Grazing Incidence Small Angle X-ray Scattering (GISAXS) at the CRG-D2AM beamline

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An advanced powerful technique to investigate nano-objects using the high brilliance and tuneability of SR

WHY?

- Statistical information on the size, shape, orientation and spatial organization of nano-objects (1-100nm) distributed in 2D or 3D.

- Grazing incidence ($\alpha_i \sim \alpha_c$): surface sensitive (enhancement of layer scattering with respect to substrate scattering)

- Element sensitive using anomalous effect

- Applicable to various systems:
  - Nanostructures supported on substrates
  - Clusters, gas bubbles, pores embedded in a matrix near the surface

- Appropriate also for in-situ investigations: growing particles in UHV chambers, sintering of particles induced by gas or shape evolution of metal particles during catalytic reaction.
Principle of GISAXS

Image of the reciprocal space around the intense specular rod hidden by a beamstop

Form factor \( F(q) \):
- shape, orientation, size distribution \((R,H)\)

Interference function \( S(q) \):
- separation distance:\( D \)

Example: Ag(2nm)/MgO(001) at 500K

\[
I(q) \approx \langle |F(q)|^2 \rangle \times S(q) \\
\text{(local monodisperse approximation)}
\]
GISAXS set-up on BM02

Typical beam size: 150x300 µm²
Energy range = 7.5 - 20 keV
Accessible q-range: 0.02 - 12 nm⁻¹

Sample chamber (10⁻⁶ torr)
DSD variable from 400 to 1200 mm
Sample transfer from UHV preparation chamber to GISAXS vessel using a vacuum suitcase

Main advantage:
Measurements on a series of sensitive samples without air exposure.
Magnetic alloy nanostructures self-assembled on low energy surfaces: NaCl(001) and WSe$_2$(0001) (future high density magnetic recording media)

**Aims of GISAXS measurements:**

- influence of the lattice symmetry of substrate on the size and shape of nanostructures
- growth mechanism for continuous deposition of metal atoms
0.5 nm CoPt₃ Tg=520K
Experimental (αᵢ=0.4°)  Simulation with IsGISAXS¹

2R=4nm  H=3.1nm, H/2R=0.8
Average volume of particles= 26nm³
Separation distance: D=8.2nm

Approximations:
- DWBA
- SSCA²

HRTEM image

For epitaxial and large (10nm) particles GISAXS sensitive to the nanostructure shape
CoPt(1nm) on $\text{WSe}_2$ at RT: dense assembly of nanostructures

\[ 2R=2\text{nm} \quad \sigma_R=1\text{nm} \]
\[ H=0.7\text{nm} \quad \sigma_H=0.8 \quad \alpha=60^\circ \]
\[ \text{VCoPt}=1.5\ \text{nm}^3 \quad H/2R=0.35 \quad D=3.2\text{nm} \Rightarrow d=0.11\text{part/nm}^2 \]

**thickness=0.15nm \ll 1\text{nm}!**
Combined GISAXS with STM measurements: CoPt (1nm) RT

Flooding at 1.3nm

Only the upper parts of nanostructures contribute to GISAXS pattern

=> GISAXS well suited for studying coalescence effects
GISAXS patterns for 3nm deposit of CoPt$_3$ on WSe$_2$(0001)

$T_d = 700K$

Triangular particles observed by Field emission-SEM image,

Low GISAXS sensitivity to the steep \{111\} side-wall facets

- $L=13nm$, $H=4.5nm$
- Aspect ratio of 0.35 $<<$ 0.8 value on NaCl
GISAXS study of size and organization of pores in low k SiOCH dielectrics prepared on Si wafers
Porous SiOCH dielectrics used in advanced microelectronic interconnections (LETI/CEA Grenoble, SIMaP)

1) Blend of a hybrid material (SiOCH skeleton) with an organic precursor as porogen by spin coating or PECVD
2) Thermal treatment (~400°C, assisted by UV or e-beam):
   - Elimination of organic molecule (pores-> low k),
   - Improvement of mechanical resistance with strong Si-O-Si bonds

Quantitative measurements of porosity since sample length (40-80mm) > footprint (35mm \( \alpha_i = 0.25^\circ \))

GISAXS patterns for different low k dielectrics

Analysis of GISAXS patterns using Babonneau’s program with refraction reflection-transmission and absorption corrections.

\[ \alpha_i > \alpha_c \text{ (Si) } > \alpha_c \text{ (SiOCH)} \]

at 8keV, \( \alpha_c \text{ (Si)} \) =0.24°

Spin coating

PECVD1 (e-beam assisted) PECVD2

Spin coating using specific polymer

Intensities divided by the probed volume

Isotropic scattering \( \Theta=4\text{nm}, d=10\text{nm} \)

Lateral order \( d=3.5\text{nm} \)

\( \Theta=0.6\text{nm}, \) vertical and lateral orders (\( d=1.75\text{nm} \))

Pore array
Anomalous GISAXS of carbon-encapsulated Au and Cu clusters.

The choice of this system is related to previous GISAXS studies performed in nanocermets giving rise to surface plasmon resonance phenomenon.
AGISAXS study of carbon-encapsulated Au & Cu clusters (PHYMAT- Poitiers, SIMaP)

C/Cu binary system

C/Au/C-Cu ternary system

C/Au binary system

Scattering ring => isotropic distribution

Interference peaks => lateral order

l=1.5nm  h=2.7nm

l=3.4nm,  h=2nm

Difference method: very efficient!

Signal 8973eV – mean signal near Cu-edge

Signal 11911eV – mean signal near Au-edge

Comparaison of horizontal cuts ($q_z=0.7\text{nm}^{-1}$) between ternary & binary systems
Summary & Perspectives

- GISAXS camera: user-friendly, variable sample-detector distance for the characterization of nano-objects with sizes 1-100nm.

- Temperature-dependent measurements under vacuum of $10^{-6}$ Torr.

- Characterization of sensitive samples introduced in the sample vessel from a vacuum suitcase.

- Taking advantage of the anomalous technique => study of core-shell systems but requires large samples for accurate normalization.