ESRF	**Experiment title:** In Situ GISAXS during Plasma-Enhanced Atomic Layer Deposition of Silver: Elementary Study of the Island Growth Mode	**Experiment number**: 26-02-779
Beamline: BM26B	**Date of experiment**: from: 20/04/2016 to: 25/04/2016	**Date of report**: 05/07/2016
Shifts: 15	**Local contact(s)**: HERMIDA MERINO Daniel	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists): **Ghent University, Dept. of Solid State Sciences** DENDOOVEN Jolien* (main proposer), DETAVERNIER Christophe* (co-proposer), MINJAUW Matthias*, RAMACHANDRAN Ranjith*, SOLANO Eduardo* (co-proposer)

***Ex situ* study of Ag PEALD –** The initial aim of this beam time was to perform an *in situ* GISAXS/XRF study of the Ag/H_2 and Ag/NH_3 PEALD processes. During the preparatory experiments in the months prior to the beam time, we found however that the processes are not reproducible. Apparently different batches of Ag precursor as obtained from the manufacturer yield different scientific results. Therefore, we decided not to waste valuable beam time on an extensive *in situ* study of these non-reproducible processes. Instead, we selected a series of samples prepared in our lab and measured them *ex situ* (Table 1). With the remaining time, we continued the *in situ* Pt ALD and annealing experiments (26-02-672/-709/-726) and obtained interesting data sets that will allow us to finalize manuscripts that are in preparation on these topics.

Table 1. Selected ex situ Ag PEALD samples

Sample #	Ag PEALD process	# cycles
1	H_2-plasma	75
2		200
3		400
4		600
5	NH_3-plasma	10
6		20
7		50
8		100

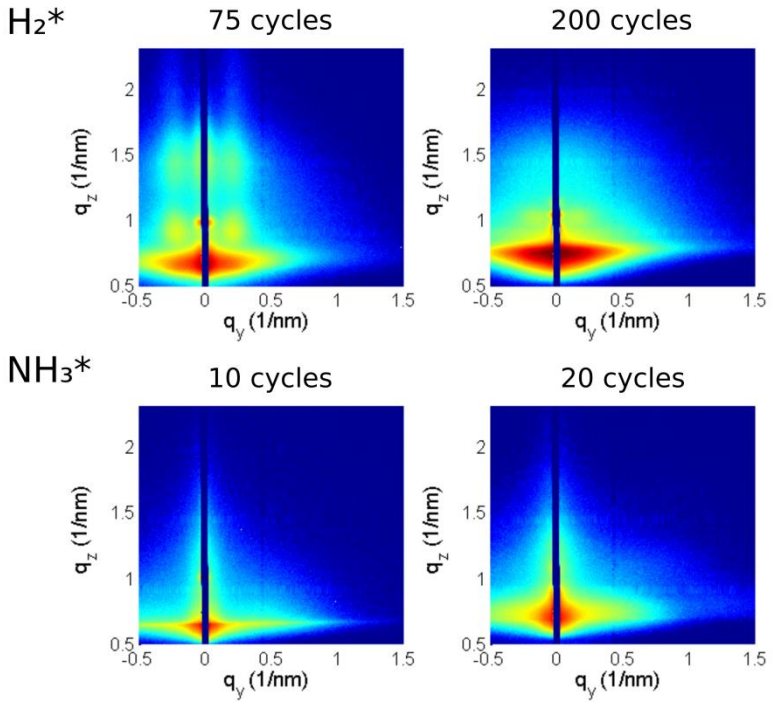

Figure 1. GISAXS data of a selection of *ex situ* Ag PEALD samples.

A selection of GISAXS data measured on the Ag samples is shown in Figure 1. For the H_2-plasma process at 75 cycles we observe multiple scattering maxima along q_z, which means that there is a good height correlation between different particles. For the sample at 200 cycles we observe a single pair of maxima, which are lying closer along q_y. This means that the inter particle spacing is larger and the particles are larger. In contrast, we have not observed any scattering maxima for the samples grown by the NH_3-plasma process. Hence, the variation in particle size and height is too strong for these samples, and we are not able to determine an average particle height or spacing.

***In situ* study of Pt thermal sintering –** A significant part of the beam time was used for a deeper investigation of the *in situ* annealing of supported ALD Pt nanoparticles, following the interesting results obtained during a previous campaign (26-02-726, June 2015). We focused on the effect of (1) the initial particle morphology and (2) the environmental O_2 concentration on the particle coarsening during the thermal annealing procedure. To this end, we prepared four distinct Pt samples with similar Pt loading but different as-deposited morphology onto a SiO_2 substrate via ALD. GISAXS corroborated the distinct initial particle morphology (Fig. 2 (left)). First, all samples were annealed in 18% O_2 in He up to 800ºC (0.2 ºC/s). By following the GISAXS peak position, $q_{y,max}$, we approximated the change in average center-to-center particle distance, $D=2\pi/q_{y,max}$. An increase in D is indicative of particle sintering. Figure 2 (middle) reveals that the onset temperature for particle coarsening depends on the initial particle morphology: smaller nanoparticles (with smaller center-to-center particle distance) sinter at lower temperature than the larger ones. In addition, the morphology of the supported Pt nanoparticles at high temperatures (> 650˚C) is observed to be independent of the initial particle morphology. Second, pieces of the same as-deposited samples were also annealed in 1.4% and 0.07% O_2 in He up to 950ºC to study the effect of the oxygen concentration on the Pt sintering behavior. Figure 2 (right) shows the results for the largest as-deposited nanoparticles (with the largest center-to-center particle distance). We observe a decrease in onset temperature for particle coarsening with decreasing O_2 concentration. A more pronounced difference, however, is that a higher O_2 concentration results in larger particles at high temperatures (> 650˚C), while for the lowest concentration a "stability plateau" is observed where no further particle sintering occurs.

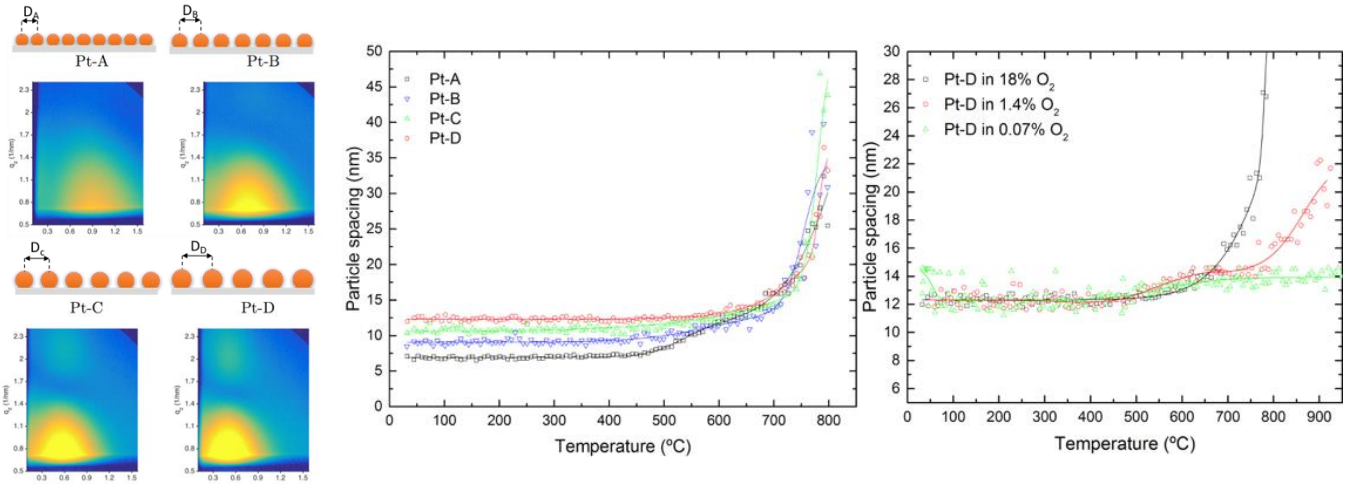

Figure 2. GISAXS images of the as-deposited supported Pt nanoparticles with similar Pt loading but distinct morphology (left). Influence of the initial particle morphology (center) and environmental oxygen concentration (right) on the particle sintering behavior during thermal annealing.

***In situ* study of Pt ALD** – As an extension of previous campaigns (26-02-672/-709), we have performed *in situ* GISAXS and XRF measurements during the initial growth stages of Pt ALD processes. We focused on the role of the Pt precursor dose on the nucleation and particle growth during the $MeCpPtMe_3/O_2$ ALD process at 300˚C. XRF and GISAXS revealed a decreasing growth rate with decreasing precursor pressure during both the nucleation and growth phase. On the other hand, GISAXS patterns obtained for the same Pt loading were identical. This indicates that, for a certain number of Pt atoms deposited on the surface, the particle shape, dimensions and areal density are equal irrespective of the precursor dose used in the ALD process. This can be understood based on our earlier findings that atom surface diffusion plays an important role during the O_2-based ALD process.

Conclusions: Although we could not execute the original beam time proposal due to reproducibility issues with the Ag PE-ALD processes, the campaign has been very successful. We collected a large amount of data for different ongoing projects in the group (ex situ Ag ALD characterization, in situ Pt annealing, and in situ Pt ALD). The results will allow us to finalize several manuscripts that are in preparation.