ESRF	**Experiment title:** In Situ GISAXS during Atomic Layer Deposition - Towards the Controlled Formation of Sintering-Resistant Pt Nanoparticles	**Experiment number**: 26-02-709
Beamline: BM26B	**Date of experiment**: from: 10/02/2015 to: 11/02/2015 (preparation) from: 12/02/2015 to: 16/02/2015 (beam time)	**Date of report**: 23/03/2015
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Atomic layer deposition (ALD) processes for Pt are often characterized by a nucleation controlled growth mode. Islands are initially formed that coalesce in a continuous film after a sufficient number of ALD cycles. To study the formation and growth of the initial nuclei and the subsequent evolution of surface morphology during Pt ALD processes, we developed a flexible ALD setup that can be installed at the DUBBLE beamline and allows performing in situ x-ray fluorerscence (XRF) and grazing incidence small angle x-ray scattering (GISAXS) measurements between subsequent deposition cycles. In a previous campaign (26-02-672 Jan 2014), we optimized our experimental setup and demonstrated the feasibiliy of our in situ approach. In the above mentioned experiment (26-02-709 Feb 2015), we aimed for a **systematic study of the effect of the underlying substrate and reactant pressure on the initial island growth mode of Pt ALD**. In addition, in view of our next beamtime (26-02-726 Jun 2015), we **optimized the measurement conditions for in situ GISAXS during post-deposition annealing (sintering) of the Pt nanoparticles**.

Results

Effect of underlying substrate on the initial growth of Pt ALD - Pt was deposited using (methylcyclopenta-dienyl)trimethylplatinum ($MeCpPtMe_3$) as the Pt precursor and O_2 gas at 1 mbar (high-P process) as the reactant on SiO_2 and Al_2O_3. Every two ALD cycles, GISAXS and XRF measurements were performed using a 12 keV beam at incidence angles of 0.5 and 1.2°, respectively. From the in situ recorded XRF spectra, the integrated counts for the Pt Lα peak were determined as a function of the number of ALD cycles. This Pt XRF intensity was then converted to a surface density of Pt atoms by remeasuring the last point of the intensity curve with an XRF spectrometer that was calibrated against Rutherford back-scattering data obtained for a series of samples with different Pt coverages. The results are shown in **Fig. 1a**. The inset shows the growth per ALD cycle (GPC) in Pt atoms/nm^2 obtained by differentiating the curves. During the initial growth stages more Pt atoms are deposited on the Al_2O_3 surface, and the maximum in the GPC is already obtained at around 30 ALD cycles as compared to ca. 60 ALD cycles for the SiO_2 surface. Because the maximum in the GPC occurs due to island-type growth, this result is a first indication of a difference in surface morphology. **Fig. 1b and c** show the GISAXS results measured at Pt coverages of 30, 60, 90 and 120 atoms/nm^2. The plotted data are vertical (1b) and horizontal (1c) cuts taken at the position of maximum intensity in the main scattering lobe. The q_y-position of the main scattering lobe in GISAXS can be correlated to the average center-to-center distance between the particles, while the average particle height and diameter can be estimated from the intensity modulations along q_z and q_y, respectively. Based on a qualitative

comparison of the GISAXS data measured on SiO_2 (dashed lines) vs. Al_2O_3 (solid lines), we can conclude that, for a same Pt surface coverage, the Pt nanoparticles formed on a SiO_2 surface are larger in height and diameter and have a larger center-to-center distance, while on Al_2O_3 a higher density of smaller particles is obtained. This difference could be related to the presence of more nucleation sites (OH-groups) on the in situ grown Al_2O_3 surface vs. the ex situ grown SiO_2 surface [Mackus et al., Chem. Mater. 2012, 24, 1752]. A second explanation could be a difference in activation energy for particle ripening processes [Zhou et al., JPCC 2012, 116, 12114]. Further analysis of the data and additional experiments are ongoing to identify the exact mechanisms that play a role.

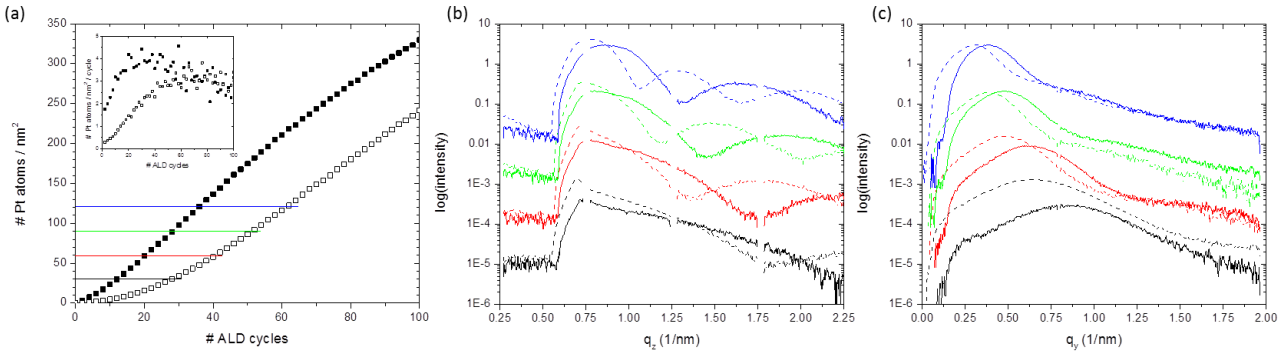
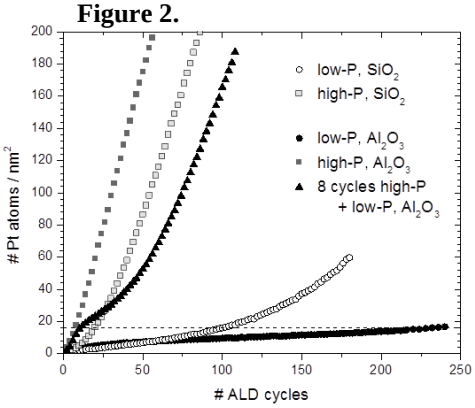


Figure 1. (a) Pt surface coverage (inset: growth per cycle) against the number of ALD cycles during growth on SiO_2 (open symbols) and Al_2O_3 (filled symbols). (b) Vertical and (c) horizontal cuts taken at the position of the main lobe in GISAXS for Pt coverages of 30 (black), 60 (red), 90 (green) and 120 (blue) atoms/nm^2 on SiO_2 (dashed lines) and Al_2O_3 (solid lines).

Figure 2.



Effect of reactant pressure on the initial growth of Pt ALD - **Fig. 2** compares the XRF growth curves for Pt ALD using high O_2 pressure (1 mbar) vs. low O_2 pressure (10^{-2} mbar) on SiO_2 and Al_2O_3 surfaces. Clearly much less Pt atoms are deposited per ALD cycle for the low-P process. Although initially more Pt atoms are deposited on Al_2O_3 than on SiO_2, the deposition slows down on Al_2O_3 while the growth rate increases on SiO_2 with increasing number of ALD cycles. Only after 240 cycles, the deposited amount of Pt on Al_2O_3 reaches the value expected for a monolayer of Pt (dashed line). On the other hand, if we first perform 8 ALD cycles of the high-P process and then continue with the low-P process, growth continues and the deposition rate becomes similar to the growth rate for the high-P process. This confirms that the O_2 pressure plays a crucial role in the formation of the first nuclei [Mackus et al., Chem. Mater. 2013, 25, 1905]. Furthermore, comparison of the GISAXS patterns measured for the high-P vs. high-P/low-P process reveals a clearly different particle morphology, thus proving that the pressure not only influences the formation of the Pt nuclei but also the particle ripening and growth process. Interpretation of the data in terms of particle size and spacing is ongoing and will provide us an in-depth understanding of the effect of the O_2 pressure on the particle formation and growth.

In situ GISAXS during post-deposition annealing - During our previous beamtime (26-02-672 Jan 2014), one proof-of-principle experiment was performed in which Pt islands were annealed in O_2 (1 bar) using a heating rate of 5°C/min. Although this result demonstrated the feasibility of the proposed in situ GISAXS approach, it also showed the necessity for further optimization of the measurement conditions in order to improve the resolution at low q_y-values and to decrease background scattering. In an optimization experiment performed in this campaign, the sample-detector distance was ca. 440 cm (vs. 155 cm before) yielding a sufficient resolution at low q_y-values to distinguish the main scattering lobe from the specular rod in GISAXS (**Fig. 3**). To decrease background scattering, mass flow controllers were used to obtain a 20% O_2 in He atmosphere at 1 bar. In our next beamtime (26-02-726 Jun 2015) the optimized conditions will be used to systematically study the Pt sintering.

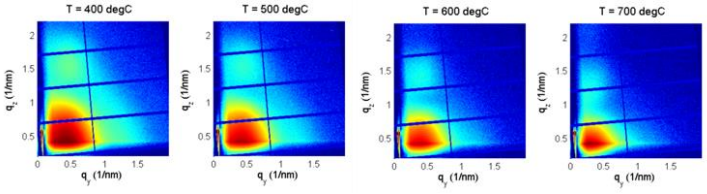


Figure 3. With increasing temperature, the main lobe shifts to lower q_y-values while the second order lobe along q_z shifts to lower q_z-values. This indicates that the average particle size and spacing increase, i.e. that particle sintering occurs.