X-ray reflectivity and Grazing Incidence Small Angle X-Ray Scattering

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European School on Magnetism
New Experimental Approaches in Magnetism

Constantza, Romania, Sept 7-16, 2005
Introduction

Nanoparticles, nanowires, thin films and multilayers... have New physical properties (e.g. magnetic, but also electronic, catalytic or photonic)

Atomic structure, size, shape & organization

Growth conditions & Morphology, temperature ... of the substrate surface

X-ray complementary to Near Field Microscopy

- non destructive - statistical information over mm scale
- depth sensitivity, from 20 Å up to several mm
- length scale probed: from a few Å to mm
- quantitative analysis
- following in-time: deposit - annealing - gas adsorption
- in situ, in UHV, during growth (and sometimes in real time)
- no charge effects: insulating samples (single crystal oxide substrates)
X-Ray Scattering

Explores Reciprocal Space

\[ \mathbf{q} = \mathbf{k}_f - \mathbf{k}_i = \mathbf{G}_{hkl} \quad \text{vector of the reciprocal space} \]
Reciprocal Space of nanostructures deposited on a substrate

MORPHOLOGY at the nm – 100 nm scale

substrate CTR

On-site M rod

Δq∥/q∥ ~ Δα∥/α∥

ATOMIC STRUCTURE OF NANOPARTICLES

diffraction by adsorbate
d

REGISTRY, i.e. location of adsorbate

Crystal Truncation Rods: interference with adsorbate ==> site, d_{interf.}

GISAXS

Specular reflectivity

z

r (z)

D

(000)

(002)

(111)

(220)

(113)

(222)

(331)

(333)
Grazing Incidence X-ray Scattering (GIXS) or GID

Structure @ atomic scale

- Structure, composition
- Epitaxial relationships
- Relaxation
  - Coherent
  - Incoherent (dislocations)
- Registry / substrate lattice
- Intermixing with substrate
- Substrate distortions
- ...

Grazing Incidence Small Angle X-ray Scattering (GISAXS) and X-R Reflectivity (XRR)

Morphology @ nanometer scale

- Shape (facets, equilibrium shape)
- Dimensions
- Size distributions
- Organization
- Growth mode
- Density profile
- Thin film thickness
- Interface roughness
- Buried layers
- ...

Grazing Incidence X-ray Scattering GIXS (or GID)

Structure @ atomic scale

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Nanostructures (nanoparticles, nanowires, thin films, multilayers ...) & x-rays

**X-RAY METHODS AT GRAZING INCIDENCE**

**STRUCTURE OF THIN LAYERS ON SUBSTRATE**

- Diffracted beam (GID)
  - Crystalline properties
- Reflected beam
  - Density profile
- Diffuse scattering (GISAXS)
  - Morphology of nano islands

Depth resolution: 10nm-200nm
X-Ray Reflectivity: Principle

Visible Light Reflectivity:

\[ n_2 > 1 \]

\[ n_1 < n_2 \]

X-Ray Reflectivity:

\[ n_2 < 1 \]

\[ n_1 > n_2 \]

adapted M. Tolan Univ. Dortmund
Reflection and refraction – Perfect surface

\[ n = 1 \]

\[ E_0 \rightarrow k_i \rightarrow \alpha_i \rightarrow k_f \rightarrow E_r \]

\[ n = 1 - \delta + i\beta \]

\[ \alpha_t = \alpha_i \]

\[ \alpha_t \]

\[ k_i \]

\[ k_f \]

\[ E_0 \rightarrow E_t \rightarrow k_t \]

\[ \exists \text{transmitted wave only if } \cos(\alpha_t) \leq 1, \text{i.e. } \alpha_i \geq \alpha_c \]

If \( \alpha_i \leq \alpha_c \),
- Incident wave totally externally reflected.
- Transmitted wave exponentially damped with \( z \).

\[ \alpha_c = \sqrt{2\delta} = \sqrt{\frac{r_0}{\pi} \times \lambda \times \sqrt{\rho}} \approx 0.1 \text{ to } 0.5^\circ \]

Snell-Descartes law: \( \cos \alpha_i = n \cos \alpha_t \)

\[ \delta = \frac{\lambda^2}{2\pi r_0 \rho} \approx 10^{-4} \text{ to } 10^{-6} \]

\[ \beta = \frac{\lambda}{4\pi \mu} \approx 10^{-6} \text{ to } 10^{-9} \]
Reflection and refraction: perfect surface

- Fresnel equations:

  Relationships between the amplitudes of incident, transmitted and reflected beam.

  Reflection

  \[ r = \frac{E_r}{E_0} = \frac{\sin(\alpha_i - \alpha_t)}{\sin(\alpha_i + \alpha_t)} \approx \frac{\alpha_i - \alpha_t}{\alpha_i + \alpha_t} \]

  Transmission

  \[ t = \frac{E_t}{E_0} = \frac{2\sin(\alpha_i)\cos(\alpha_i)}{\sin(\alpha_i + \alpha_t)} \approx \frac{2\alpha_i}{\alpha_i + \alpha_t} \]

  Amplitude

  Intensity

  \[ R = \left| \frac{E_r}{E_0} \right|^2 \]

  \[ T = \left| \frac{E_t}{E_0} \right|^2 \]
Limiting and asymptotic values for Fresnel equations

Transmission

\[
t = \frac{2\alpha_i}{\alpha_i + \sqrt{\alpha_i^2 - 2\delta}} \approx \frac{2\alpha_i}{\alpha_i + \alpha_i(1 + \frac{1}{2}\frac{2\delta}{\alpha_i^2})}
\]

\[t \approx \frac{2\alpha_i}{\alpha_i + \frac{2\delta}{\alpha_i}} \approx \frac{\alpha_i}{\delta} \quad \text{for} \quad \alpha_i < \sqrt{2\delta}
\]

\[t \approx \frac{2\alpha_i}{2\alpha_i} = 1 \quad \text{for} \quad \alpha_i >> \sqrt{2\delta}
\]

Reflection

\[
r = \frac{\alpha_i - \sqrt{\alpha_i^2 - 2\delta}}{\alpha_i + \sqrt{\alpha_i^2 - 2\delta}} \approx \frac{\alpha_i - \alpha_i(1 + \frac{1}{2}\frac{2\delta}{\alpha_i^2})}{\alpha_i + \alpha_i(1 + \frac{1}{2}\frac{2\delta}{\alpha_i^2})}
\]

\[r = 1 \quad \text{for} \quad \alpha_i << \sqrt{2\delta}
\]

\[r \approx \frac{\delta}{2\alpha_i^2} \quad \text{for} \quad \alpha_i >> \sqrt{2\delta}
\]

Amplitude

Intensity

\[Q_z = \frac{4\pi}{\lambda} \sin \Theta_1\]

\[T(q_z) = t^2\]

\[T = t^2\]

\[R_F = r^2\]

\[R_F(q) = \frac{64\pi^4}{\lambda^4} \frac{\delta^2}{q^4}\]

\[Q_c = \frac{4\pi}{\lambda} \sin \Theta_1\]
Exact evaluation of Fresnel reflectivity

\[ R_F(\alpha_i) = |r|^2 = \frac{(\alpha_i - p_+)^2 + p_-^2}{(\alpha_i + p_+)^2 + p_-^2} \]

\[ \alpha_t = p_+ + i p_- \]

\[ p_{+/\text{--}}^2 = \frac{1}{2} \left\{ \sqrt{\left( \alpha_i^2 - \alpha_c^2 \right)^2 + 4\beta^2} \pm (\alpha_i^2 - \alpha_c^2) \right\} \]

→ Absorption \( \beta \) also play a significant role
Fresnel Reflectivity: $R_F(\alpha_i)$ with absorption

Total External Reflection Regime

$Q_z^{-4} = (4\pi/\lambda \sin \alpha_i)^{-4}$
Transmission Function with absorption

\[ T_F = |t|^2 \]
Penetration Depth with absorption

\[ L_{i,f} = \frac{1}{\text{Im}(k_{t,z})} = \frac{\lambda}{2\pi l_{i,f}} \]

\[ l_{i,f} = \frac{1}{\sqrt{2}} \left\{ \left( 2\delta - \sin^2 \alpha_{i,f} \right) + \left[ (\sin^2 \alpha_{i,f} - 2\delta)^2 + 4\beta \right]^{1/2} \right\}^{1/2} \]
The geometry of X-ray reflectivity

Transferred momentum:
\[ \vec{q} = \vec{k}_f - \vec{k}_i \]

Reflectivity:
\[ q_x = q_y = 0 \]
\[ q_z = \frac{(4\pi/\lambda)}{\sin \alpha_i} \]

Diffuse Scattering:
\[ q_x, q_y \neq 0 \]
\[ q_z = \frac{(4\pi/\lambda)}{\sin (\alpha_i + \alpha_f)/2} \]

\[ \alpha_i, \alpha_f < 5^\circ \]
Helmholtz equation

\[
\Delta E(\vec{r}) + k^2 n_X^2(\vec{r}) E(\vec{r}) = 0
\]

Formal solution:

\[
n(z) = 1 - \frac{\lambda^2}{2\pi} r_e \varrho(z) + i \frac{\lambda}{4\pi} \mu(z)
\]

- Electron density profile

- X-ray reflectivity: main equation

Adapted from M. Tolan, Univ. Dortmund
Reflectivity from multilayers

Multiple scattering (dynamical calculation)

Matrix formalism:

Parrat iterations
Parrat, 1954

adapted M. Tolan  Univ. Dortmund
Reflectivity used as an everyday laboratory tool to measure the thickness of layers deposited on a substrate.

Ref: M. Tolan, Univ. Dortmund

Reflectivity from layer on substrate. Ex: PS on Si

\[ d = \frac{2\pi}{\Delta q_z} = \frac{\lambda}{2\Delta \alpha_i} \]

- \( E = 8 \text{ keV} \)
- \( d = 800\text{Å} \)
- \( \lambda = 1.54\text{Å} \)
Rough interfaces: statistics

\[ n_j = 1 - \delta_j + i\beta_j \]

\[ n_{j+1} = 1 - \delta_{j+1} + i\beta_{j+1} \]

Probability Density

\[ P_j(z) = \frac{1}{\sqrt{2\pi}\sigma_j} \exp\left(\frac{-z^2}{2\sigma_j^2}\right) \]

Integration

Refractive Index Profile \( n(z) \)

Electron Density Profile \( \rho(z) \)

adapted M. Tolan   Univ. Dortmund
Reflectivity by a rough surface: which roughness?

Same Roughness $\sigma$ & Refractive Index Profile $n(z)$!

Lateral Structure Different

Different Averaging Procedures: $\sigma/\xi_p < 1$ or $\sigma/\xi_p > 1$
Roughness in multilayers?

Beckmann-Spizzichino Result (1963):

\[
\begin{align*}
\tilde{r}_{j,j+1} &= r_{j,j+1} e^{-2k_{z,j}^2 \sigma_j^2} \\
\tilde{t}_{j,j+1} &= t_{j,j+1} e^{-(k_{z,j} - k_{z,j+1})^2 \sigma_j^2/2}
\end{align*}
\]

Nevot-Croce Result (1980):

\[
\begin{align*}
\tilde{r}_{j,j+1} &= r_{j,j+1} e^{-2k_{z,j} k_{z,j+1} \sigma_j^2} \\
\tilde{t}_{j,j+1} &= t_{j,j+1} e^{+(k_{z,j} - k_{z,j+1})^2 \sigma_j^2/2}
\end{align*}
\]

\( \sigma_j \rightarrow \text{Exponential Damping of Reflectivity!} \)
\[ R(q_z) = R_F(q_z) \exp(-q_z^2 \sigma^2) \]

- Reflectivity very efficient to measure (small) (statistically averaged) roughness of surfaces or interfaces.
Roughness at several interfaces

**Parratt-Iteration & Roughness:**

\[
\sigma_1 \quad \sigma_2
\]

Interference:
\[
d = \frac{2\pi}{\Delta q_z} = \frac{\lambda}{(2\Delta \alpha_i)}
\]

Damping:

Roughness \( \sigma_1, \sigma_2 \)
Thin film with surface and interface roughness. Example: PS layer on Si, with roughness

Effects of surface and interface roughness very different

$\sigma_1$, $\sigma_2$ and $d$ can be determined independently
Reflectivity calculation for arbitrary density profiles

\[ \delta(z) \approx \sum_j (\delta_j - \delta_{j-1}) \]

- Slicing & Parratt-Iteration
- Reflectivity from Arbitrary Profiles!
- Drawback: Numerical Effort!
Example of fit of reflectivity curve:

adapted M. Tolan  Univ. Dortmund
Simpler approach: Kinematical approximation

\[ \bar{q} \]

\[ d \bar{l} \sim \rho(\bar{r}) \, dV \]

\[ I(\bar{q}) \propto \left| \int \rho(\bar{r}) \exp(i \bar{q} \cdot \bar{r}) \, d\bar{r} \right|^2 \]

Multiple Scattering Negligible!
The «master» formula

\[ I(\vec{q}) \propto \left| \int \varrho(r) \exp(i \vec{q} \cdot \vec{r}) \, d\vec{r} \right|^2 \]

Reformulation for Interfaces

\[ R(qz) = R_F(qz) \left| \frac{1}{\varrho_\infty} \int \frac{d\varrho(z)}{dz} \exp(i qz z) \, dz \right|^2 \]

Fresnel-Reflectivity of the Substrate

Electron Density Profile

Example: roughness

\[ \rho'(z) = \frac{1}{\sqrt{2\pi} \sigma} \exp\left(-\frac{z^2}{2\sigma^2}\right) \Rightarrow R(q) = R_F(q) \exp\left(-q^2 \sigma^2\right) \]
Kinematical versus dynamical calculation

\[ R(q_z) = R_F(q_z) |F(q_z)|^2 \]

„Phase Problem“ Data Fitting!
Pb: Loss of the phase:

Different ways to solve the phase problem:
- Inclusion of pre-knowledge
- Anomalous reflectivity
Ex: Multilayers:

- Complex index profile

\[ \sin \theta_B = \frac{\lambda}{2d} \]

\[ \Delta \theta = \frac{\lambda}{2Nd} \]

\[ x_N \]

X-ray reflectivity used to characterize the thickness, period and roughnesses of multilayers.
Rough surfaces $\rightarrow$ diffuse scattering

$Lateral$ $features$ $of$ $the$ $roughness$ $–$ $Height$-$height$ $correlations$
Ex.: Roughness correlations in multilayers?
Conclusions on reflectivity

Specular reflectivity measures
- average density (mass and electron density)
- layer thicknesses
- interface roughness

Off-specular reflectivity probes
- Height-height correlations
- lateral order at nanometer-micrometer scale

- Refraction under grazing incidence
  ➔ tuneable scattering depth
**Why GISAXS?**

**GISAXS**
- Statistical information
- Lateral and vertical correlation
- Shape as seen by x-rays: input for diffraction experiments
- Information about buried objects

**AFM / STM**
- Local information
- Detailed shape
Example: 20 Å Ag/MgO(001) 500K

Anisotropic islands: truncated square pyramids with (111) facets

Standard 3D growth (Volmer-Weber)

2D image around direct beam: Fourier transform of objects

Morphology
- Shape
- Sizes
- Size distributions
- Particle-particle pair correlation function

Grazing Incidence Small Angle X-ray Scattering (GISAXS)

Principle
Off-specular reflectivity:

Probed length scales?
La géométrie de diffusion : GISAXS et réflectivité

Le GISAXS ou comment mesurer des distances de l’ordre du nanomètre avec des rayons X ?

Le transfert de moment : grandeur pertinente ?

\[ \vec{q} = \vec{k}_f - \vec{k}_i \]

### GISAXS

\[ \lambda = 1 \text{Å} - E = 12 \text{keV} \]
\[ \alpha_i = \alpha_f / 2 = 0.2^\circ \]
\[ 2 \theta_f = 1^\circ \]
\[ q_x = -0.011 \text{ nm}^{-1} \Rightarrow d_x = 580 \text{nm} \]
\[ q_y = 1.1 \text{ nm}^{-1} \Rightarrow d_y = 5.7 \text{nm} \]
\[ q_z = 0.66 \text{ nm}^{-1} \Rightarrow d_z = 9.5 \text{nm} \]
Small angles of incidence and exit: plane of incidence

\[ \mathbf{q} = \mathbf{k}_f - \mathbf{k}_i \]

Specular direction: \( \alpha_f = \alpha_i \):
\[ q_z = \frac{4\pi}{\lambda} (\sin \alpha_i) = \frac{2\pi}{d} \]

\[ q_x = \left(\frac{2\pi}{\lambda}\right)(\cos \alpha_f - \cos \alpha_i) \]
\[ q_z = \left(\frac{2\pi}{\lambda}\right)(\sin \alpha_f + \sin \alpha_i) \]

Lengthscales \( d \): lateral and vertical

\[ \lambda = 1.54 \text{Å} \quad \alpha_i = 0.5^\circ \quad d_x = 2\pi/ q_{x, \text{max}} \leq \lambda / (\cos \alpha_f - 1) \approx 10 000 \text{ Å} \]

\[ d_z = 2\pi/ q_z, \approx 20 \text{ Å for} \quad \alpha_f = \alpha_i \]
GISXAS or how to measure \textbf{nm} lateral lengthscales

\[ Q = k_f - k_i \]
\[ q_x = \frac{2\pi}{\lambda} (\cos \alpha_f \cos 2\theta - \cos \alpha_i) \]
\[ q_y = \frac{2\pi}{\lambda} (\cos \alpha_f \sin 2\theta) \]
\[ q_z = \frac{2\pi}{\lambda} (\sin \alpha_f + \sin \alpha_i) \]

Lengthscales \( d \): lateral
\[ \lambda = 1.54\text{Å} \quad 2\theta = 2^\circ \quad \alpha_f = 0.5^\circ \]
\[ d_y = \frac{2\pi}{q_y} \leq \frac{\lambda}{(\cos \alpha_f \sin 2\theta)} \approx 44 \text{ Å} \]

Out-of-plane scattering suited for nanostructure investigations
“No” limitation in \( 2\theta \): \( d \) from 100nm to 0.1nm
\[ Q_x = 2k \sin \theta \sin (\omega - \theta) \]
\[ Q_z = 2k \sin \theta \cos (\omega - \theta) \]

As the scattered intensity usually drops quite fast as a function of \( Q_z \), the range of lateral momentum transfer is limited. Typically achievable scattering angles are in the order of \( 2\theta = 3^\circ \). This puts an upper limit to the accessible range of lateral structure dimension:

\[ dq > \frac{2\pi}{|Q_{x,\text{max}}|} \approx \frac{\pi}{k \sin^2 \theta} \]

Using \( 2\theta = 3^\circ \) and \( k \approx 4 \text{ Å}^{-1} \) (for copper radiation), we obtain \( |Q_{x,\text{max}}| \approx 0.005 \text{ Å}^{-1} \), i.e., XRR is suitable only for the investigation of lateral structures with dimensions \( d \geq 1000 \text{ Å} \) (this value depends, of course, on the wavelength and on how rapidly the intensity drops with \( Q_z \), which depends, e.g., very sensitively on surface and interface roughnesses).

usually named \( \alpha_i \), the exit angle is \( \alpha_f \) correspondingly. The reciprocal space coordinates are given by the relations

\[ Q_x = k(\cos \alpha_i - \cos \alpha_f \cos 2\theta) \]
\[ Q_y = k \cos \alpha_f \sin 2\theta \]
\[ Q_z = k(\sin \alpha_i + \sin \alpha_f) \]

\( Q_z \) is equivalent to the corresponding expression in XRR, Eq. (2.2), but now \( Q_z \) is very small, zero, and \( Q_y \) is finite instead. Hence for the determination of parameters of the very fine sample structure, XRR and GISAXS are equivalent. However, as is obvious from Fig. 10, no restriction of \( Q_y \) due to the Laue zones exists, and consequently GISAXS is the method of choice for the investigation of small lateral structures \( (d < 1000 \text{ Å}) \). As a "prize" for the enlarged range of lateral momentum transfer, the lateral resolution is much smaller than for XRR:

\[ |\Delta Q_y| = |\frac{\partial Q_y}{\partial \theta}| \Delta \theta + |\frac{\partial Q_y}{\partial \alpha_f}| \Delta \alpha_f = \]
\[ = 2k \cos \alpha_f \cos 2\theta \Delta \theta + k \sin \alpha_f \sin 2\theta \Delta \alpha_f \]
\[ \approx 2k (\Delta \theta + \alpha_f \theta \Delta \alpha_f) \]
\[ |\Delta Q_y| \approx 1.5 \cdot 10^{-3} \text{ Å}^{-1} \]
Quantitative analysis of GISAXS

\[ I(q_{//}, q_{\perp}) \approx \left\langle |F|^2 \right\rangle \times S(q_{//}) \]

Form factor: a kind of shape FT with refraction effects

Interference function: FT of pair correlation function

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

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

- Cylinder
- Troncated sphere
- Pyramid
- Tetraedron
- Cubooctaedron

\[ F_{DWBA}(q_{//}, k_i, k_f) \]
Analyse quantitative du signal GISAXS

$I(\vec{q}) = \left| F \right|^2 S(q_{||})$

Facteur de forme

- $k_f^z - k_i^z$
- $k_f^z + k_i^z$
- $k_i^z - k_f^z$
- $k_i^z + k_f^z$

Forme, taille et orientation

- cylindre
- sphère tronquée
- pyramide
+ distributions

Fonction d'interférence

$S(q_{||}) = TF \left\{ \text{Fonction de corrélation de paires} \right\}$

Arrangement spatial

- réseau
- modèle de désordre (paracristal...)

distance moyenne + distribution de distances

/SGISAXS program :
http://www.esrf.fr/computing/scientific/joint_projects/IsGISAXS/
Growth of Au on TiO$_2$(110)

STM pictures

Goodman et al.

12 Å flashed annealed @ 800K

Experiment

Simulation

α$_f$

\( q_y \) (nm$^{-1}$)

\( q_z \) (nm$^{-1}$)

\( \sin(2\theta) \times 10^3 \)

\( \sin(\alpha_f) \times 10^3 \)

\( R = 2.9 \text{ nm} \ s_R(\text{log normal}) = 1.2 \)

\( H = 4.9 \text{ nm} \ s_H(\text{gaussian}) = 0.1 \)

\( r = 9.1 \times 10^{11} \text{ part/cm}^2; q_c = 132^\circ \)
Equilibrium shape of particles. Ex: 1.5nm Pd/MgO @ 650 K

Fit with truncated octaedron

Equilibrium island shape

D=22±0.2nm

d=11.4±0.4nm - σ_{FWHM}=6nm

h=6.2±0.4nm - σ_{FWHM}=0.8nm

h_{(001)}/d=0.46

h/d=0.62 ±0.2

H/d = cte = 0.62

Wulff’s construction

Adhesion energy from GISAXS:

β=1.12 J/m²

To be compared with TEM : β = 0.95 J/m²

GISAXS → Equilibrium shape, in situ, non destructively during growth


Self-organized growth: systems

3 main types of surface structuration

Surface reconstruction
Co dots on Au(111)
B. Voigtländer et al.

Vicinal surface
Co wires on Pt(997)
P. Gambardella et al.
Nature 416 (2002) 301

Dislocation Network
Fe islands on a bilayer of Cu/Pt(111)
H. Brune et al.
• Self-organized growth of cobalt islands on a 
  –Au(677) kinked surface
The kinked Au(677) surface

STM image (S. Rohart (GPS, Paris))

Scattering rods from steps

Ordered kinks

Reconstruction period ~ 8 nm

3D Measurements of reciprocal space by GISAXS

Map of reciprocal space at $q_\perp=0$

- $\omega+0^\circ$
- $\omega+1^\circ$
- $\omega+2^\circ$
- $\omega+3^\circ$
- $\omega+4^\circ$
- $\omega+6^\circ$
- $\omega+7^\circ$
- $\omega+8^\circ$
- $\omega+9^\circ$
- $\omega+10^\circ$
- $\omega+11^\circ$
- $\omega+12^\circ$
- $\omega+13^\circ$
- $\omega+14^\circ$

Intensity (log)

$K_1$ (nm$^{-1}$)

$\pi/2 - \epsilon$

(11)

(12)

(10)

(20)

(02)

(01)

Steps

$K_2$ (nm$^{-1}$)

$q_x$ (nm$^{-1}$)

$q_\parallel$ (nm$^{-1}$)

$\alpha$

$\omega$
Modelisation of a kinked Au(677) surface

**Principle:** Paracrystal

**Steps**
- \( D_{\text{step}} = 3.42 \pm 0.23 \text{ nm} \)

**Kinks position**
- \( D_{\text{kink}} = 8.04 \pm 0.62 \text{ nm} \)
- \( L = 0 \pm 0.3 \text{ nm} \)

**Kinks size**
- \( k = 0.7 \pm 0.35 \text{ nm} \)

Determined by the reconstruction

Monoatomic kinks
- Packed by 3\( \pm 1.5 \)

**Shape and size of kinks**

\[
I(\vec{q}) = \left[ 4 \sin \left( \frac{q_z h}{2} \right) \sin \left( \frac{q_x k}{2} \right) \right]^2 \frac{q_x q_y q_z}{q_x q_y q_z}
\]

**Elementary object**

\( h \)

\( k \)
GISAXS data and fits

(10L) rods: steps

(01L) rods: kinks

(11L) rods: crossed

Data

Intensité (photons)

Fits

Intensité (photons)

Δq_// (nm⁻¹)

q_⊥ (nm⁻¹)

q_∥ (nm⁻¹)
Co growth at room temperature

STM image
S. Rohart (Au(788) surface)

0.5ML

100 nm

Model

Top view
Side view

Shape and size

Position

Island position
• in between kinks
• at the step edge

Shape and size
• anisotropic growth
• bilayer islands

STM image

0.5ML

100 nm

Shape and size

Position

Island position
• in between kinks
• at the step edge

Shape and size
• anisotropic growth
• bilayer islands
Self-organized growth: Systems

3 main surface structuration

Surface reconstruction
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Vicinal surface
Co wires on Pt(997)

Dislocation Network
Fe islands on a bilayer of Co dots on a dislocation network buried at the Ag/MgO(001) interface
• Self-organized growth of cobalt islands on a dislocations network at the Ag/MgO(001) interface
Ordering of nanostructures induced by a dislocation network: principle

- Misfit dislocation network

\[
\frac{a_{\text{MgO}} - a_{\text{Ag}}}{a_{\text{Ag}}} = 3\%
\]

\[\Delta = 10 \text{ nm}\]

- Significant surface strain if: \( H < \Delta \)
Ag/MgO(001) ultra-thin film: *in situ* GIXS, XRR and GISAXS

1. Growth of 100 nm Ag(001)/MgO

![Diagram showing growth of Ag(001)/MgO](image)

- 10 nm Ag film of homogeneous thickness, with an ordered array of dislocations
- Very low roughness
- Large terraces (100 nm)

2. Annealing 900 K

![Graph showing dislocation peaks](image)

- Ordered dislocation network
- Very low roughness
- Large terraces (100 nm)

3. Ion Beam thinning down to 5 nm while keeping large terraces and low roughness.

![Diagram showing ion bombardment](image)

4. Co Deposition

- Room temperature: trap energy >> thermal energy
- Deposition rate (0.05 Å/min): diffusion length of Co adatoms >>10 nm

![Graph showing reflectivity](image)
Self-organized growth of magnetic cobalt dots on an interfacial dislocation network: Co/Ag/MgO(100)
Position of Co islands / dislocation cores

\[ I(\vec{q}) - I_{\text{disloc}}(\vec{q}) = I_{\text{Co}}(\vec{q}) + 2\sqrt{I_{\text{disloc}}(\vec{q}) \times I_{\text{Co}}(\vec{q}) \times \cos q} \]

After - before negligible

Intensities (photons)

Simulations
Size and shape evolution of Co dots upon deposition time

\[ I_{\text{interference}}(\vec{q}, \text{time}) = 2 \sqrt{I_{\text{disloc}}(\vec{q}) \times \cos(\vec{q}_//d_// + q_\perp H)} \]

Interference\( (q_\perp, \text{time}) \)

Fit: 2ML height islands
Conclusions

GISAXS for the first time in situ during growth
- Combined with GIXS → Atomic structure + Morphology
- Quantitative information on nano-particles shape/size/ordering
- Very sensitive to the ordering of nanostructures

In situ surface X-ray diffraction and GISAXS combined for determining conditions for ordering of Co islands on a Ag/MgO dislocation network

Determination of the nucleation site, size and shape of islands during organized growth of:
- Co on Au(111)
- Co on kinked Au(677) : in between kinks and at the step edges
- Co on Ag/MgO(001) : upon the dislocation core
Potential and future directions

- GISAXS extremely sensitive to the very premisses of organization
  - used to monitor organized growth in real-time and quickly reach the right thermodynamical and kinetic conditions for the organization.

- *In situ* studies during
  - surface reactivity (e.g. catalytic reactions, annealings ...)
  - growth (during MBE, (MO)CVD, LPE);
  - use of gaseous, liquid or solid surfactants, at High p, T ...

- Eventually probing the shape & 2D organization of biological molecules deposited on surfaces?
  
  ➔ Conformation and function of selected bio-molecules?
La section efficace de diffusion en GISAXS et l’approximation de l’onde distordue DWBA

- « petits angles »  
  - pas d’effets de polarisation  
  - diffusion par des écarts $\delta \rho$ à la densité électronique moyenne = rugosité ou des variations de contraste électronique

- formulation cinématique de la diffusion (expression volumique)
  \[ \frac{d\sigma}{d\Omega} \propto \left| \int \delta\rho(\vec{r}) \exp(iq\vec{r}) \right|^2 \]

- $\alpha_t$ et $\alpha_r$ proches de l’angle critique de réflexion totale extense = effet de réfraction du faisceau ou pic de Yonêda

- DWBA = combinaison du traitement dynamique et cinématique de la diffusion  
  - réflexion-réfraction aux interfaces  
  - traitement cinématique de la diffusion par $\delta \rho$, sans inclure les effets de diffusions multiples  
  - approche similaire en réflexion neutronique  
  - section efficace calculée au premier ordre en théorie des perturbations par rapport au système idéal

Historique
Formulation de la DWBA

Point de départ : équation de Helmholtz pour l’onde électromagnétique

\[ \left( \nabla^2 + k^2 \right) \psi = V(r) \psi \]

Potentiel diffusant

\[ V(r) = k^2 \left[ 1 - n(r)^2 \right] = \overline{V(r)} + \delta V(r) \]

Élément de matrice de transition

\[ \langle f | T | i \rangle = \langle \tilde{\psi}_f | V | \phi_i \rangle + \langle \psi_f | \delta V | \chi \rangle \approx \langle \tilde{\psi}_f | V | \phi_i \rangle + \langle \psi_f | \delta V | \psi_i \rangle \]

Les ondes

\[ \phi_i(r) = \exp(ik_i \cdot r) \]

\[ \psi_i(r) = T_i \exp(i \mathbf{k}_i \cdot \mathbf{r}) + R_i \exp(i \mathbf{k}_i' \cdot \mathbf{r}) \]

\[ \tilde{\psi}_f(r) = T_f^* \exp(i \mathbf{k}_f \cdot \mathbf{r}) + R_f^* \exp(i \mathbf{k}_f' \cdot \mathbf{r}) \]

Onde incidente

Vecteurs propres du système idéal avec renversement temporel

\[ \frac{d\sigma}{d\Omega} \propto \left\langle |i | T | f \rangle^2 \right\rangle = \left\langle |V_{if} + \delta V_{if}|^2 \right\rangle \]

Règle d’or de Fermi

\[ \frac{d\sigma}{d\Omega}_{\text{spec}} \propto |V_{if} + \langle \delta V_{if} \rangle|^2, \quad \frac{d\sigma}{d\Omega}_{\text{diff}} \propto \left\langle |\delta V_{if}|^2 \right\rangle - \left| \langle \delta V_{if} \rangle \right|^2 \]
**Quelques exemples de sections efficaces en GISAXS**

Développement suivant la géométrie du potentiel de diffusion

\[
\frac{d\sigma}{d\Omega} \propto |T_i(\alpha_i)|^2 S(q) |T_f(\alpha_f)|^2 \quad \Rightarrow \quad \text{Pic de Yonèda}
\]

\[
S(q) = \frac{(\Delta \rho)^2}{|q|^2} \exp\left(-\frac{\left(q_x^2 + q_z^2\right)^2}{2}\right) \int \exp\left\{i \left(q_x \cdot \mathbf{r}_i\right)\right\} \int \exp\left\{-i \left(q_x \cdot \mathbf{r}_i\right)\right\} d^2 \mathbf{r}_i
\]

Remarques : principe de réciprocité
- Cas limites : \( \alpha_i, \alpha_f, \sigma, q_z \), et \(|T| \) - approximation de Born valide
- \( q_z, \sigma \) - TF de la fonction d’auto-corrélation de la rugosité

**Multicouches rugueuses corrélées**

Traitement analogue mais plus complexe !
- Point de départ = optique des multicouches
- Complexité = corrélation hauteur-hauteur inter-couches

**Inclusions sous la surface**

\[
\frac{d\sigma}{d\Omega} \propto |T_i(\alpha_i)|^2 S(q_{\parallel}, q_{\pi}) |T_f(\alpha_f)|^2
\]

\[
S(q) = \int \exp\left(i \mathbf{q} \cdot \mathbf{r}\right) d^2 \mathbf{r} \quad \text{Transformée de Fourier de la forme de l'objet diffusant}
\]

**Programme d’analyse IsGISAXS**

- Cas approfondi par la suite !
Coherent interferences between 4 waves with different $q_z$!

1$^{st}$ term: $q_z = k_{fz} - k_{iz}$
2$^{nd}$ term: $q_z = k_{fz} + k_{iz}$
3$^{rd}$ term: $q_z = -k_{fz} - k_{iz}$
4$^{th}$ term: $q_z = -k_{fz} + k_{iz}$

Modulus square of the each term

DWBA form factor of a cylinder

+ Phases

« Yoneda peak»

Minima depend on $\alpha_i$

Scattered intensity along $\alpha_i$
Diffuse scattering due to size distributions, and sizes-distances and sizes-sizes correlations

Two usual extreme approximations neglecting correlations:

1 – DA (Decoupling Approximation):
Size and positions completely un-correlated

\[ I(q_\parallel, q_\perp) \propto \langle |F|^2 \rangle - \langle |F|^2 \rangle^2 + \langle |F|^2 \rangle \times S(q_\parallel) \]

Diffuse scattering Coherent scattering

2 - LMA : Local monodisperse approximation

\[ I(q_\parallel, q_\perp) \propto \langle |F|^2 \rangle \times S(q_\parallel) \]

Coherency zones of the X-ray beam

• Correlations deduced from analysis of TEM images Pd/MgO(001)

No sizes-sizes correlation \( \square \) LMA wrong

Sizes-separations correlations
In plane scattering: coherent versus incoherent?

\[
\frac{d\sigma}{d\omega} \propto \frac{1}{N} \left| \sum_i F_i(\bar{q}_\parallel, k_{fz}, k_{iz}) \exp(i\bar{q}_\parallel \cdot \bar{r}_{i\parallel}) \right|^2
\]

Configuration average over the coherently illuminated areas.

Knowledge of all the partial pair correlation functions?

Decoupling approximation DA

\[
\frac{d\sigma}{d\Omega} \propto \left( \langle |F|^2 \rangle - \langle |F| \rangle^2 \right) + \langle |F| \rangle^2 \times S(q_\parallel)
\]

Incoherent scattering Coherent scattering

2 simple limit cases

Local Monodisperse Approximation LMA

\[
\frac{d\sigma}{d\Omega} \propto \langle |F|^2 \rangle \times S(q_\parallel)
\]

Incoherent sum of scattering from Monodisperse domains

Total disorder – no correlations

X-ray coherent area
Result from scattering theory

\[ \left( \frac{d \sigma}{d \omega} \right)_{\text{diff}} = \text{const.} \sum_{p} \left| A_p F \left( Q_p \right) \right|^2 P \left( Q_p \right) \]

over the processes

form factor of a single object

correlation function of the positions

amplitude of the \( p \)-th process

\( P(Q_p) = \text{FT of pair correlation in real space} \)

Short range order  Long range order

Courtesy of V. Holy
Lateral size distribution and zeros of the form factor

Cylindrical particles and gaussian distributions

In ISGISAXS: distributions of lateral sizes, of heights, of orientations, of incidence angles, of wavelengths

Porod regime: a signature of the shape!
Late stages of facetting: Large nano-pyramids

\[
|\langle Q \rangle| = \left| F_{DWBA}(Q, k_i^z, k_f^z) \right|^2 S(Q)
\]

Shape: \( F_{DWBA} \)
Evolution of facetting as a function of annealing time
"Super-cristallography" of the Co cluster lattice on Au(111) before coalescence

Analysis parameters
- rectangular 2D paracrystal (ΔK) with three variants oriented at 120°
- Triangular islands (R, H and size distribution)
- Centering of the mesh δy

Rebuild cross section of the reciprocal space around q_z = 0

Experiment

Simulation
GISAXS on Bimolecules B. Krause, ID01

Model: Formfactor of double-disk

$R_0 = 270 \, \text{Å}$  \hspace{1cm} $H = 170 \, \text{Å}$

$R_1 = 130 \, \text{Å}$  \hspace{1cm} 10 % size distribution
Scans in 3D reciprocal space

- Information on shape \( q_{\text{angular}} \)
- Information on strain \( q_{\text{radial}} \)
- Information on depth \( q_z \)

Radial direction: \( q_r \)  
Angular direction: \( q_\alpha \)

GISAXS
Results: data analysis ISS

Linear relation between strain and size is found from fits at all radial positions.
Example III: composition of Ge domes on Si

GID with contrast variation using anomalous ISS

Energy dependence

\[ f(Q,E) = f_0(Q) + f'(E) + i f''(E) \]

For Si negligible

Use energy and Q dependence to amplify contrast: measure at high Q!

anomalous correction enhanced at high Q
higher resolution for $\Delta a/a = -q_r/Q$
Si content from deviation of $I_{E1}/I_{E2}$ for pure Ge
All possible GID reflections should be measured
Si interdiffusion: vertical composition profile from (A)-GID at (800)

RESULTS

- Sharp Si/Ge interface
- Ge plateau at 85%
- \(\Delta a/a\) monotonic
- dot is highly strained

“Nano-Tomography”: 3D real space image shape, size, strain and composition of Ge/Si alloy islands

11.2 ML Ge domes on Si (001) grown by CVD at 600°C

Results:
the lateral variation of the Ge concentration changes with height
Si rich core covered by Ge rich alloy
concentration from pure Si at bottom to pure Ge at top

A. Malachias et al. PRL91, 176101 (2003)
Oxide layer and crystalline core

amorphous oxide layer (2-3 nm)

oxidation $\Rightarrow$ foot of the dot was part of the substrate

Marquez et al., APL 78 (16), 2310 (2001)
Oxide layer and crystalline core

amorphous oxide layer (2-3 nm)

oxidation \Rightarrow \text{foot of the dot was part of the substrate}

Marquez et al., APL 78 (16), 2310 (2001)
Magnetic resonant X-ray scattering from an array of CoPt multilayers

Away from L₃ Co edge 770 eV

Specular peak

Structural peaks

At L₃ Co edge 780 eV

Magnetic peaks

Peak from AF magnetic order

Pinhole 20 µm

K. Chesnel at al, PRB 2003
Coherent scattering on magnetic microstructures

- Magnetic satellite
- Specular spot
- Speckle
- Interference fringes
- Pinhole 20 µm
- 22 µm
- 8 µm

FePd thin film, perp. magn. AF order
Beutier – Chesnel

CF les PRBs.
Grazing Incidence X-ray Scattering

In UHV *in situ* during growth

**GID**
Strain state
In-plane lattice parameter

**GISAXS**
Shape, size

2D image around direct beam:
Fourier transform of the objects

to decrease the bulk scattering as much as possible
(to be sensitive to surface)
Coherent Diffraction from a $5\mu$m made of Au

Christian Schroer, Edgar Weckert, Andreas Schropp, I. Vartanyants, Hasylab and ID01

Next steps
Phase retrieval and reconstruction

Measurement

Simulation
General references

Aknowledgments

F. Leroy, C. Revenant, A. Létoublon, T. Schülli, M. Ducruet, O. Ulrich, CEA-Grenoble (France)

C.R. Henry, C. Mottet
CRMCN, Marseille (France)

O. Fruchart,
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R. Lazzari, S. Rohart, Y. Girard, S. Rousset
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A. Coati, Y. Garreau
LURE, Orsay (France)

Thank you for your attention