ESRF	**Experiment title:** GISAXS study of silver nanoparticles aligned on rippled Al_2O_3 films produced by low-energy ion erosion	**Experiment number**: SI 1839
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Names and affiliations of applicants (* indicates experimentalists):

V. Antad*, D. Babonneau*, S. Camelio*

Laboratoire PHYMAT

UMR 6630 CNRS – Université de Poitiers

Bvd M. et P. Curie, BP30179

86962 Futuroscope Chasseneuil Cedex, France

Report:

The goal of our project was to investigate by GISAXS the nanostructure of (i) periodic ripples produced by Xe^+ erosion of dielectric thin films and of (ii) silver nanoparticles deposited onto such surfaces by ion-beam sputtering under grazing incidence. These sytems present a structural anisotropy, which results in a dependence of their optical response to the orientation of the electric field. From the quantitative analysis of the GISAXS data, which are complementary to local AFM and TEM observations, we expected to obtain valuable information on the morphology and organization of the Ag nanoparticles onto the rippled surfaces in order to explain their dichroic optical properties dominated by a surface-plasmon resonance phenomenon in the visible range.

Al_2O_3, Si_3N_4, and BN thin films were patterned by Xe^+ etching at room temperature and oblique incidence (35° with respect to the surface) with the aim of producing ripples with controlled lateral periodicity and vertical amplitude. Then, these patterned surfaces were used as templates to direct the self-organized growth of Ag nanoparticles deposited at room temperature or at 200°C by ion-beam sputtering under grazing incidence of 5°. The effective Ag thickness t_{Ag} was varied between 1 and 4 nm, and the nanoparticles were subsequently covered with a 20 nm-thick Al_2O_3 cap.

The surface topography of the free-particles patterned surfaces was investigated by GISAXS experiments performed on the ID1 beamline at 7.750 keV with a grazing angle α_i being varied between 0.15° and 0.5°. Moreover, to characterize the in-plane anisotropy of the samples, series of 2D GISAXS patterns were collected rotating the sample from $\varphi = 0°$ (direction parallel to the ripples) to $\varphi = 90°$ (direction perpendicular to the ripples) by increments of 1°, so allowing to obtain 3D maps of the reciprocal space. As a typical example, Figs. 1a and 1b show the out-of-plane (at $\varphi = 0°$) and the in-plane (at $\alpha_f = 0.4°$) GISAXS maps of an as-etched Si_3N_4 film, which reveals the formation of ripples with long-range order by the presence of two intense and sharp vertical streaks located at $2\theta_f \approx \pm 0.41°$ when $\varphi < 15°$. In addition, it is worth noting that the GISAXS intensity is not symmetric, i.e. $I(2\theta_f) \neq I(-2\theta_f)$, which can be ascribed to an asymmetric profile of the rippled surface. The quantitative analysis of the data was performed in the framework of the distorted wave-Born approximation assuming an asymmetric sawtooth surface profile with a positive slope γ_+ and a negative slope γ_-, and with a ripple length $L_{//}$, an amplitude h, and a Gaussian probability of the ripple spacing (period $L_\perp$ and standard deviation $\sigma_\perp$). In the case of the maps shown in Fig. 1, the best-fit parameters are $L_{//}$ = 75 nm, $L_\perp$ = 20.0 nm, $\sigma_\perp$ = 4.2 nm, h = 3.7 nm, γ_+ = 23.7°, and γ_- = 17.3°. Similar results were obtained for Al_2O_3 films, while for BN films etched under the same conditions, the period of the ripples was found to be smaller and the asymmetry higher.

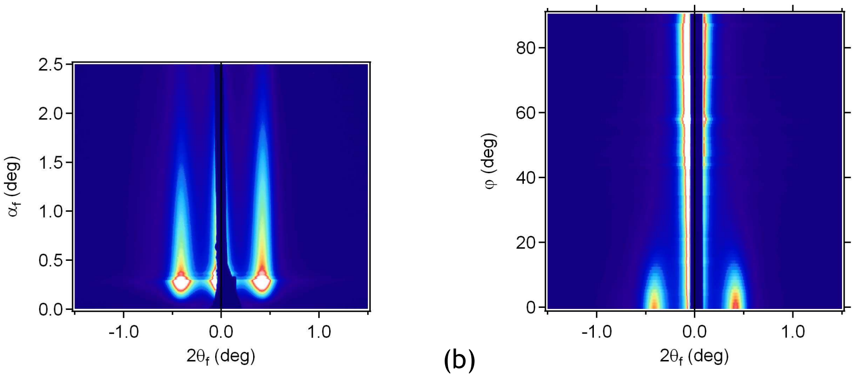

Fig. 1: (a) Out-of-plane (at φ = 0°) and (b) in-plane (at α_f = 0.4°) GISAXS maps of an as-etched Si_3N_4 film.

The morphology and the organization of the Al_2O_3-capped Ag nanoparticles deposited onto rippled surfaces were also studied by GISAXS experiments rotating the sample from φ = 0° to φ = 90° by increments of 1°. For comparison, one nanocomposite film deposited onto a plane Al_2O_3 surface was also measured, showing no sensitivity to azimuthal rotation. Fig. 2 displays typical out-of-plane (at φ = 0° and φ = 90°) and in-plane (at α_f = 0.4°) GISAXS maps of Al_2O_3-capped Ag nanoparticles deposited at room temperature onto an etched Al_2O_3 film with t_{Ag} = 2 nm. As for the case of the as-etched Al_2O_3 films, two intense and sharp streaks are exhibited on both sides of the vertical beam stop at $2\theta_f \approx \pm 0.84°$ indicating that the Ag nanoparticles replicate the long-range order between ripples in the lateral direction with an interparticle distance similar to the ripple period $L_\perp$. The asymmetry of the scattering intensity can be ascribed to a preferential nucleation of the Ag nanoparticles on the facets of the rippled surface that are illuminated during the Ag deposition owing to shadowing effects (i.e., the nanoparticles are not nucleated in the trough of the wavy surface). Moreover, modulations of intensity coming from correlated roughness effects are generated in the vertical direction, indicating that the topography of the Ag nanoparticles is partially replicated to the surface of the Al_2O_3 capping layer. In contrast, the 2D GISAXS pattern obtained with the x-ray beam perpendicular to the ripples (Fig. 2c) shows two broad lobes typical of a short-range order between nanoparticles in the direction parallel to the ripples with an interparticle distance much smaller than $L_\perp$ in this direction. Thus, the GISAXS experiments clearly demonstrate that the in-plane organization of the nanoparticles is anisotropic, in agreement with our optical measurements. Full quantitative analysis of the data is under progress: our first results tend to show that both the organization and the shape of the particles are anisotropic, with the shape anisotropy being enhanced at low deposition temperature and high effective Ag thickness.

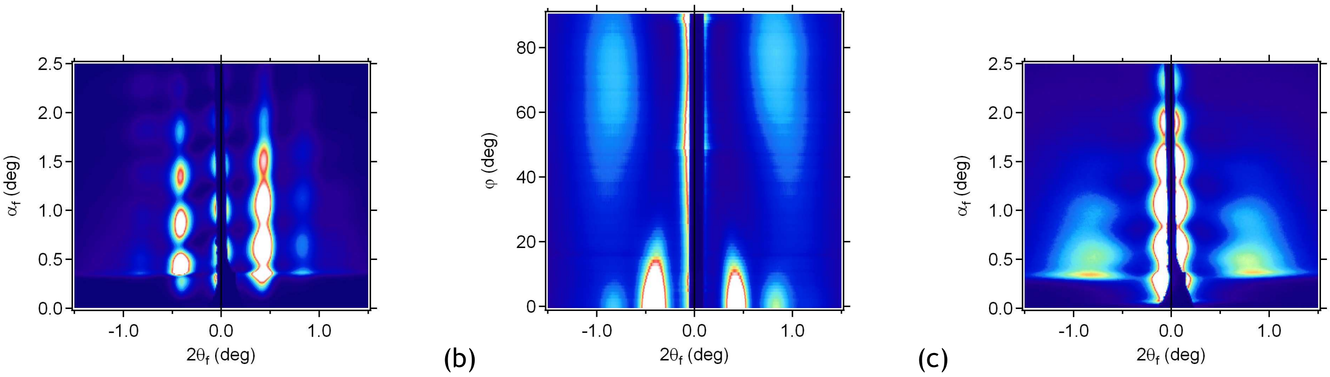

Fig. 2: (a) out-of-plane (at φ = 0°) and (b) in-plane (at α_f = 0.4°) GISAXS maps of Al_2O_3-capped Ag nanoparticles deposited onto an etched Al_2O_3 film. (c) Out-of-plane GISAXS map with φ = 90°.