ESRF	**Experiment title: Self-organized growth of Ag nanoclusters on vicinal surfaces investigated by grazing incidence small-angle x-ray scattering**	**Experiment number**: 02-01-691
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Report:

The control of the shape and organization of nanoparticles is of great interest for both fundamental and technological reasons (high-density magnetic data storage, optical devices, etc.). In particular, the control of the optical response of noble-metals nanoparticles – characterized by a surface-plasmon resonance (SPR), which consists of a collective oscillation of the electrons of conduction under the influence of the incident electromagnetic wave – is a great challenge that number of physicists in the field of nanoplasmonics try to recover. Our study is focused on the investigation of Ag nanoparticles dispersed in dielectric matrices (BN, Al_2O_3 et Y_2O_3) grown by alternate deposition and the aim of this project was to investigate by grazing incidence small-angle x-ray scattering (GISAXS):

i) the capping-layer effects on the morphology of Ag nanoislands deposited onto plane surfaces;
ii) the self-organized growth of Ag nanoislands deposited onto vicinal surfaces.

1) Ag nanoislands deposited onto plane surfaces: capping-layer effects

Ag nanoislands have been deposited onto flat SiO_2 substrates by ion-beam sputtering and electron-beam evaporation at 200 °C and subsequently covered by 20-nm thick dielectric caps (BN, Al_2O_3, and Y_2O_3). The influence of the nature of the cap on the morphology of the Ag nanoislands has been investigated by GISAXS experiments carried out on the D2AM beamline at 8 keV. As a typical example, Fig. 1 shows the GISAXS patterns (grazing angle ~ 0.4°) of Ag 3 nm / X 20 nm bilayers with X = BN, Al_2O_3, and Y_2O_3. Quantitative analysis has been performed in the framework of the distorted-wave Born approximation in order to determine the size and the shape of the nanoislands. The results – confirmed by complementary STEM-HAADF experiments – provide evidence for a decrease of the nanoisland aspect ratio H/D with their in-plane diameter D. In addition, the D-dependence of H/D is not governed by the deposited Ag amount, but strongly relies on the nature of the matrix. Therefore these measurements demonstrate that capping-layer effects can be used to modify the shape and the size of the nanoislands, and thus the spectral position of the SPR.

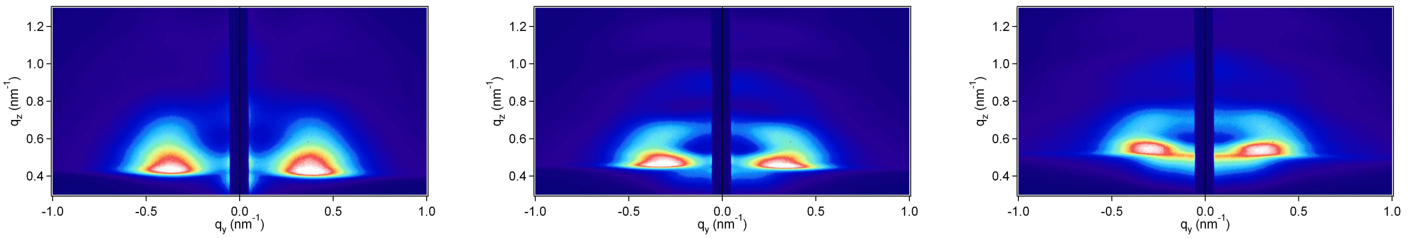

Fig. 1 : GISAXS patterns of Ag 3 nm / X 20 nm bilayers with X = BN (left), Al_2O_3 (center), and Y_2O_3 (right)

2) Ag nanoislands deposited onto vicinal surfaces under normal incidence

Ag nanoislands covered with Al_2O_3 caps has been grown onto vicinal Al_2O_3, $SrTiO_3$ and MgO surfaces, with the Ag flux parallel to the direction of the substrate normal. The substrates present terrace widths and step heights varying from 20 nm to 100 nm and from 0.4 nm to 4 nm, respectively, and have been chosen for their transparency in the visible range (required for optical transmission measurements), their different refraction indices and crystallographic structures. To characterize the in-plane anisotropy of the samples, GISAXS experiments have been carried out with the incident x-ray beam oriented in the direction either perpendicular or parallel to the steps. For comparison, bilayers deposited onto plane Al_2O_3, $SrTiO_3$ and MgO surfaces has been also measured by GISAXS. As seen in Figure 2, GISAXS patterns enable to characterize (i) the structure of the vicinal surfaces (the distance between the intense rods obtained with x-rays parallel to the steps yields the width of the terraces) and (ii) the morphology and the organization of the nanoislands in both directions parallel and perpendicular to the steps (by the lateral and vertical extensions of the diffuse scattering). However, our results show that under normal incidence deposition, self-alignment of the Ag nanoislands along the steps of the vicinal surfaces is not obtained and that the macroscopic organization remains isotropic.

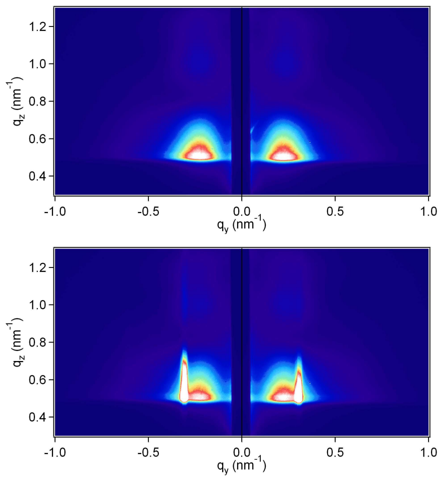

Fig. 2 : GISAXS patterns of a Ag 6 nm / Al_2O_3 20 nm bilayer deposited under normal incidence onto a $SrTiO_3$ vicinal surface with x-rays perpendicular (top) and parallel (bottom) to the steps.

3) Ag nanoislands deposited onto vicinal surfaces under grazing incidence

To produce self-organized arrays of Ag nanoislands on vicinal surfaces, another approach consists in performing the Ag deposition under grazing incidence to exploit self-shadowing effects. Our results shows that depending on the orientation of the substrate with respect to the Ag flux, only selected facet types can be exposed to the atomic beam, resulting in linear arrays of nanoisland chains or stripes. This structural anisotropy is clearly illustrated in Fig. 3 showing the GISAXS patterns of a Ag 3 nm / Al_2O_3 20 nm bilayer deposited under grazing incidence onto an Al_2O_3 vicinal surface with x-rays perpendicular and parallel to the steps. These results are in agreement with the optical properties of such self-organized nanosystems, which are dominated by a SPR whose spectral position depends on the polarization of the incident light (parallel or perpendicular to the facets of the vicinal template) and that can be attributed to a strong electromagnetic coupling between the individual nanoislands.

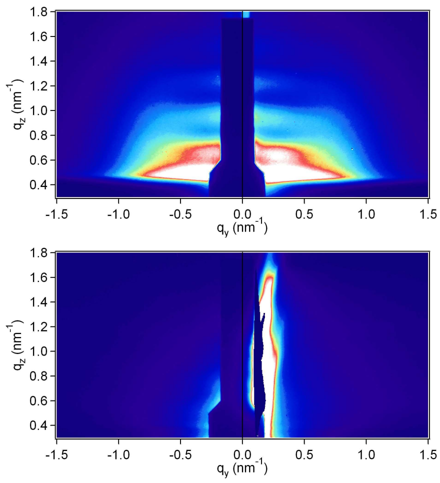

Fig. 3 : GISAXS patterns of a Ag 3 nm / Al_2O_3 20 nm bilayer deposited under grazing incidence onto an Al_2O_3 vicinal surface with x-rays perpendicular (top) and parallel (bottom) to the steps.