

# **Grazing-Incidence SAXS: Basic Principles and Applications**

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### Introduction

**GISAXS** combines the accessible length scales of small-angle X-ray scattering (**TSAXS**) and the surface sensitivity of grazing incidence X-ray techniques (GID, XRR, etc.)





A look back at the origins of GISAXS

J. Appl. Cryst. (1989). 22, 528-532

#### Grazing-Incidence Small-Angle X-ray Scattering: New Tool for Studying Thin Film Growth



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#### Abstract

Grazing-incidence small-angle X-ray scattering (GISAXS) is introduced as a method of studying discontinuous thin films. In this method, the incident beam is totally externally reflected from the substrate followed by small-angle scattering of the refracted beam by the thin film. The experiment described establishes the ability of GISAXS to provide size information for islands formed in the initial stages of thin film growth. The data presented are for gold films of 7 and 15 Å average thicknesses on Corning 7059 glass substrates. The advantages of this technique are that it is non-destructive, can be done *in situ*, provides excellent sampling statistics, does not necessarily require a synchrotron source, and is not limited to thin or conducting substrates.







- Rotating anode ( $\lambda = 0.154$  nm)
- Linear position-sensitive detector
- Grazing incidence and exit angles  $\rightarrow \phi_i = \phi_f = 0.229^{\circ}$



Fig. 2. TEM micrograph of 15 Å Au film.

Fig. 3. Scattered intensity from clean Corning 7059 glass and from 15 Å Au on glass.



Introduction

#### Brief overview of bibliographic data (1989–2024)









Limitations of transmission SAXS at normal incidence

• Small size of the incident beam limits the volume irradiated

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· Absorption causes a strong decrease of the signal-to-noise ratio



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- $q_z \approx 0$ 
  - $\checkmark$  In-plane information only





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- Absorption causes a strong decrease of the signal-to-noise ratio
- $q_z \approx 0$ 
  - ✓ In-plane information only
  - ✓ SAXS patterns are centrosymmetric

$$I\left(q_{\mathrm{x}}, q_{\mathrm{y}}\right) = I\left(-q_{\mathrm{x}}, -q_{\mathrm{y}}\right)$$







Advantages and added values of GISAXS ( $\alpha_i < 1^{\,\circ})$ 

- Increased footprint of the primary beam at the sample surface
- Reduced depth of penetration (typically a few nanometers below  $\alpha_c$ )







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- Enhancement of surface sensitivity •



$$I_{t}(z, \alpha_{i}) = |t_{0,1}(\alpha_{i})|^{2} \exp\left(-\frac{z}{z_{1/e}}\right)$$

$$\alpha_{c} = \sqrt{2\delta}$$
**10 keV**

$$a_{c} = \sqrt{2\delta}$$





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In-depth distribution of electric field intensity can be varied in a controlled way, enabling enhancement of the scattering from **supported** or **buried** nanostructures



 $\alpha_{i}$ 

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- Scattering vector

$$\vec{q} = \frac{2\pi}{\lambda} \mathcal{Q}_{z} \left( \varphi \right) \begin{bmatrix} \cos \left( 2\theta_{f} \right) \cos \left( \alpha_{f} \right) - \cos \left( \alpha_{i} \right) \\ -\sin \left( 2\theta_{f} \right) \cos \left( \alpha_{f} \right) \\ \sin \left( \alpha_{f} \right) + \sin \left( \alpha_{i} \right) \end{bmatrix}$$

✓ In-plane and out-of-plane information are made accessible





Advantages and added values of GISAXS





 $\alpha_{i}$ 

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- $\checkmark~$  Full 3D reciprocal space mapping by changing  $\phi~(\pm 180^{\circ})$

$$\checkmark q_{\rm z} \neq 0 \Rightarrow I(q_{\rm x}, q_{\rm y}, q_{\rm z}) \neq I(-q_{\rm x}, -q_{\rm y}, q_{\rm z})$$



## Why using grazing incidence conditions ?

Advantages and added values of GISAXS



## Why using grazing incidence conditions ?

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## **GISAXS: some points of vigilance**

Influence of the angle of incidence







Influence of the angle of incidence





Influence of the sample length





Influence of the sample curvature





Influence of the sample curvature



















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#### Gold islands sandwiched between carbon layers Institut Pprime 3.5 3.0 System Si // Ni / C / Au / C 800 Density (µm<sup>-2</sup>) 2.5 600 S(q // ) 2.0-1.5-400 1.0 200 0.5 50 nm 0 0.0 0 2 4 6 8 0 2 6 4 q∥ (nm<sup>-1</sup>) Babonneau et al., Phys. Rev. B 80 (2009) 155446 Diameter (nm) 12 10<sup>0</sup> 12 Ele Electric field intensity 0.37° 10 C capping-layer C-Au Óepth (nm) 10<sup>-2</sup> tric field intensity Reflectivity C buffer-layer 20-8 SiO<sub>2</sub>--8 Si substrate 6 10<sup>-4</sup> 40 0.41° -4 2 <u>E = 6.99 ke</u>V 10<sup>-6</sup> 60 0 0.5 1.5 2.0 2.5 0.8 0.2 0.8 1.0 0.2 0.4 0.6 0.0 0.4 0.6 0.0 $\alpha_i$ (deg) $\alpha_i$ (deg) $\alpha_i$ (deg)

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# Gold islands sandwiched between carbon layers





LETTERS

Multicolour photochromism of TiO<sub>2</sub> films loaded with silver nanoparticles



Ohko *et al.*, Nat. Mater. **2** (2003) 29 Naoi *et al.*, J. Am. Chem. Soc. **126** (2004) 3664

nature materials | VOL 2 | JANUARY 2003 | www.nature.com/naturematerials



- **Vis. light**: Size-selective Ag oxidation by photo-induced electron transfer at the localized surface plasmon resonance
- UV light: Photocatalytic reduction of the Ag<sup>+</sup> ions to metallic Ag



#### ADVANCED MATERIALS

Mabrials Views www.MaterialsViews.com

Reversible and Irreversible Laser Microinscription on Silver-Containing Mesoporous Titania Films









Crespo-Monteiro *et al.*, Adv. Mater. **22** (2010) 3166 Diop *et al.*, Appl. Spectrosc. **6** (2017) 1271



*t* = 160 nm

Real-time investigations under UV and visible laser irradiation

Coll. N. Destouches







Ag nanoparticles grown in a nanoporous  $TiO_2$  film by reduction after immersion into an aqueous ammoniacal silver solution

- Film thickness: ~160 nm
- Pore diameter: ~8 nm



Real-time investigations under UV and visible laser irradiation

Coll. N. Destouches







*E* = 11.5 keV



Babonneau et al., Nano Futures 2 (2018) 015002



Real-time investigations under UV and visible laser irradiation





Real-time investigations under UV and visible laser irradiation





Real-time investigations under UV and visible laser irradiation

Coll. N. Destouches







*E* = 11.5 keV

Babonneau et al., Nano Futures 2 (2018) 015002





- Repeatable photochromic behavior with a good contrast between the colored and colorless states
- Photo-oxidation process (X-ray + vis.) is always faster than the photocatalytic reduction process (UV)
- Efficiency of the photo-activated reduction process (UV exposure) is degraded after 2 cycles





Kim et al., Mater. Res. Bull. 149 (2022) 111703

LOW-E GLASS



Simonot et al., Appl. Surf. Sci. 544 (2021) 148672

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Room temperature magnetron sputtering deposition Si<sub>3</sub>N<sub>4</sub> / Ag ( $t_{A\alpha}$ ) / Si<sub>3</sub>N<sub>4</sub>

- Early stages dominated by strong optical absorption (localized surface plasmon resonance) and high electrical resistivity
- Growth strategies needed for producing conductive and transparent Ag layers  $\Rightarrow$  use of gas additives (*e.g.*, O<sub>2</sub>, N<sub>2</sub>, etc.)



- Simultaneous measurements during magnetron sputtering Ag deposition on SiO<sub>x</sub>/Si
  - GISAXS: island morphology and organization
  - GID: crystal structure, grain size and orientation...
  - Substrate curvature measurements: stress evolution







- Simultaneous measurements during magnetron sputtering Ag deposition on SiO<sub>x</sub>/Si
  - GISAXS: island morphology and organization
  - GID: crystal structure, grain size and orientation...
  - Substrate curvature measurements: stress evolution









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A. Coati, Y. Garreau, A. Resta, A. Vlad (SOLEIL)

Yun et al., Nanoscale 12 (2020) 1749



# Gold NPs in topological defects of smectic films

Coll. E. Lacaze





# Gold NPs in topological defects of smectic films

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## Gold NPs in topological defects of smectic films

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## Gold NPs in topological defects of smectic films







