

	Experiment title: Investigation of solvent-evaporation-induced nanoparticle self-assembly at liquid/vapour and solid/vapour interfaces	Experiment number: SC3039
Beamline: ID10B	Date of experiment: From: 22/09/2010 to: 27/09/2010	Date of report: 16/08/2011
Shifts: 18	Local contact(s): Alexei Vorobiev	<i>Received at ESRF:</i>
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Report:

We have investigated the self-assembly of nanoparticles (NPs) using our hermetic wetting cell. The cell is designed to allow: (i) deposition of NP dispersions onto solid substrates, (ii) controlled macroscopic solvent evaporation, and (iii) nano-scale solvent adsorption/desorption onto the pre-assembled NP films.

We devoted particular attention to the investigation of an unexpected phenomena of NP segregation at the solvent/vapor interface, that we observe after each fresh NP solution injection onto a solid substrate. The injection is performed in condition of high solvent humidity inside the cell, so that the macroscopic solvent evaporation is negligible and the NP solution/vapor interface is stable.

We have characterized the structure of the interfacial NP films by X-Ray Reflectivity (XR) and Grazing Incidence Small Angle X-Ray Scattering (GISAXS) performed with a X-ray beam of energy 8 keV. We used a vertically mounted 1D detector for XR measurements, and a 2D detector for GISAXS measurements.

We injected onto a 2''-diameter Silicon wafer 1 mL of a 6.5 nm core-size decane-thiol (DT) Au NPs dispersion in toluene. The volume injected contained a total number of NPs to cover the whole wafer surface with a single layer. Fig. 2 shows the measured Reflectivity R normalized by the Fresnel Reflectivity R_f at different stages of the experiment. The first curve (black) is measured at the bare silicon wafer surface, before NP solution injection. The other three curves, scaled for clarity, are measured at the NP-solution/vapor interface 1 hour (blue, $\cdot 1e^{-1}$), 2 hours and 30 minutes (red, $\cdot 1e^{-3}$) and 4 hours (green, $\cdot 1e^{-5}$) after the injection. The blue curve exhibits a clear bump at low q_z values, with an intensity higher than 1. This bump indicates the presence of a NP film. The corresponding GISAXS pattern (Fig.1a) does not show clear signatures of in-

plane correlation, even though a faint shoulder can be recognized at $q_{xy} \approx 0.08 \text{ \AA}^{-1}$. 1 hour and a half later, the bump in the R/R_f becomes less intense, indicating a less dense interfacial film. The GISAXS pattern becomes more isotropic (Fig. 1b), indicating an higher in-plane disorder. 4 hours after the injection, the R/R_f is practically flat, with a decay due to solvent/vapor interfacial roughness, and the corresponding GISAXS pattern is completely isotropic (Fig. 1c). The NP segregation at the solvent/vapor interface is therefore only a transitory effect, and after some hours the particles are dissolved again into the bulk solvent. The causes of this phenomena are not clear at the moment, but this layering effect is reproduced after each new injection of fresh NP solution. Further investigations carried out with an high-energy X-ray beam (70 keV, ID15A) showed that no accumulation of NPs is present, at any moment, at the buried substrate/NP-solution interface.

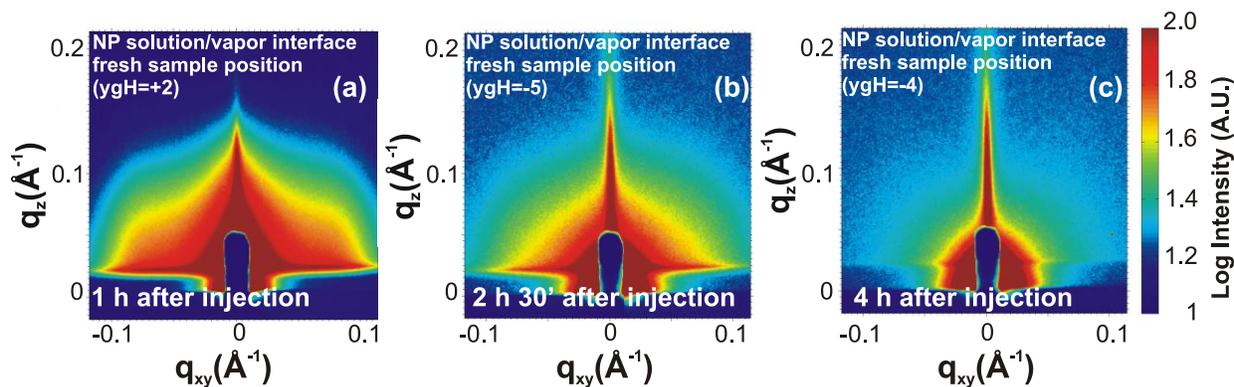


Figure 1 – GISAXS patterns measured at the stable NP solution/vapor interface.

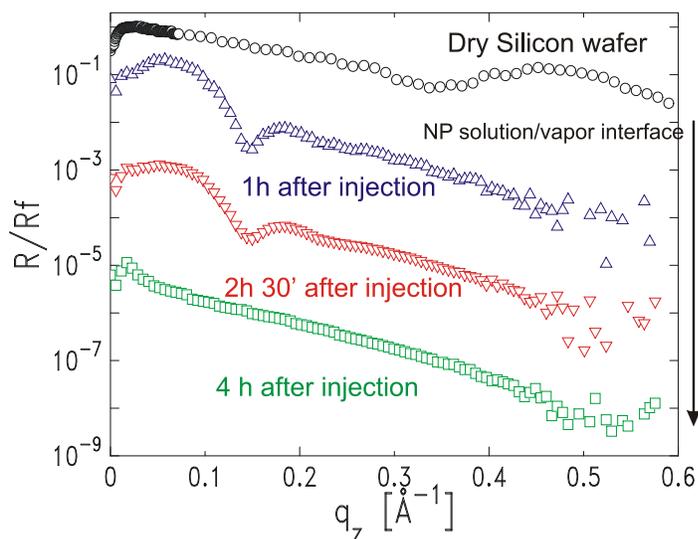


Figure 2 – XR measurements at the bare silicon surface (black) and at the stable NP solution/vapor interface 1 hour (blue, $\cdot 1e^{-1}$), 2 hours and 30 minutes (red, $\cdot 1e^{-3}$) and 4 hours (green, $\cdot 1e^{-5}$) after the NP solution injection.

We dedicated the second part of the beamtime to the investigations of the NP films resulting from the fast macroscopic solvent evaporation of different NP dispersions, and to the study of the effects of subsequent nano-scale solvent adsorption/desorption. The selected rate for the macroscopic evaporation determines a recession of the solvent/vapor interface in the direction perpendicular to the substrate plane of about $120 \mu\text{m}/\text{min}$. In particular, we have grown and

characterized a monolayer of 6.5 nm core-size DT-Au NPs (Fig. 3a), a multilayer of a 2.8 nm and 6.5 nm core-size DT-Au NPs mixture (number ratio small-NPs:large-NPs 60:40, Fig. 4a),

and a nanocrystal superlattices made of 8.2 nm core size oleic-acid (OA) capped PbSe NPs (Fig. 3b).

Fig. 4 shows an example of controlled nano-scale solvent adsorption study performed on the film composed of a mixture of 2.8 nm and 6.5 nm core-size Au NPs. The solvent adsorption onto the substrate is achieved by controlling the temperature offset ΔT between the sample and the toluene vapour inside the cell, in thermal equilibrium with a liquid toluene reservoir. Toluene films of thickness ranging from about 1 nm to 2.5 nm can be adsorbed onto a flat silicon surface

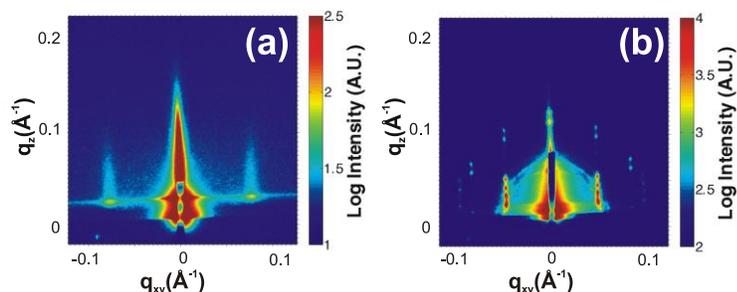


Figure 3 – Two examples of NP film obtained by fast macroscopic solvent evaporation: (a) monolayer of 6.5 nm core-size DT-Au NPs; (b) multilayer of 8.2 nm core size OA-PbSe NPs.

as ΔT is changed from 2.7 K to 140 mK. After fast evaporation, in almost dry conditions ($\Delta T=2.7$ K), the GISAXS pattern shows a large $q_{xy}\approx 0.18 \text{ \AA}^{-1}$ isotropic ring, indicating small NPs disorder, and two faint rods at smaller $q_{xy}\approx 0.08 \text{ \AA}^{-1}$, indicating in-plane correlation of the large NPs. Qualitatively, as ΔT is decreased and more solvent is adsorbed onto the NP film, the in-plane organization of the large NPs

is enhanced (Fig. 4c), and the correlation rods at $q_{xy}\approx 0.08 \text{ \AA}^{-1}$ becomes better defined, while the small NPs gives only an isotropic signal. The evolution of the GISAXS pattern indicates a structural reorganization of the NP superlattice at the nano-scale level. This is another intriguing process that deserves deeper investigations.

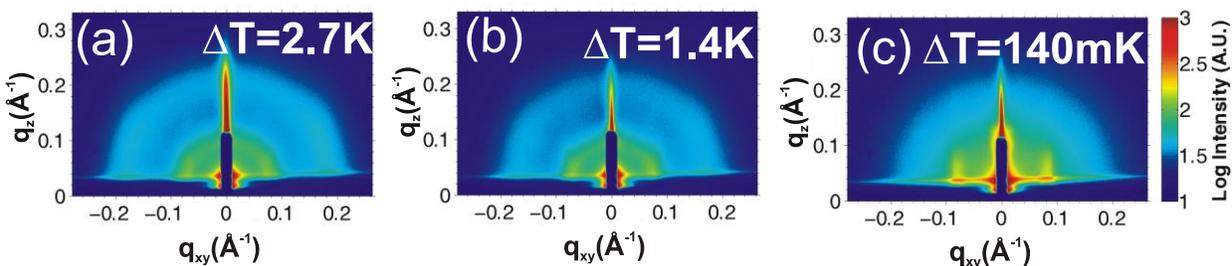


Figure 4 – GISAXS patterns showing three different stages of the solvent rewetting study of the NP film made of 2.8 nm and 6.5 nm core-size Au NPs. The first patterns corresponds to the film after fast evaporation and stabilization of ΔT to 2.7 K. Decreasing ΔT more solvent is adsorbed onto the film, yielding structural transformations in the NP superlattice.