ESRF	**Experiment title:** Pd nanoparticles by atomic layer deposition: In situ GISAXS study of the growth and thermal stability	**Experiment number**: 26-02-872
Beamline: BM26B	**Date of experiment**: (including 1 preparation day) from: 04/06/2018 to: 12/06/2018	**Date of report**: 01/10/2018
Shifts: 15	**Local contact(s)**: HERMIDA-MERINO Daniel	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists): DENDOOVEN Jolien*[1] (main proposer), DETAVERNIER Christophe[1] (co-proposer), FENG Ji-Yu*[1], MINJAUW Matthias*[1], SOLANO MINUESA Eduardo*[1,2], VAN DAELE Michiel*[1]

[1] CoCooN group - Department of Solid State Sciences, Ghent University. Krijgslaan 281, S1. 9000-Ghent, Belgium

[2] ALBA Synchrotron Light Source – NCD Beamline, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallès, Spain

Introduction

During the last decade, ALD has emerged as an effective method to deposit noble metal nanoparticles (NPs) with a precise control of the particle morphology (size and areal density), which has promising potential applications in heterogeneous catalysis (Pt, Pd) and plasmonics (Au, Ag). Here, our home built ALD system enabling *in situ* monitoring of the NP morphology and loading by GISAXS and XRF measurements has been exploited to study the nanoparticle nucleation and formation during ALD growth of Pd. Preceding work revealed that the use of different plasma reactants influences the growth rate during steady Pd growth (Pd on Pd). Furthermore, it had been reported in literature that a trimethylaluminium (TMA)-based treatment can improve the nucleation on Al_2O_3 surfaces.[1] During this synchrotron campaign, we aim to figure out how these different processes influence the Pd NP growth and morphology evolution.

Experimental

GISAXS patterns were recorded using the Pilatus 1M detector of the beamline, using an acquisition time of 30s. The X-ray energy was set to 11.9 kev. The distance between sample and detector was 4.4m, while the incident angle was 0.5°. XRF spectra were simultaneously recorded using a Vortex detector. Pd NPs were deposited on Al_2O_3 (7nm ALD deposited) and native SiO_2/Si substrates at 150°C by alternating exposure of Palladium(II)hexafluoroacetylacetonate $Pd(hfac)_2$ and H_2, H_2+O_2, O_2+H_2 plasma as reactants. In some cases a pretreatment based on TMA was used.

Results

First, in situ GISAXS was used to monitor the island density as a function of the reactant choice (H_2 plasma, H_2+O_2 plasma or O_2+H_2 plasma) and on different substrates (7nm Al_2O_3 on Si and SiO_2). The deposition temperature was kept constant at 150°C. Figure 1 shows the results for Pd NPs deposited on Al_2O_3 by different plasma combinations. The Pd loading, derived from the in situ XRF measurements, versus ALD cycles graph shows that Pd NPs grown with H_2 plasma and O_2+H_2 plasma have a similar nucleation delay at lower loadings while Pd NPs grown with H_2+O_2 nucleate faster in the beginning. At higher loadings, the 3 processes show a growth rate which matches our earlier steady growth study. The GISAXS patterns recorded *in situ* for the 3 processes reveal a clear difference in the morphological evolution of the Pd NPs, where we estimate the center-to-center distance (D) between neighboring NPs as $2\pi/q_{y,max}$, with $q_{y,max}$ the q_y–position of the main scattering peak. The particle density (estimated as $1/D^2$ with D equal to the center to center distance plotted in Figure 1) is different for the three processes, with the H_2+O_2 plasma process yielding the highest particle density. The process that uses only H_2 plasma also shows a more static growth, with an almost constant particle density, while for the processes with O_2 plasma the particle density gradually decreases (somewhat similar to previous results obtained for Pt ALD).[2] Also the shape of the scattering signal is different for the pure H_2 plasma process, showing a

clear interference ring, while this scattering ring is less prominent when O_2 plasma is incorporated. This indicates for a different shape of the NPs. More detailed analysis of these results is ongoing.

Secondly, the combination of processes with H_2 plasma and H_2+O_2 plasma was also performed during this campaign (scattering patterns not shown). The main conclusion is that by combining the processes, we can tune the nucleation areal density and morphology evolution of the ALD Pd NPs. However, the tuning range is rather limited and this motivated the next study, focused on introducing TMA exposures during the first Pd ALD cycles.

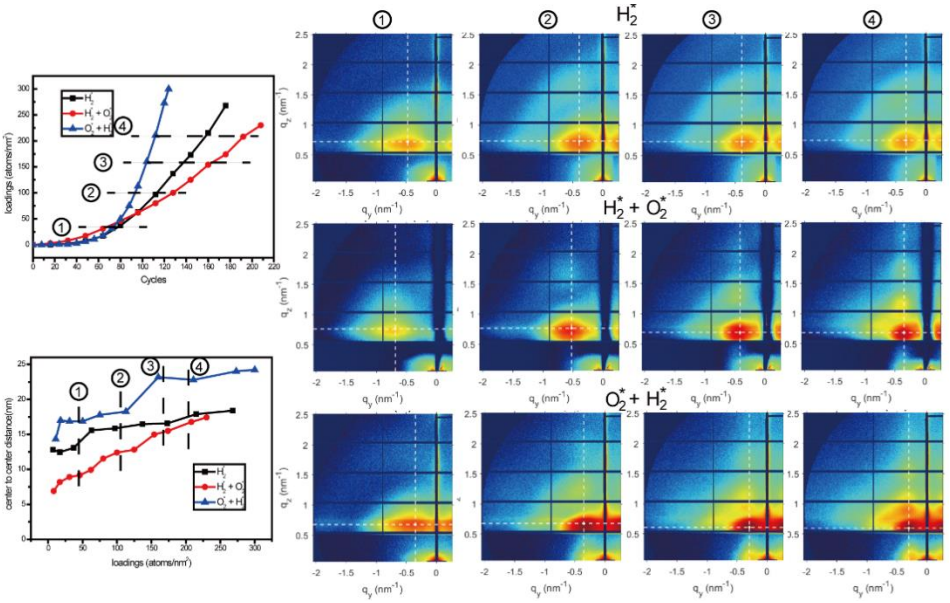

Fig. 1: PE-ALD of Pd NPs on Al_2O_3 substrates with H_2, H_2+O_2 and O_2+H_2 plasma. Left up: Pd loading as a function of cycles. Left down: center-to-center distance as a function of Pd loading. Right: GISAXS patterns at the indicated Pd loadings.

Indeed, thirdly, in Figure 2, Pd NPs were deposited on Si using the H_2 plasma-based process with and without TMA pulse in the first ten ALD cycles. The Pd NPs growth with TMA treatment shows an obvious faster nucleation than the growth without TMA treatment, whose long nucleation delay is due to the surface poisoning generated from reaction between the surface and ALD byproducts. By introducing a TMA pulse during the first cycles, these poisoning surface groups could effectively be removed. Moreover, GISAXS patterns at similar loading throughout both processes show quite different morphology of the Pd NPs when grown with or without TMA treatment. The estimated center-to-center distance (D) between neighboring NPs shows that Pd NPs with TMA treatment in the first ALD cycles have a denser distribution with small particle size, while Pd NPs without TMA treatment show a dispersed distribution with larger particle size at the same Pd loadings. This difference in particle density has been confirmed by ex situ SEM images. More detailed analysis of the GISAXS data is ongoing, together with the preparation of a manuscript on this topic.

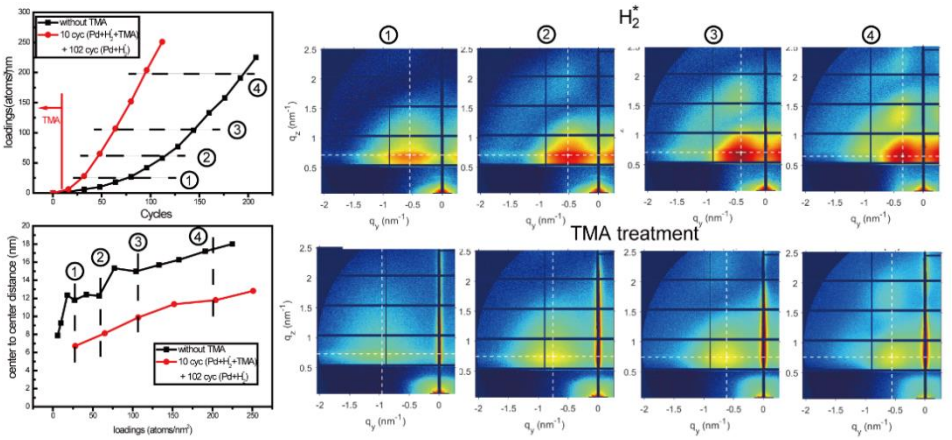

Fig. 2: PE-ALD of Pd NPs on SiO_2 substrates with and without TMA pretreatment. Left up: Pd loading as a function of cycles. Left down: center to center distance as a function of Pd loading. Right: GISAXS patterns at the indicated Pd loadings.

Finally, Pd NPs grown with different cycles of TMA treatment (0, 1, 3, 10) at the same loading were measured with *ex situ* GISAXS (scattering patterns not shown). The data show that the areal density of the Pd NPs can be varied between the two processes analyzed *in situ* (Figure 2).

Conclusion

The synchrotron campaign allowed us to perform a rather complete study of Pd NP ALD. Simulations to complement the quick GISAXS analysis shown here are ongoing, and the work is in progress of being written down in a publication.

[1]Goldstein et al., Appl. Phys. Lett. 95, 143106 (2009). [2]Dendooven et al., Nature Communications 8, 1074 (2017).