ESRF	**Experiment title:** In situ GISAXS study of atomic layer deposition of Pd and its combination with atomic layer deposition of Pt to synthesize supported Pt/Pd and Pd/Pt core/shell nanoparticles	**Experiment number**: 26-02/818
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Introduction

Over the past decade, atomic layer deposition (ALD) has proven to be a promising method to deposit noble metal nanoparticles (NPs) with precise control over the size and composition. This has attracted wide interest from the fundamental heterogeneous catalysis research field. During previous DUBBLE campaigns, we collaborated with the DUBBLE team to develop and apply a unique *in situ* XRF-GISAXS approach during ALD and annealing of Pt NPs. This work provided insights in the tuning opportunities of Pt ALD as well as the coarsening mechanism at high temperatures, and resulted in recent publications in Nature Communications[1] and Nanoscale[2].

During our recent campaign, 26-02/818, we aimed to extend this successful work to the Pd system and 1) study the morphology evolution during ALD of Pd NPs using different plasma reactants, 2) combine Pt and Pd ALD to deposit Pd/Pt core/shell nanoparticles and 3) study the thermal stability of ALD-grown Pd NPs during annealing.

Experimental

Pd NPs were deposited on planar Al_2O_3 and SiO_2 substrates using palladium(II)hexafluoroacetylacetonate [$Pd(hfac)_2$] as precursor and NH_3, H_2 and $H_2 + O_2$ (three steps process) plasmas as reactants at 100°C, while *in situ* XRF spectra and GISAXS patterns were recorded using 30 s measurements (E = 12 keV, α_i = 0.5°, sample-detector distance = 3.2 m). In addition, *ex situ* measurements were performed on Pd samples that were prepared in our homelab using the same ALD setup. Core/shell Pd/Pt NPs were synthesized by depositing Pt on pre-prepared Pd NPs using (methylcyclopentadienyl)trimethylplatinum [$MeCpPtMe_3$] as precursor and NH_3 plasma or O_2 gas as reactant at 300°C and monitoring the Pt deposition *in situ*. For the annealing experiments, pre-prepared Pd NPs were annealed to 1000°C with a ramp rate of 0.2 °C/s in 21% or 2.1% O_2/He atmosphere, while *in situ* GISAXS patterns were recorded.

Results

In situ characterization of Pd NP ALD

Figure 1 shows a selection of GISAXS patterns recorded during a first deposition of Pd NPs on Al_2O_3 using NH_3 plasma as reactant at 100°C (Fig. 1(a)). The scattering along q_z near the beam stop (q_y = 0 nm^{-1}) in the initial pattern originates from the Al_2O_3 substrate (Fig. 1(a1)). With increasing number of Pd ALD cycles, additional scattering maxima appear along q_z, which means that the height of the Pd NPs increases. The position of the main scattering peak along q_y shifts slightly to lower value during the first ca. 100 ALD cycles and then remains at a fixed position, meaning that the centre-to-centre distance between the Pd nuclei increases slightly at first and remains stable then. This trend is clear in the 2D color map shown in Fig. 1(b1). In the case of the H_2 plasma (Fig. 1(b2)) and $H_2 + O_2$ plasma (b3) processes, the main scattering peak shifts slowly to lower q_y values during the 200 recorded ALD cycles. Overall, we conclude that the **Pd NPs grow at a mainly static mode** with no obvious cluster mobility or particle ripening during the ALD process. This is in contrast to the Pt ALD process which showed very clear dynamic, diffusion-mediated particle growth when O_2 gas or O_2 plasma are used as reactant.[1]

However, when we repeated the NH_3 plasma process again, the Pd growth curve obtained from XRF revealed a degradation of the Pd deposition (Fig. 1(c)), likely due to an unexpected **degradation of the $Pd(hfac)_2$ precursor**. It is unclear why the chemical degraded during the synchrotron campaign (similar experiments were done in our homelab during the past year without problems). In any case, for future campaigns, we will bring two spare precursor containers that will be thoroughly tested in advance in Gent.

[1]Dendooven et al., Nature Communications, Accepted Manuscript, 2017. [2]Solano, Dendooven et al. Nanoscale 9, 13159, 2017.

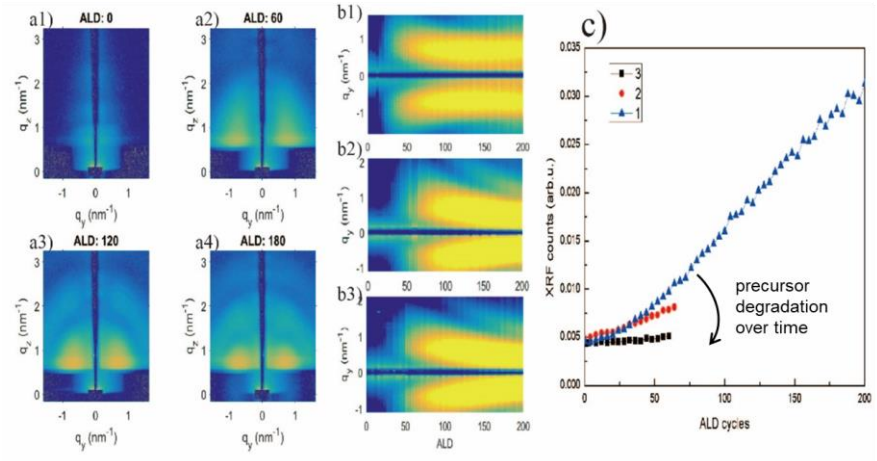

Figure 1 (a) GISAXS patterns recorded during NH_3 plasma–based Pd ALD on Al_2O_3 at 0 (a1), 60 (a2), 120 (a3) and 180 (a4) cycles. **(b)** 2D color maps showing the evolution of the main scattering peak along q_y (1D line profiles along the Yoneda peak position) for Pd ALD on Al_2O_3 with NH_3 plasma (b1), H_2 plasma (b2) and H_2 + O_2 (b3) plasma. **(c)** Pd XRF counts against the number of ALD cycles for three identical depositions using NH_3 plasma (growth curve 1 corresponds to the experiment in (a) and (b1)).

<u>*Ex situ* characterization of Pd NP ALD</u>

Because of the degradation of the Pd precursor, the original plan to perform *in situ* experiments during Pd NP growth on SiO_2 substrates could not be carried out. As a backup, pre-prepared samples were measured *ex situ* with GISAXS. **Figure 2** compares two of the measured images for Pd samples grown with the NH_3 plasma process with the same Pd loading on a SiO_2 vs. Al_2O_3 substrate. On Al_2O_3 the scattering peak appears at a larger q_y value (~0.7 nm^{-1}) than on SiO_2 (~0.5 nm^{-1}), which reveals a smaller NP center-to-center distance and thus **larger Pd NP areal density on Al_2O_3 than on SiO_2.**

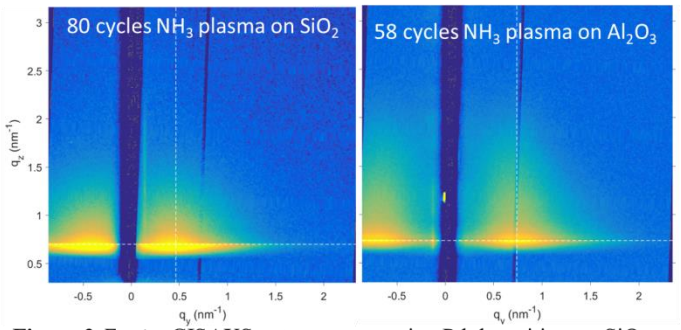

Figure 2 *Ex situ* GISAXS patterns comparing Pd deposition on SiO_2 vs. Al_2O_3. The Pd loading (XRF counts) was the same for both samples.

<u>Pd/Pt core/shell NPs</u>

Pre-prepared Pd NPs on Al_2O_3 were overgrown with Pt to synthesize Pd/Pt core/shell NPs. **Figure 3** shows the GISAXS patterns before and after 32 cycles of Pt ALD using NH_3 plasma (top) and O_2 gas (bottom). The final GISAXS pattern is very different for the two selected reactants. After the Pt-NH_3 plasma process, the main scattering maximum remains at the same q_y position as the original scattering feature of the Pd core particles. In addition, another scattering peak appears at larger q_y values. After the Pt-O_2 gas process, the main scattering peak has shifted to lower q_y values and a scattering ring has appeared. The different GISAXS patterns are to be explained by a *difference in selectivity* for the Pt ALD growth on Pd vs. the Al_2O_3 substrate (O_2 gas process is likely more selective) and by a *difference in surface diffusion* during the Pt ALD growth (O_2 gas process likely induces more mobility on the surface). Post-characterization of the synthesized samples with TEM is ongoing. This will provide us with the required info to proceed with the analysis of the *in situ* GISAXS images.

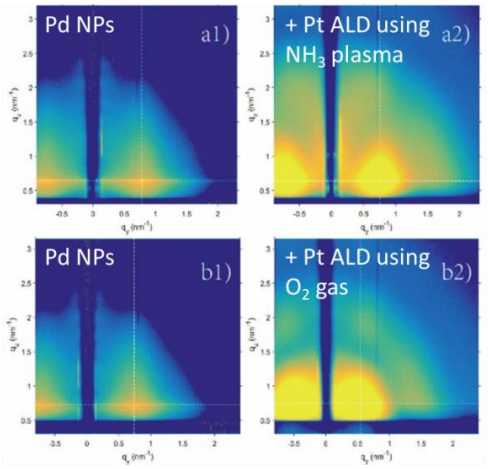

Figure 3 GISAXS pattern recorded before and after 32 Pt ALD cycles on Pd NPs using different reactants: NH_3 plasma (a1 and a2) and O_2 gas (b1 and b2).

<u>*In situ* GISAXS during annealing of Pd NPs</u>

At last, annealing experiments were carried out to study the coarsening mechanism of pre-prepared Pd NPs. Samples grown with the NH_3 plasma process with different Pd loading (i.e. different initial particle size) and different substrate (SiO_2 vs. Al_2O_3) were selected. Annealing experiments were performed under 21% and 2.1% O_2 in He atmospheres (1 bar pressure). All samples showed a **remarkable stability** in 21% O_2 in He atmosphere and particle coarsening only started at 1000°C. This is in large contrast to Pt NPs of similar sizes for which coarsening started at temperatures between 450 and 600°C.[2] Decreasing the O_2 partial pressure to and 2.1% O_2 in He, decreased the onset temperature for NP coarsening to 900°C. This is in line with our Pt work that revealed a decreasing onset temperature with O_2 partial pressure.[2] However, to obtain a deeper understanding of the particle coarsening mechanism of Pd NPs, **additional experiments are needed at even lower O_2 partial pressures**.

Conclusion

This campaign focused on ALD of Pd NPs. Though the Pd process failed, limiting the number of *in situ* studies that we could perform, important insights have been obtained providing a firm basis for the design of follow-up experiments. Surprising differences with the previously studied Pt system were found: (1) static growth was observed for Pd ALD, even when O_2 plasma was used; (2) Pd NPs show a much higher thermal stability than Pt NPs with comparable size. In addition, the Pd NP areal density is significantly higher on Al_2O_3 than on SiO_2. Pd/Pt core/shell NPs were synthesized using different Pt ALD chemistries. Their different growth behaviour remains to be analyzed.

[1]Dendooven et al., Nature Communications, Accepted Manuscript, 2017. [2]Solano, Dendooven et al. Nanoscale 9, 13159, 2017.