enhance surface scattering !



Example: Quantum Dots studied by GISAXS

II-VI semi-conductors Nanostructures: what for ?

quantum confinement of excitons,
increase of the energy gap



- variable length optical absorbers
- high-speed non-linear optical switches
- photoluminescence with variabel wavelength by changing particle size (-> quantum dot laser)
- formation of nanoparticles in dielectrics and non-absorbing materials

BUT: working devices will depend on a precise control of size and density of an ensemble of Quantum Dots (QD)!

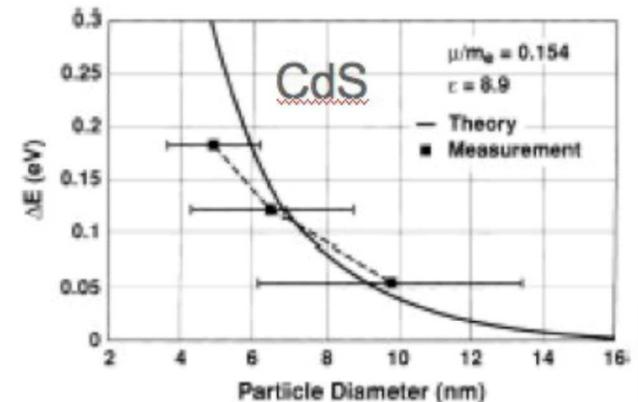
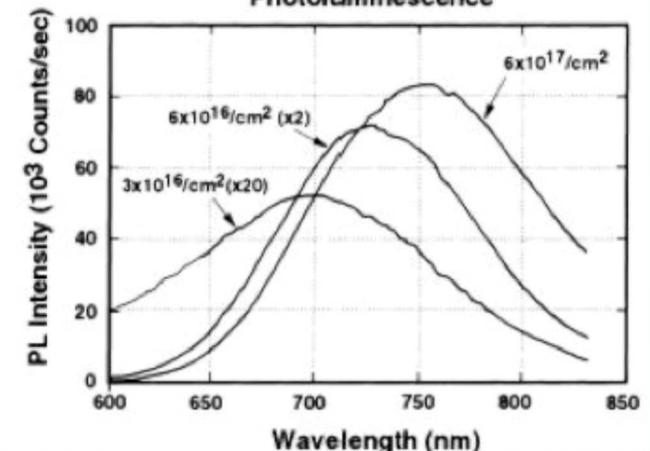


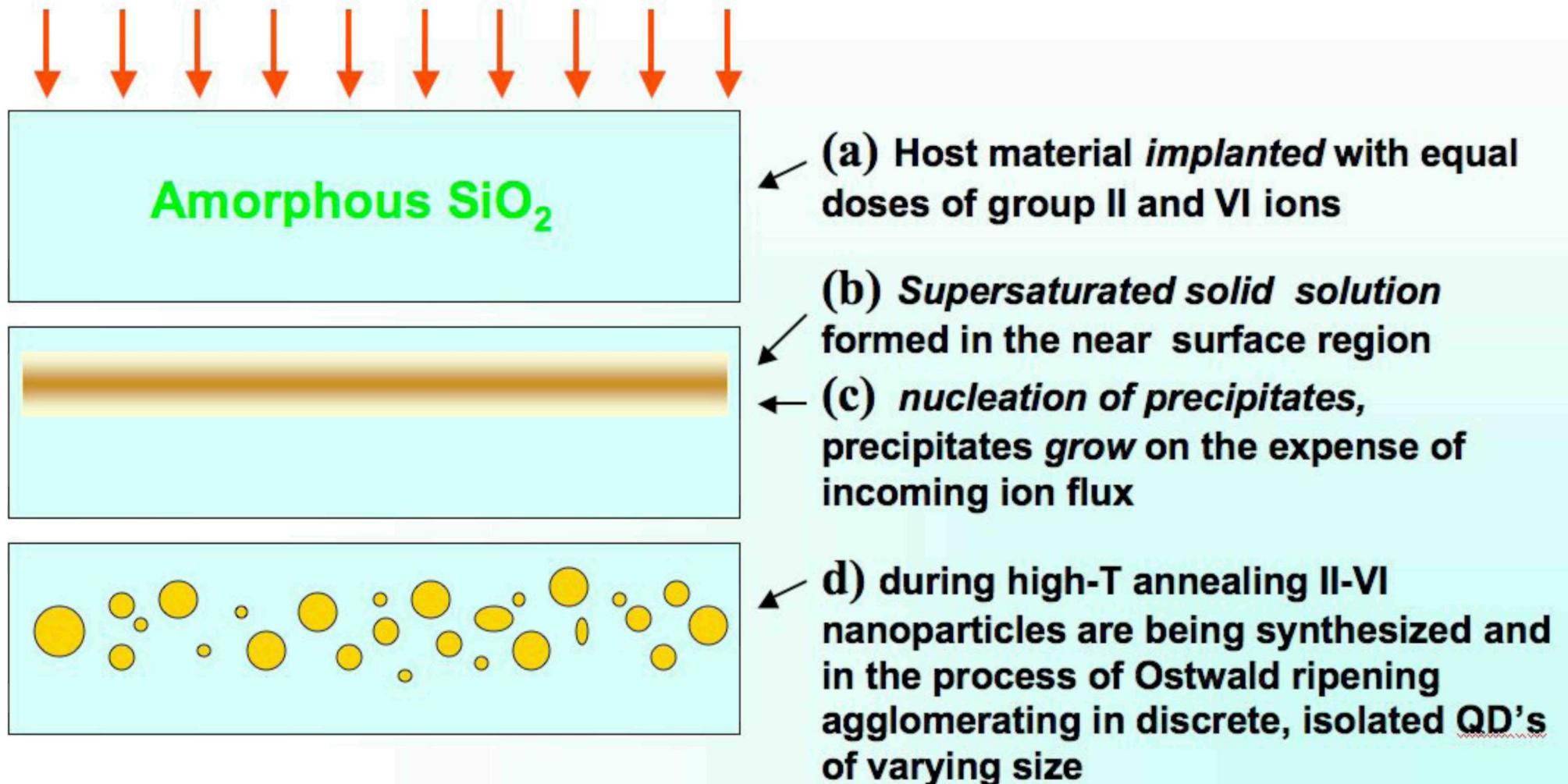
Fig. 5. Calculated and measured bandgap shift for CdS nano-crystals. The solid line is calculated from Eq. (2). The points are measurements of the bandgap shift from Eq. (1) for the samples in Fig. 4.

Si (400keV, RT) Implanted Fused Silica
(Annealed 1100°C/1h)
Photoluminescence

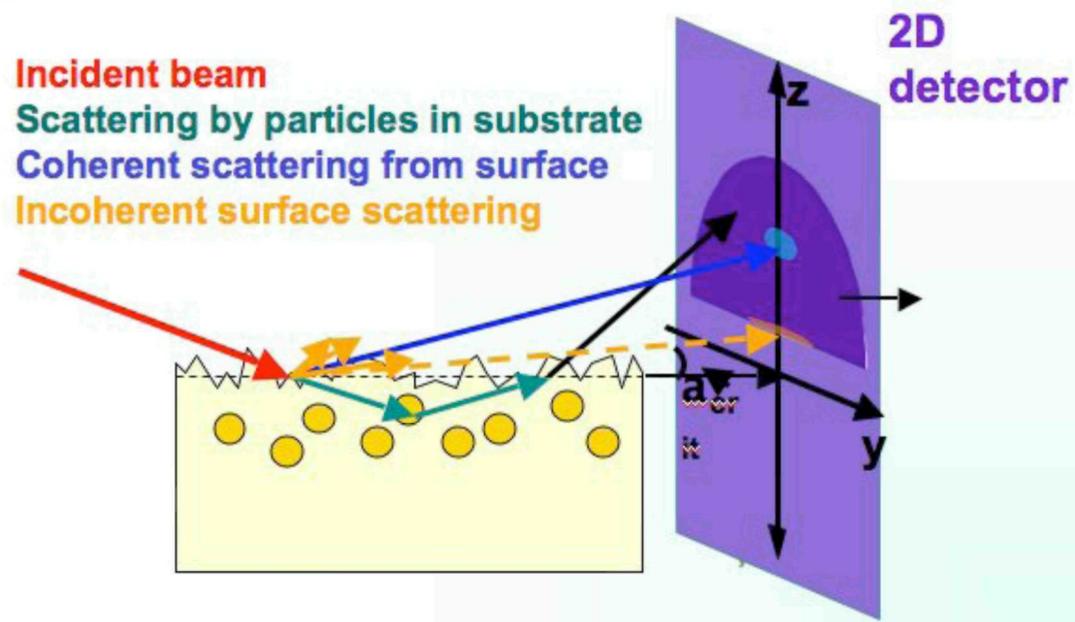


Nanocrystals in Substrates

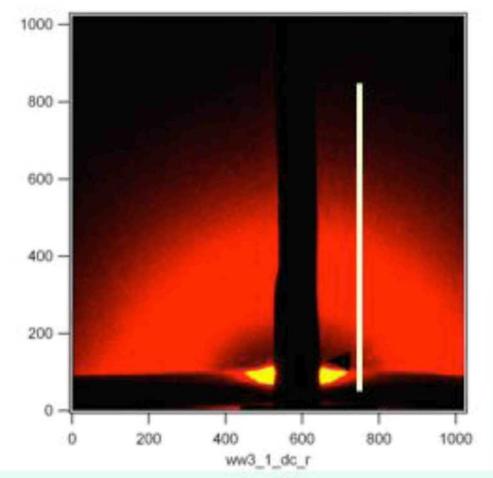
Schematic of the ion implantation technique for NC production



GISAXS: what information do we get ?

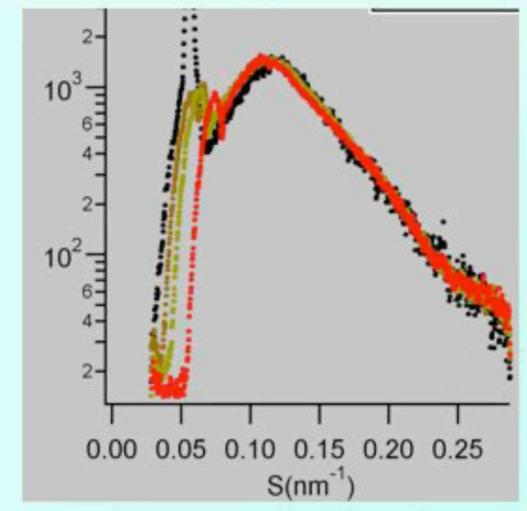


2D GISAXS pattern



$\Lambda = 2\pi/q_m$, $\Lambda =$ average nanocrystals distance -
 obtained from interference peak, q_{max}

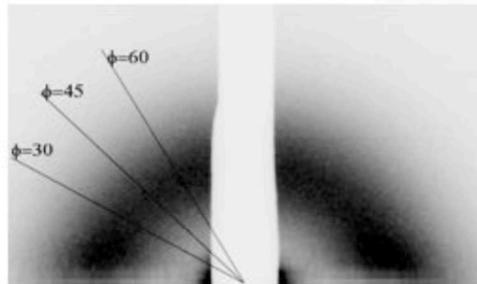
$R_g =$ radius of gyration
 $\Rightarrow D =$ average cluster diameter
 obtained from slope of linear region of
 $I(q)$ versus q^2



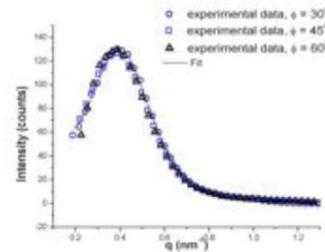
Synthesis and growth of CdS Quantum Dots in SiO₂

GISAXS-pattern

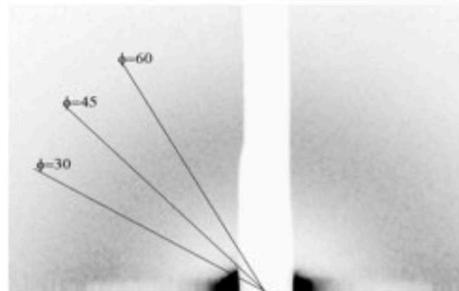
Intensity profiles



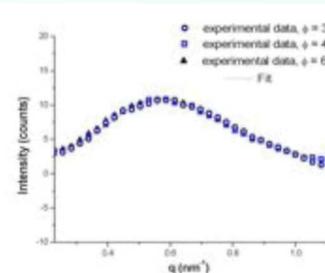
Concentration $5.3 \times 10^{21}/\text{cm}^3$



Isotropical distribution of spherical QDs with average diameter 8.8 nm, and with average distance of 10.8 nm



Concentration $2.0 \times 10^{21}/\text{cm}^3$



Isotropical distribution of spherical QDs with smaller average diameter and larger distance

LMA approximation, and DWBA formalism -> scattered intensity is:

$$I(q) \propto |T(\alpha_i)|^2 |T(\alpha_f)|^2 \int_0^\infty P(q, D) S(q, D_{hs}, \eta_{hs}) N(D, w) dD$$

GISAXS data evaluation

Scattering from embedded particles: Local Monodisperse Approximation - LMA

- system is approximated by monodisperse subsystems, weighted by the size distribution
- positions of the particles are completely correlated with their sizes

$$I(q) \propto |T(\alpha_i)|^2 |T(\alpha_f)|^2 \int_0^\infty P(q,D) S(q, D_{hs}, \eta_{hs}) N(D,w) dD$$

$T(\alpha_i)$ and $T(\alpha_f)$ - Fresnel transmission coefficients for angle of incidence α_i and exit α_f

$P(q,D)$ - form factor of a homogeneous sphere of diameter D , ($D=2R$);

$S(q, D_{hs}, \eta_{hs})$ - structure factor (η_{hs} - volume fraction and diameter of the hard spheres)

$N(w,D)$ - Gaussian size distribution function

Surface Scattering: Distorted Wave Born Approximation - DWBA

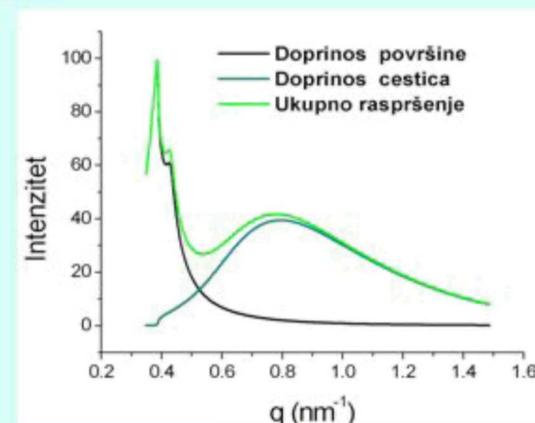
$$I_{total} = I_{LMA} + I_{surface}$$

Distorted Wave Born Approximation:

Vineyard 1982, Shinha et al. 1988

M. Rauscher, T. Salditt and H. Spohn, Phys. Rev. B 52, 16855 (1995)

M. Rauscher et al., J. Appl. Phys. 86 (12), 6763 (1999)



Quantitative analysis of GISAXS

$$I(q_{//}, q_{\perp}) \approx \langle |F|^2 \rangle \times S(q_{//})$$



Form factor :

a kind of shape FT
with refraction effects

Interference function:

FT of pair
correlation function

×

IsGISAXS program :

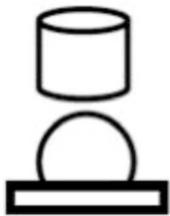
http://www.esrf.fr/computing/scientific/joint_projects/IsGISAXS/

R. Lazzari, J. Appl. Cryst. 35, 406 (2002)

F. Leroy, R. Lazzari and G. Renaud, Acta. Cryst. A 60, 565, (2004)

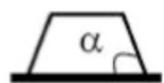
$$S(q_{//}) = 1 + \rho_S \int (g(r) - 1) e^{-iq_{//}r} d^2r$$

$$F_{DWBA}(q_{//}, k_i, k_f)$$

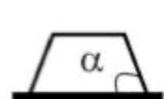


•Cylinder

•Truncated
sphere



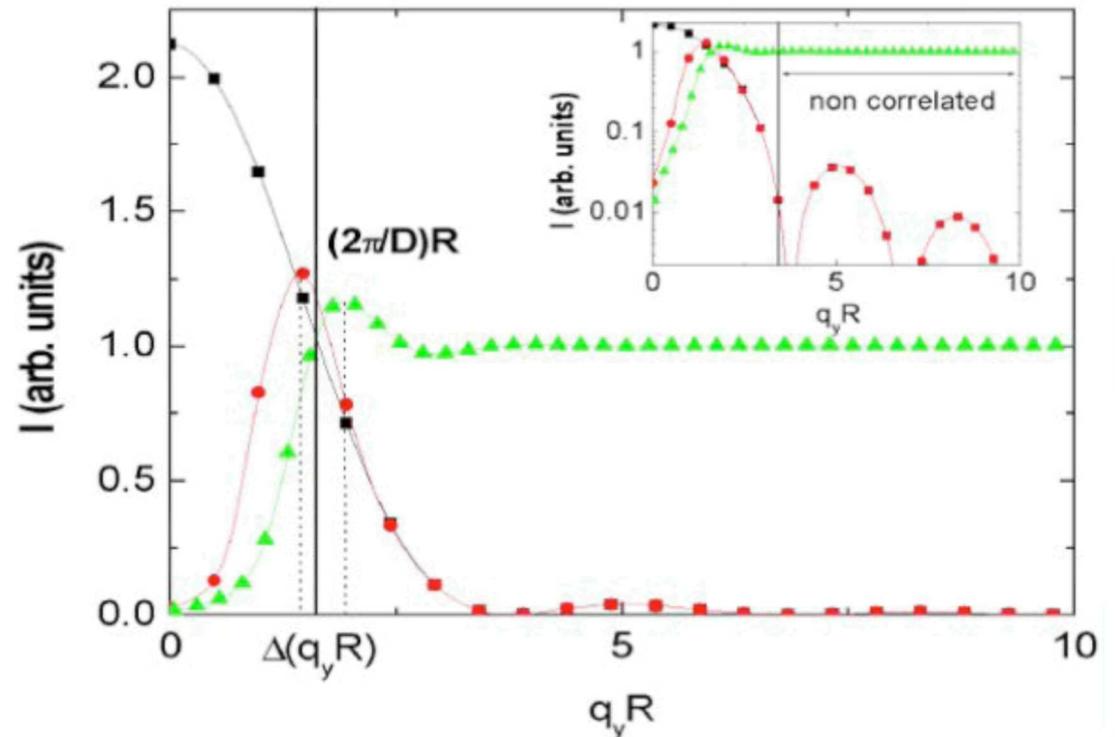
•Pyramid



•Tetraedron



•Cubooctaedron



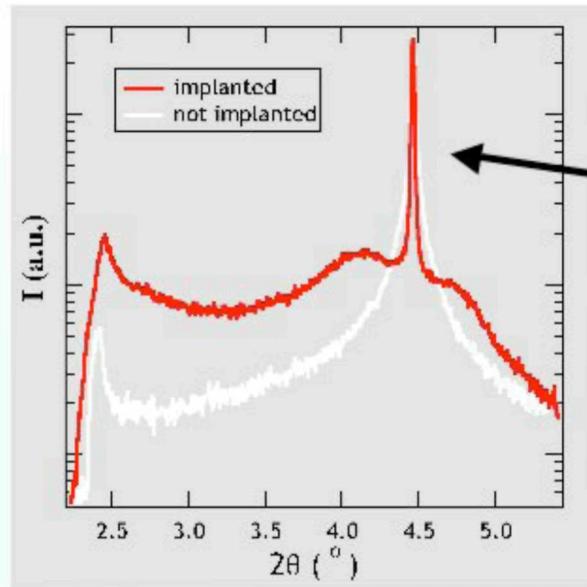
Synthesis and growth of CdS Quantum Dots in SiO₂

GISAXS

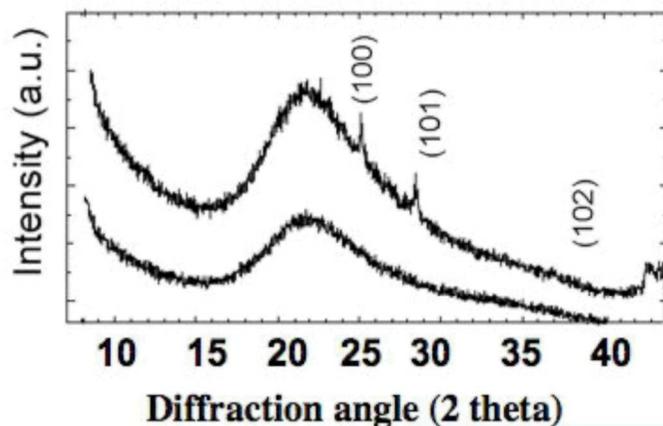
(grazing angle 2.25°) vs. total scattering angle.

Yoneda Peak

(at α_c , due to the maximum in the Fresnel transmission function)



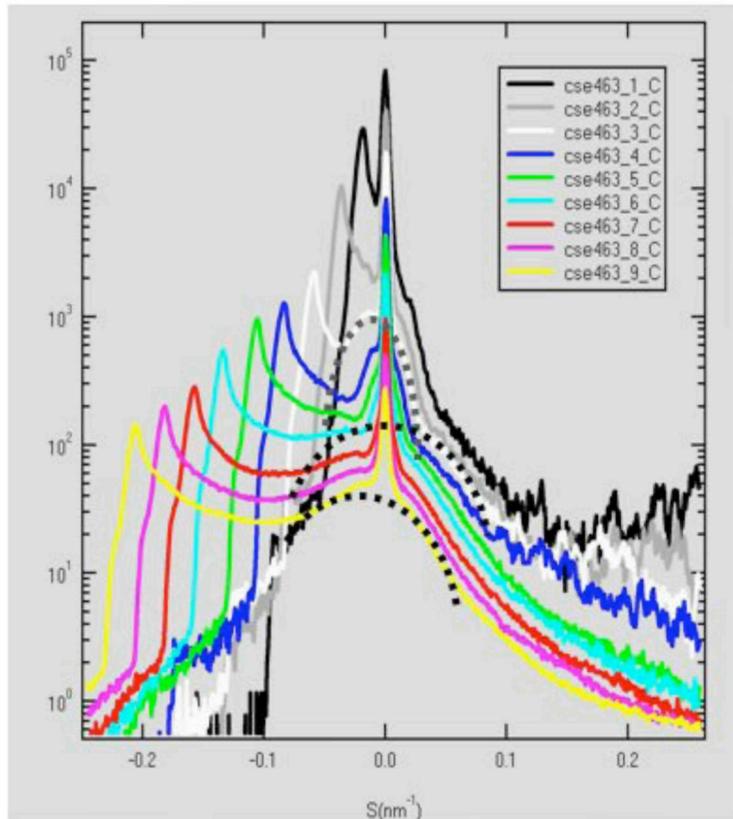
Sharp specular peak
(due to Fresnel reflectivity)



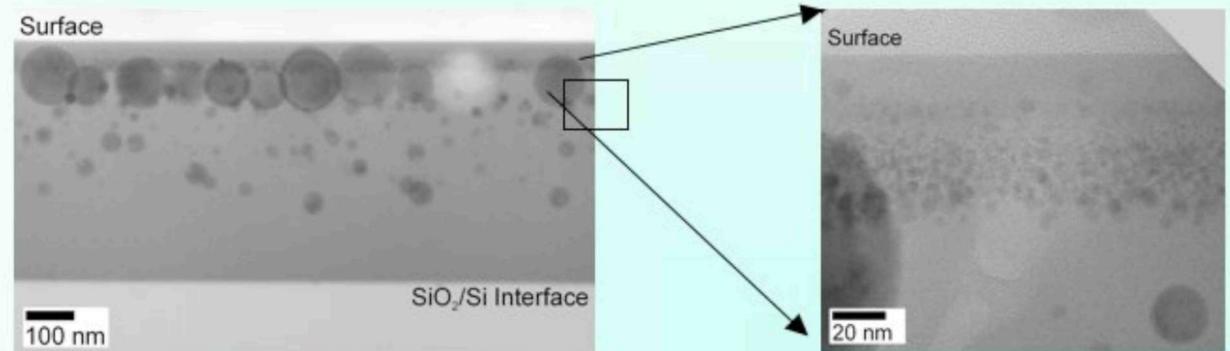
X-ray Diffraction

- Broad signal from amorphous SiO₂ substrate
- Superimposed: sharp peaks identified as CdS (hexagonal)
- Determination of average nanocrystal size (from the broadening of lines)

Bimodal size distribution of particles: GISAXS + TEM



→ depth profiling by small increase of the incidence angle (0.02° step) ↓
closely spaced population of large particles with narrow size distribution $R_G \approx 50 - 60$ nm
shoulder - second group of smaller particles of broader size distribution $R_G \approx 5 - 7$ nm
(**CdSe in SiO₂**, +0% Cd, 800 °C in Ar+H₂)

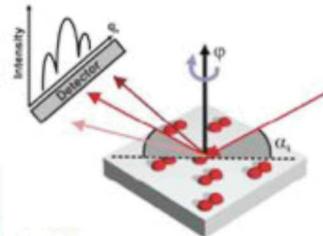


Cross-sectional **TEM** image:

Size distribution for **ZnSe nanocrystals in SiO₂** after annealing at 1000 °C, 30s, Ar. Sample was implanted with 33% surplus Cd. Among large particles positioned at approx. 100nm, there is also a band of small particles with diameters below 10 nm

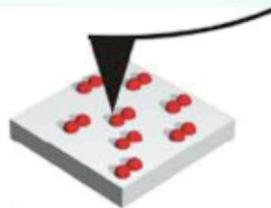
Complementary Methods

GISAXS:

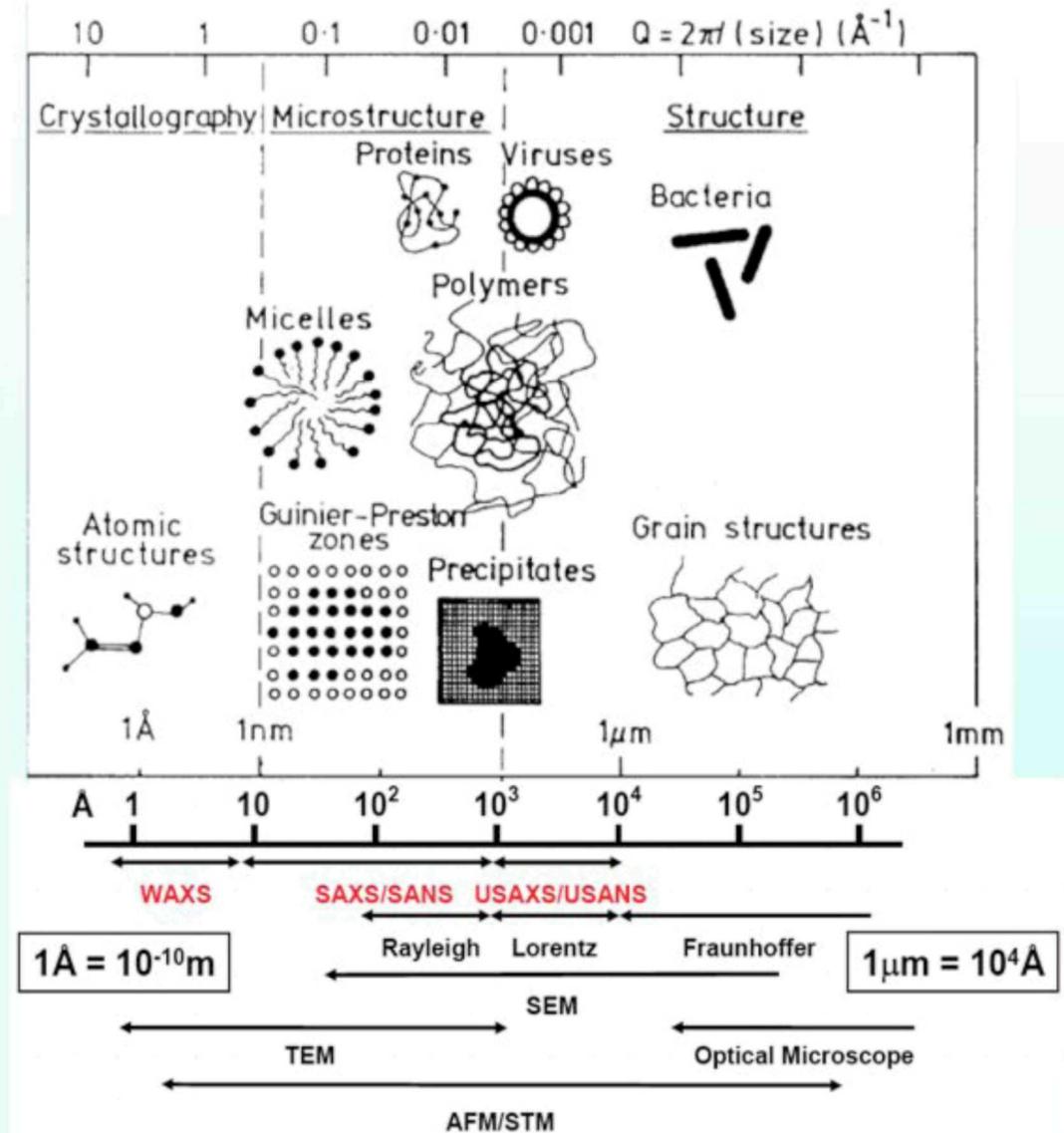


- averages over macroscopic areas, but still yields microscopic information
- lateral and vertical correlations
- intrinsically sensitive to strain
- information about buried objects
- gives reciprocal space information: GISAXS is an indirect method, to find proper models for the data evaluation is crucial
- width of Bragg peaks in X-ray scattering depends not only on the size of the crystalline regions but also on their perfection

Microscopy (AFM, STM, ...):



- sees shape of QD (faceted pyramids, hut clusters, dome-like structures, ...)
- gives real space surface images
- too small sampling statistics for getting size distribution and ordering effects
- strain cannot be detected
- buried dots are not accessible



GISAXS study of Ge islands on a Si(111) substrate

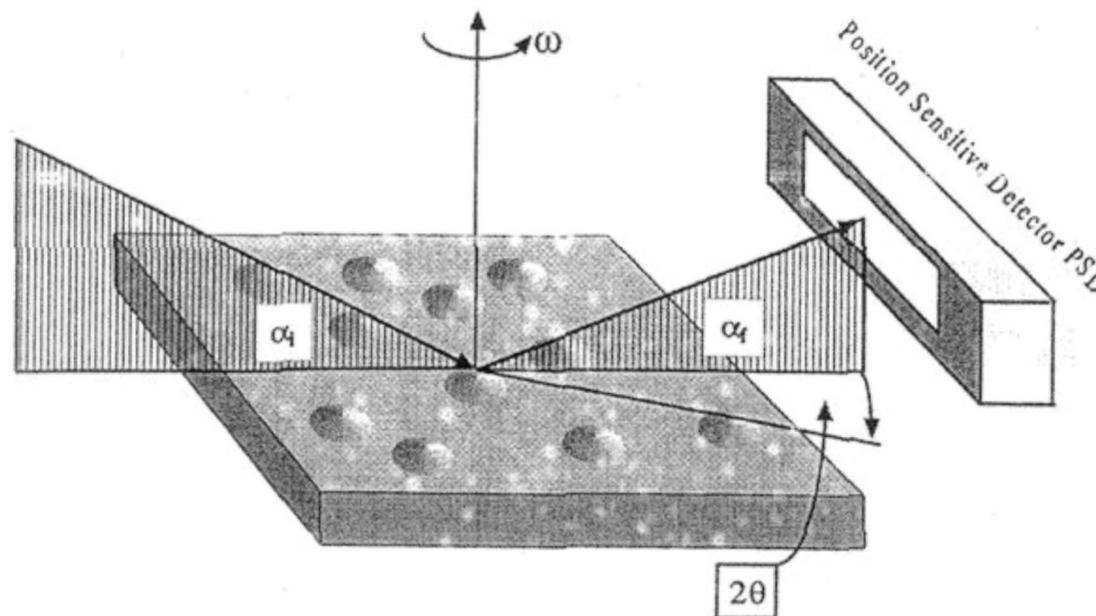
Sample prepared by molecular beam epitaxy at substrate temperature 530°C



15 nm Ge

1/3 layer Boron ($\sqrt{3} \times \sqrt{3}$ reconstruction on Si (111))

150 nm Si

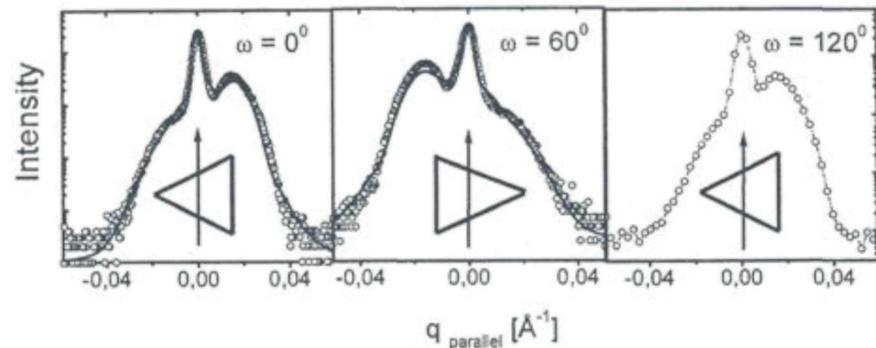


Rotate azimuthal angle ω keeping all other angles unchanged \rightarrow axial symmetry of QD since $q_z \neq 0$

Not possible with transmission SAXS ($q_z = 0$) !

Scattering geometry for grazing incidence small angle scattering (GISAXS). The PSD is placed parallel to the sample surface : collects the small angle signal as a function of $q_{\parallel} = 2\pi/\lambda \sin(2\theta)$ at constant angles of incidence and exit, $\alpha_i \neq \alpha_f$. The axial symmetry the quantum dots are studied by rotating the azimuthal angle ω .

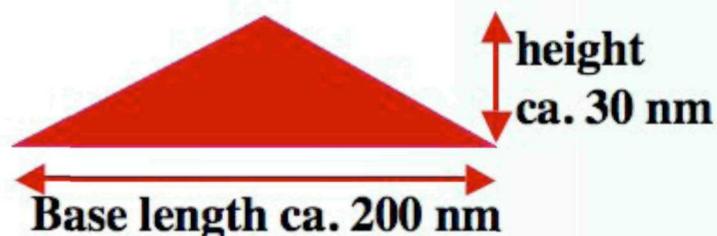
GISAXS study of Ge islands on a Si(111) substrate



GISAXS signal from Ge pyramids on Si(111) for different azimuthal angles as a function of q_{\parallel} . The pyramids possess a threefold symmetry. The full curve is a fit to the experimental data (○○○○) using the structure factor of a pyramid

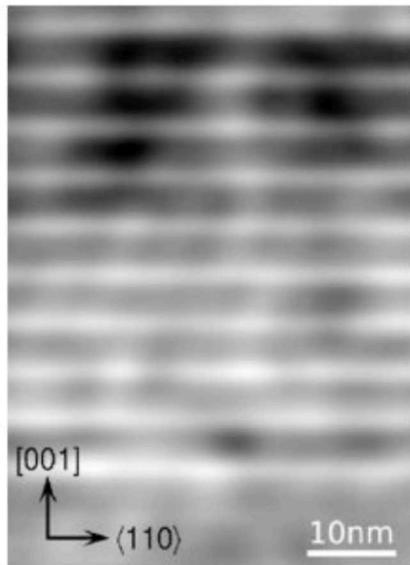
3-fold symmetry of scattering pattern
means
3-fold symmetry of triangular pyramids

- Relation of ω and known cleavage edge direction of the sample -> sides of pyramids are aligned along all possible $\langle 110 \rangle$ directions in the (111) oriented surface plane
- Fit of structure factor to experimental data -> dimensions of the pyramids



AFM (atomic force microscope) -> islands have pyramidal shape with well defined {113} facets; some exhibit also a small (111) terrace on a truncated top

Towards Quantum Dot Laser: the samples



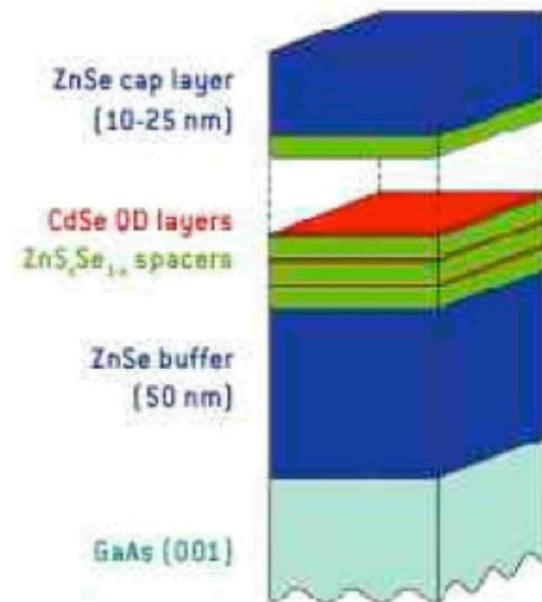
14.5 nm
average QD
distance

← **N QD containing CdSe layers**
← **N+1 strain compensating ternary
spacer layers of thickness d**

Cap layer

Buffer layer

Substrate



**Z-contrast cross section
TEM for 10-fold stack
sample (QD layers: 0.6
nm, spacer: 4.2 nm
 $T_{\text{growth}} = 280 \text{ }^\circ\text{C}$)**

**Samples grown by migration enhanced
molecular beam epitaxy with:**

N = 3, 5 or 10

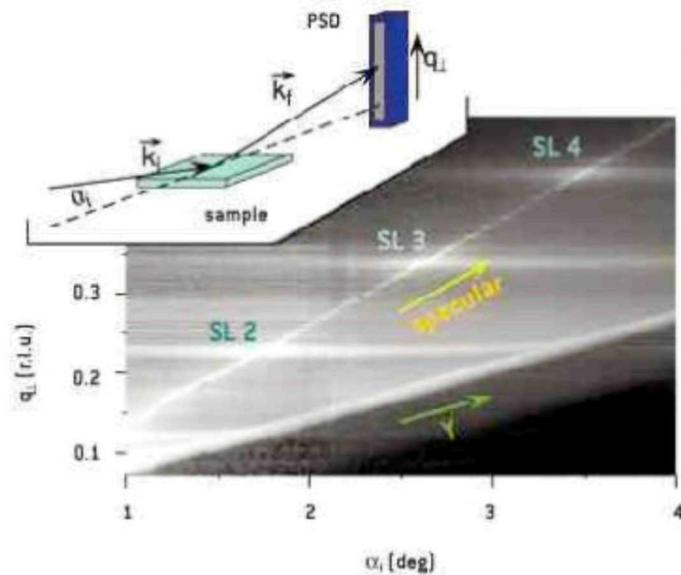
CdSe layers thickness: 1.8 monolayers (i.e. 0.5-0.6nm)

d_{spacer} = fix value in the range 2.0 nm - 8.0 nm

Substrate temperature: 230, 280 or 310 $^\circ\text{C}$

Th. Schmidt et al., Physical Review B72,
195334 (2005)

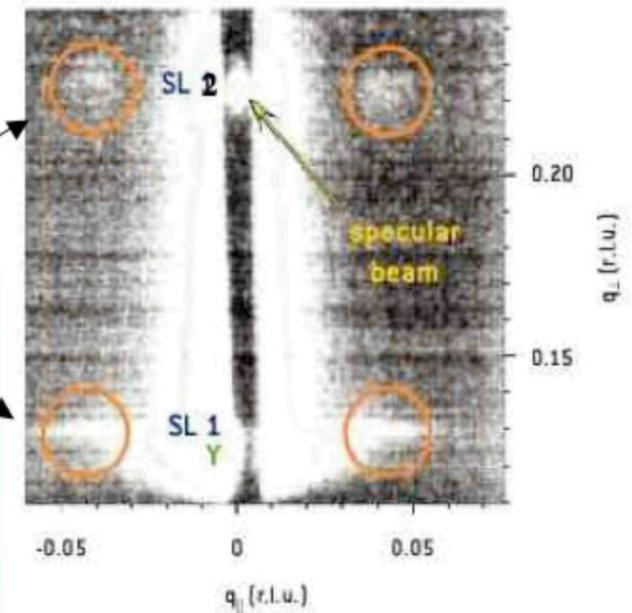
GISAXS reveals CdSe/ZnSse Quantum Dot ordering



Pseudo 2D presentation of 1D spectra taken in dependence of α_i

Bragg peaks of super lattice

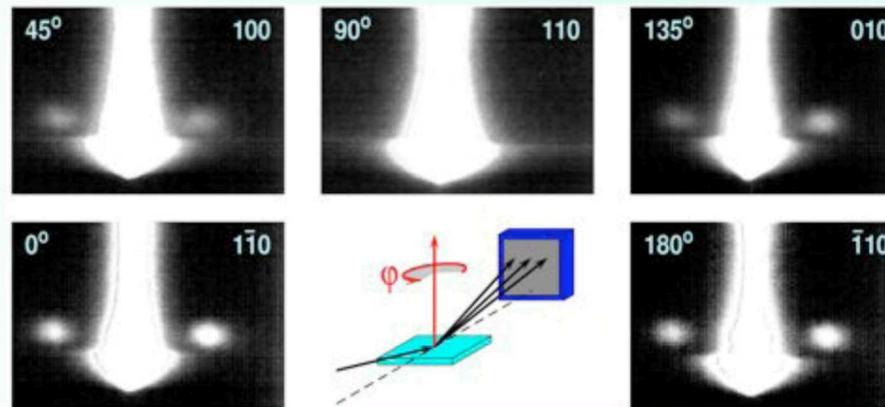
2D GISAXS pattern taken at $\alpha_i = 1.4^\circ$



QD superlattice: degree of ordering depends strongly on growth parameters.

High ordering for:

- Many QD layers
- Adequate layer thickness
- High growth T



10 QD layers a 0.6 nm
4.2 nm spacer

$T_{\text{growth}} = 280^\circ\text{C}$



14.5 nm average QD distance, shape anisotropy

Th. Schmidt et al., Physical Review B72, 195334 (2005)

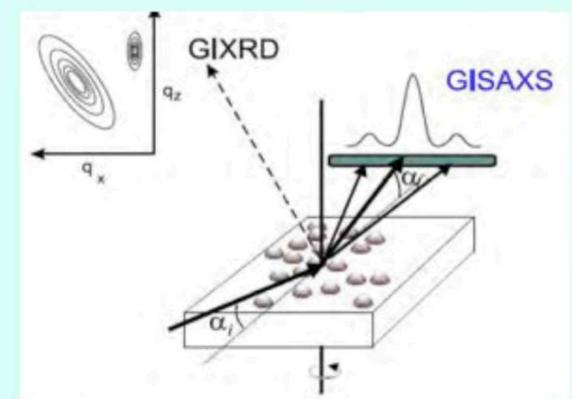
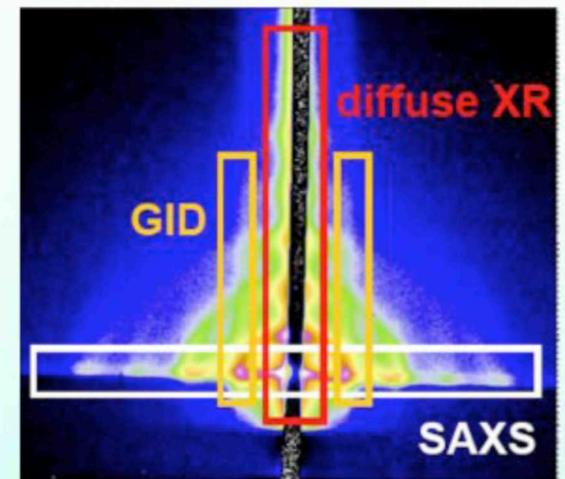
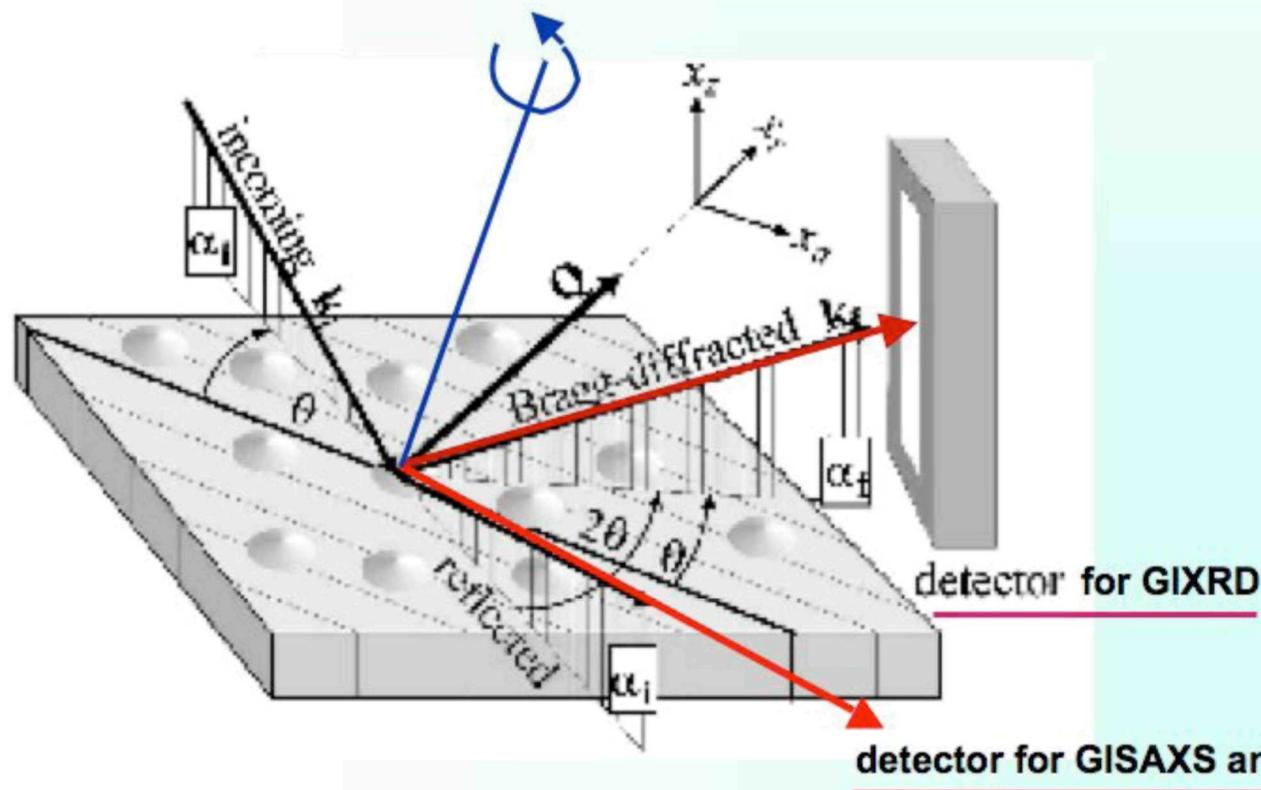
Th. Schmidt, T. Clausen, J. Falta, G. Alexe, D. Hommel, S. Bernstorff, *Elettra Highlight* 2004, p. 63

Grazing Incidence Diffraction (GID)

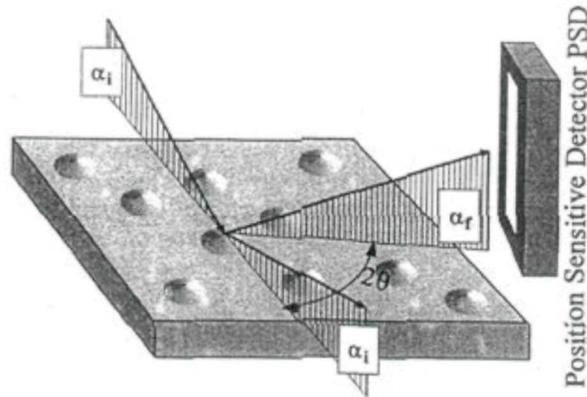
Scattering geometry: defined by directions of incident beam and detector position

To reach diffraction condition: rotate sample about its surface normal so that net-planes make angle Θ with respect to both incident and scattered beam \rightarrow probe long range periodicity parallel to sample surface

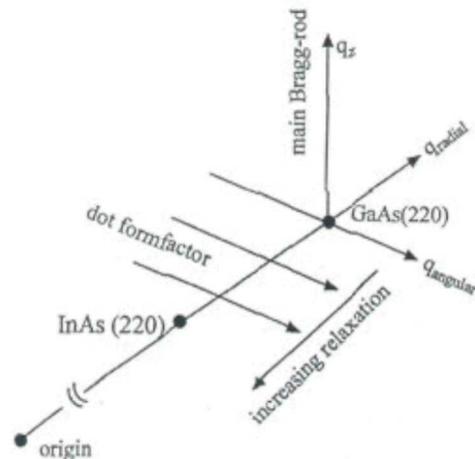
To see reflected beam: $\alpha_i = \alpha_f$, $2\Theta = 0$



Grazing Incidence Diffraction (GID)



Scattering geometry for grazing incidence diffraction to study the crystalline properties of quantum dots. Three-dimensional reciprocal space maps are recorded in this geometry by collecting the scattered intensity as a function of the exit angle α_f , the scattering angle 2θ and the sample angle θ .

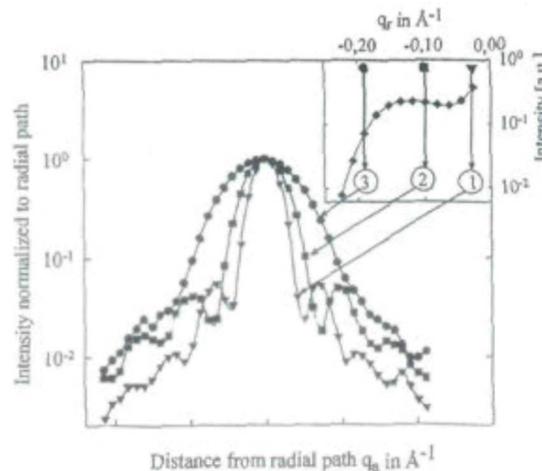


Important directions in reciprocal space close to the (220) surface Bragg reflections of GaAs and InAs. By adjusting q_r the lattice relaxation in the dots is measured, along q_s information on the lateral form factor of the dots is obtained, the q_z -dependence determines the maximum depth and reveals the form factor of the dots in the growth direction.

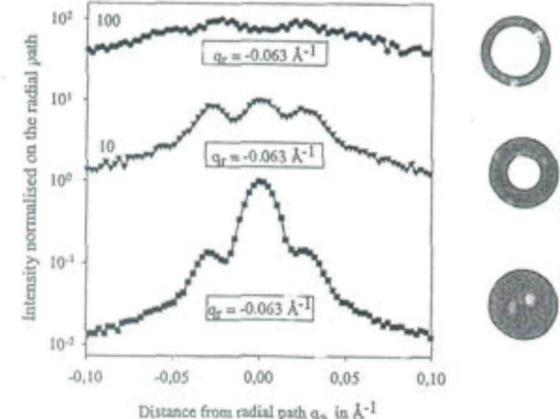
InAs islands grown by molecular beam epitaxy on GaAs(100) at 530°C substrate temperature

GID -> crystalline properties of coherent quantum dots

Analysis of reciprocal space maps -> interdependence of shape and elastic strain within the quantum dots



'Isostrain-scattering' between the (220) surface Bragg reflections of GaAs and InAs. The intensity distribution in angular scans is shown for different radial positions (q_r) as indicated in the inset. The angular dependence (q_s) of the scattering signal is characteristic for the lateral shape of the InAs dots. The central maximum broadens with increasing relaxation $|q_r|$.



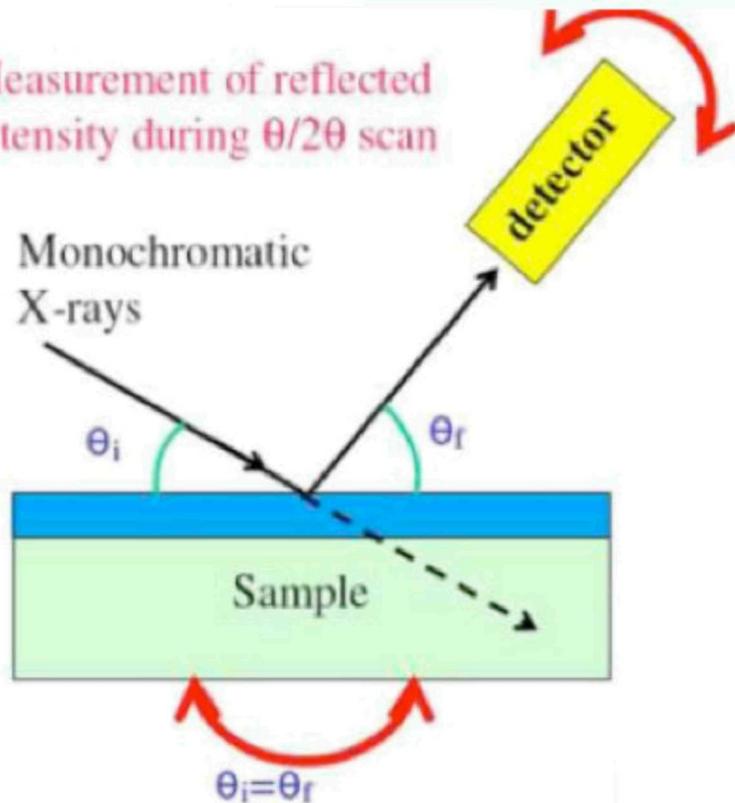
Form factor-induced scattering signal as a function of q_s for ring-shaped InAs islands overgrown by GaAs as a function of the relaxation q_r . The corresponding shapes of the islands are indicated schematically on the right-hand side.

X-ray Reflectivity measurements

Determine

- Surface / interface roughness
- Layer thickness

Measurement of reflected intensity during $\theta/2\theta$ scan



Why layer thickness ?

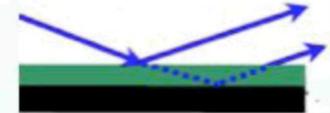
Because function of devices depends on thickness:

- IC (semiconductors)
- Solar cells (photovoltaic materials)
- Displays (liquid crystals)
- Data storage (magnetic multilayer)
- Biomaterial (proteins, lipids -> biochip)
- LED (electroluminescence)
- Coatings and platings (optical materials)

X-ray Reflectivity measurements

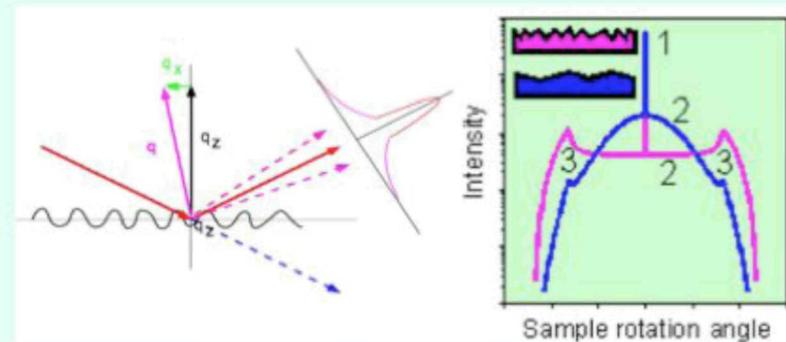
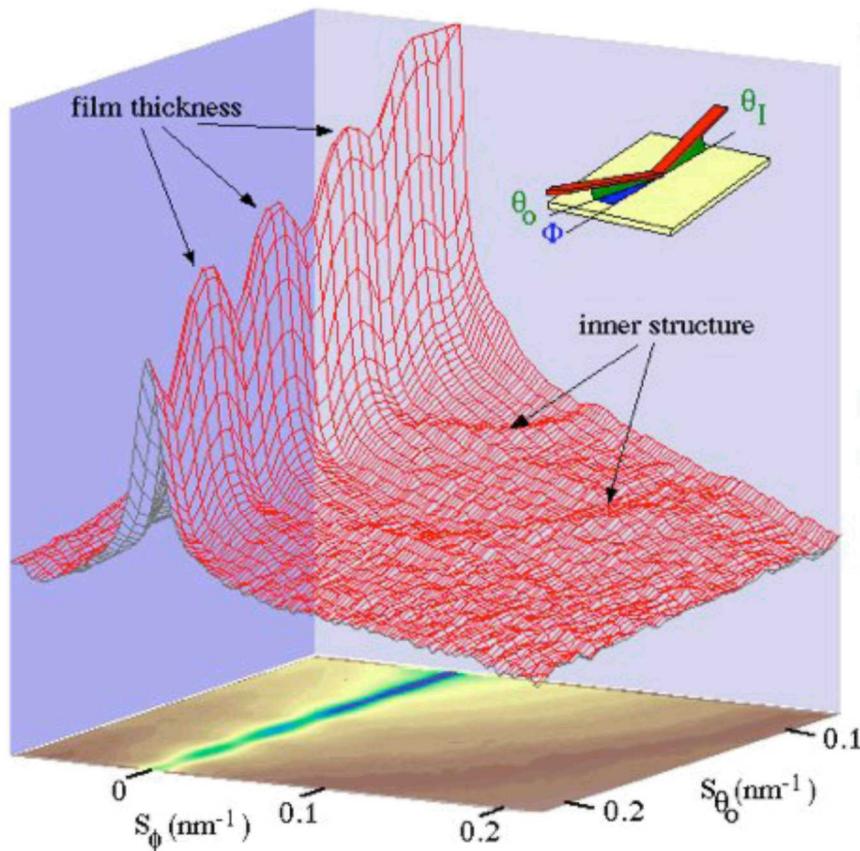
Thin films on substrates:

high correlation between
the film and substrate surface



- interference patterns in the specular plane
- precise film thickness determination

concentric rings around the direct beam direction
correspond to inner structure of the film



Rough surfaces -> diffuse scattering
-> lateral features of the roughness: height-height
correlations

Basic experimental considerations

High photon flux is needed for GI-scattering: Nr. of atoms in interfaces / surfaces is \ll as in bulk ! -> use rotating anodes or synchrotron sources !

Critical angles for e.g. 8 kV photons: --> • very flat substrates needed (e.g. silicon wafers, float glass)
• very flat films (spin coating, dip coating, implanting, ...) needed

organic films $ac = 0.1^\circ \leftrightarrow 1.7 \text{ mrad}$
substrates $ac = 0.2^\circ \leftrightarrow 3.4 \text{ mrad}$

Sample size (length L x width W):

accepted beam height $H = L \times a$

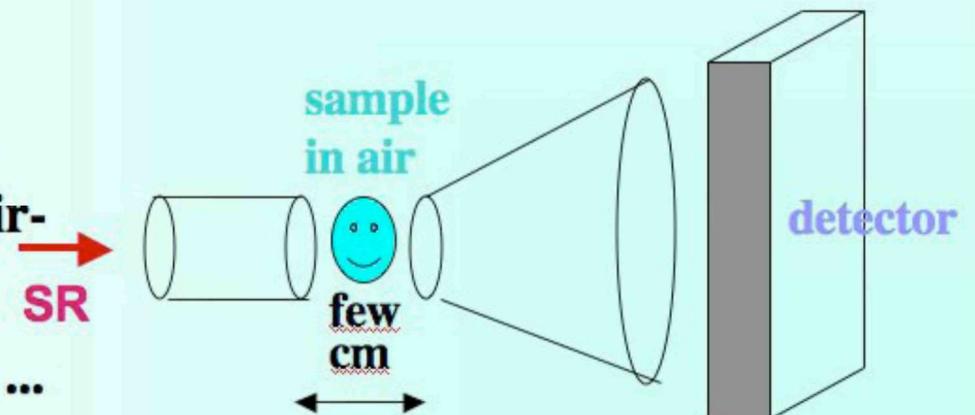
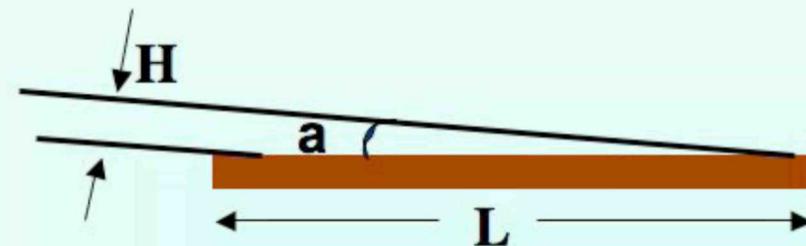
$L = 20 \text{ mm}$, $a = 0.2^\circ \rightarrow H = 70 \text{ mm}$

$W >$ beam width of ca. 5 mm

Sample surrounding

avoid photons scattered from air -> work in vacuum, He-atmosphere, or use very short air-paths

avoid photons scattered from slits, windows, ...



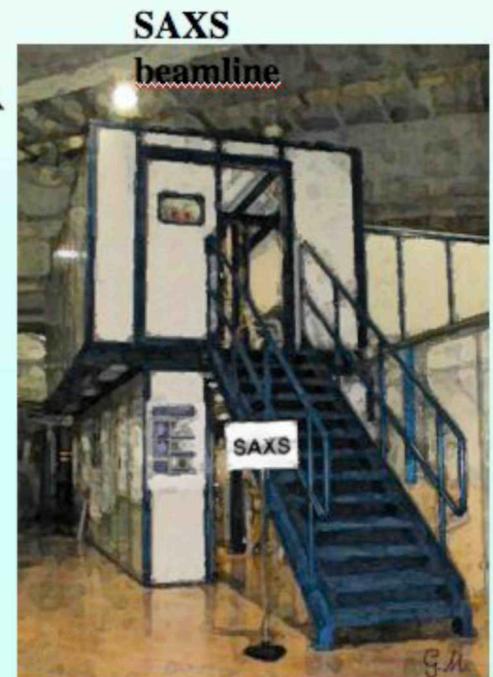
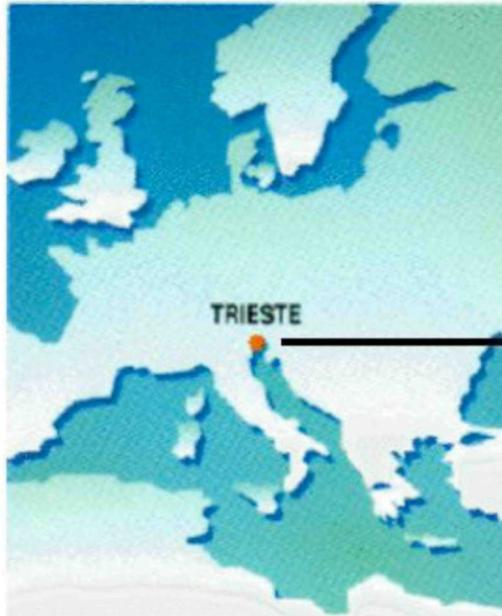
GISAXS is an ideal tool to study:

- non-destructive
- no special sample preparation / samples as prepared (implanted, spin / dip coating, ...)
- in ambient conditions, or under vacuum
- mesoscopic scale: from molecular size to ca 150 nm
- extremely sensitive to lateral and normal structure
- accurate statistical average
- compatible with in-situ experiments (parameters can be temperature, shear, tear, chemical mixing, ...)
- Low-contrast systems possible
- very weakly-scattering samples possible (probe shape and 2D organization of interfaces and QD, of biological molecules deposited on surfaces - > bio-chips, function of selected bio-molecules)

ESSENTIAL

- source providing high flux / brilliance
- 2D detector with high dynamic range, and very low background / noise

Thank you for your attention !



If you now want to perform your own SAXS or GISAXS experiment with SR:

Info: www.elettra.trieste.it
www.ibn.oeaw.at/beamline/

you are also welcome to e-mail me at

bernstorff@elettra.trieste.it

Some useful literature ...

SAXS:

- A. Guinier and G. Fournet, "Small-Angle Scattering of X-rays", Wiley, New York, 1955
- O. Glatter and O. Kratky, editors of "Small-Angle X-Ray Scattering", Academic Press, New York 1982
- L. Feigin and D. Svegun, "Structure Analysis by Small-Angle X-Ray and Neutron Scattering, Plenum Press, New York, 1987
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- H. Brumberger, editor of "Modern Aspects of Small-Angle Scattering", NATO Advanced Series, Kluwer, Dordrecht, 1993
- Manfred's homepage <http://scattering.tripod.com/>

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- T H Metzger, I Kegel, R Paniago and J Peisl, "Grazing incidence x-ray scattering: an ideal tool to study the structure of quantum dots", J. Phys. D: Appl. Phys. 32 (1999) A202-A207
- Till Hartmut Metzger, Tobias Urs Schuelli and Martin Schmidbauer, "X-ray Methods for Strain and Composition Analysis in Self-Organized Semiconductor Nanostructures", lab-neel.grenoble.cnrs.fr/pageperso/fruche/crphys/contrib/metzger.pdf
- Lazzari R., IsGISAXS: a program for grazing-incidence small-angle X-ray scattering analysis of supported islands, J. Appl. Cryst. 35, (2002) 406.
- Salditt T., Metzger T.H. and Peisl J., Kinetic Roughness of Amorphous Multilayers Studied by Diffuse X-Ray Scattering, Phys. Rev. Lett. 73, (1994) 2228.
- Vineyard G. H., Grazing-incidence diffraction and the distorted-wave approximation for the study of surfaces, Phys. Rev. B 26, (1982) 4146.
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- M. Rauscher et al., J. Appl. Phys. 86 (12), 6763 (1999)

Infos on Austrian SAXS beamline at ELETTRA: <http://www.ibn.oeaw.ac.at/beamline/>