

We have realized a first test experiment of GISAXS on D2AM during 02/2010 on films constituted with metallic nanoparticles in an hybrid silica-polymer matrix. During this first experiment, very promising results have been obtained. About 25 samples have been observed. Signals were in each case significant. We present some qualitative results and quantitative analysis will be done later.

These films form silica sol and block copolymers where metallic nanoparticles (silver NP) were grown by thermal treatment or chemical reactions. Different commercial block copolymers have been used : P123 (PEO₂₀-PPO₇₀-PEO₂₀), F127 (PEO₁₀₆-PPO₇₀-PEO₁₀₆) and Brij56 (C₁₆H₃₃-EO₁₀), which are called respectively, F, P and B polymers.

These three different polymers are constituted with both hydrophilic and hydrophobic parts. Then, they form micelles which organize into cubic or into hexagonal arrangements, depending on the conditions used. It allows to get different silica mesostructures. A silica sol is prepared from these kinds of polymer and a silicon alkoxide. Moreover, a silver salt is introduced in the sol which can modify significantly the silica organization. A galvanic replacement of silver with gold is then performed.

For instance, by using the F polymer, a GISAXS 2d image (figure 1a) has been obtained which reveals a complex 3D organization in which silver nuclei are inserted. This complex structure will be changed when replacement of silver with gold is performed as shown in figure 1b.

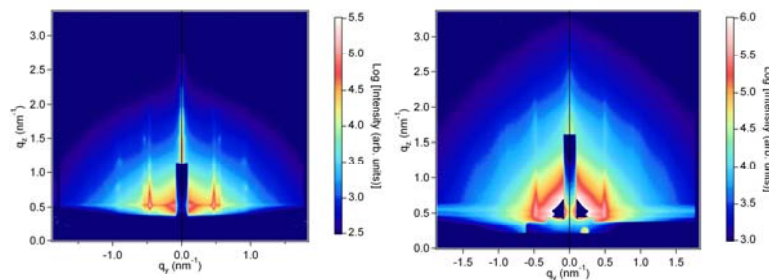


Figure 1: F-silica-Ag film before and after gold replacement.

By using the P polymer, another GISAXS 2d image (figure 2a) has been obtained which reveals an hexagonal 2D organization, with cylindrical micelles parallel to the substrate, in which silver nuclei have been grown. The figure 2b represents the picture when gold nanostructure has grown inside these cylindrical micelles.

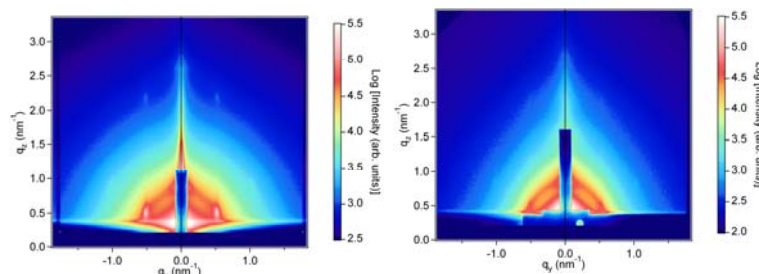
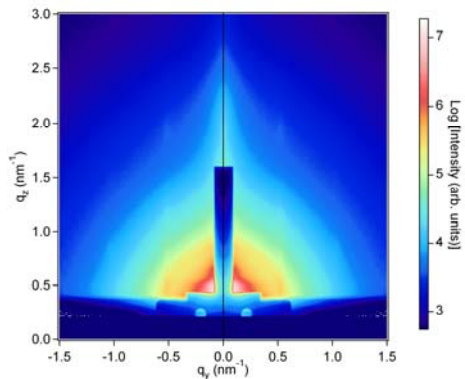
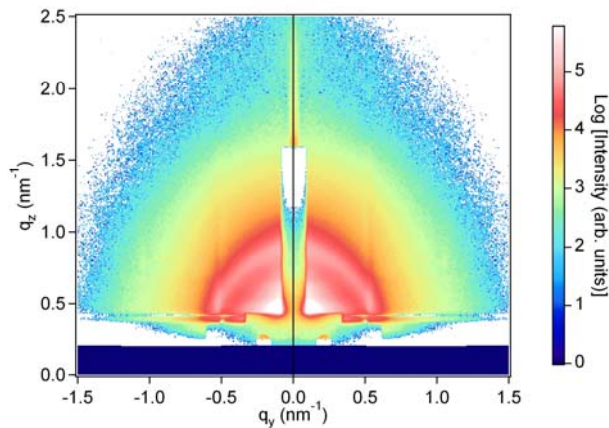


Figure 2: P-silica-Ag film before and after gold replacement.

On a sample containing Au clusters which are formed inside a P-silica films with cylindrical micelles, we have been tried to construct a bimetallic nanostructure, with a gold core and a silver shell. The GISAXS image presents an isotropic signal strongly decreasing with q and a strike at $q_x \sim 0.5 \text{ nm}^{-1}$.



The profile is an azimuth average outside the strikes, i.e. in the $70\text{-}85^\circ$ range with respect to q_x . A hump is observed which superimposes to the intensity decrease. The data are corrected from the footprint volume, although it is not valid at 0.15° since beam overflow the sample. Anomalous GISAXS was recorded at five energies near the L_{III} Au edge (11919eV), 11788, 11857, 11889, 11904 & 11911eV with respectively $f' = -12, -13.5, -14.9, -16.3$ & -17.4 following the methodology of JAC **42** (2009) 312-322. Next figure and profile show an example of $I(q, 11788\text{eV}) - \langle I(q) \rangle_{5\text{energies}}$, where the halo is well extracted near 0.7nm^{-1} .



As these samples contain metallic nanostructures (core/shell : gold /silver) inserted inside a silica and polymer ordered mesostructure, which are give tractable signal for Anomalous GISAXS .

Then, we hope that original anomalous GISAXS analysis of bimetallic nanostructures could be obtained from this data and further acquisitions on D2AM beamline