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Experiment Report Form

ESRF	**Experiment title:** Fundamental Study of the Initial Nucleation during Atomic Layer Deposition of Pt: In Situ GISAXS Study of the Island Growth Mode	**Experiment number**: 26-02-672
Beamline: BM26B	**Date of experiment**: from: 16/01/2014 to: 20/01/2014 (preparation) from: 21/01/2014 to: 25/01/2014 (beamtime)	**Date of report**: 25/03/2014
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Report:

Objectives

For atomic layer deposition (ALD) processes of Pt, a clear nucleation controlled growth is typically observed on oxide surfaces. This initial islandlike growth mode can be used advantageously for the fabrication of nanoparticles, e.g. for applications in catalysis. However, due to experimental difficulties, obtaining an in-depth understanding and control over the nanoscale structure and morphology during the early stages of ALD growth has proven very difficult. The main objective of experiment 26-02-672 was to develop and optimize a novel approach to systematically study the initial growth mode of Pt ALD by means of *in situ* grazing incidence small angle x-ray scattering (GISAXS) and x-ray fluorescence (XRF) measurements at the BM26B beamline. Secondly, we aimed at a detailed study of how the morphology during Pt ALD is affected by the underlying substrate (SiO_2 vs. TiO_2), the reactant gas (O_2 vs. O_3) and the growth temperature (150°C vs. 300°C).

Results

✓ Succesfull installation of the ALD setup at the DUBBLE SAXS/WAXS beamline

For the purpose of this experiment, a dedicated pump-type ALD reactor with three Be windows for the x-rays to enter and exit the chamber was developed. Figure 1 shows pictures of the setup installed on the sample pillar at the DUBBLE beamline. The Vortex XRF detector was fixed on a mounting plate and installed on the chamber. The Pilatus 1M detector for GISAXS was positioned at the calculated optimum distance of 155 mm from the sample. To decrease background scattering in GISAXS, adjustable horizontal Mo slits and a rod-like W beam stop (BS1) were placed inside the vacuum at the entrance and exit side respectively. A second beam stop (BS2) was positioned in front of the detector to completely mask the direct beam and specular rod.

✓ Optimization of the alignment strategy

To optimize the measurement conditions, a native SiO_2/Si substrate with a 10 nm ALD grown Pt layer was placed on a Mo sample plate and positioned horizontally in the beam. The chamber was pumped down to its base pressure (10^{-6} mbar). The energy of the x-rays was fixed at 12 keV, above the Pt L3 edge (11.6 keV). At this energy, the critical angle of Pt is 0.38°. The size of the x-ray beam was 0.38 x 1.3 mm^2 at the detector position. After alignment of the sample and BS2 with respect to the beam, we optimized the position of the in vacuum slits and BS1, so as to minimize background scattering arising from the Be windows (Figure 1).

✓ In situ GISAXS and XRF during ALD of Pt

ALD of Pt was performed on (in situ O_2 plasma cleaned) SiO_2 and TiO_2 substrates using trimethyl(methyl-cyclopentadienyl)platinum ($MeCpPtMe_3$) as Pt source and O_2 or O_3 as reactant gas. The growth temperature was either 150 or 300 °C. Every two ALD cycles, the sample was exposed to x-rays and in situ XRF and GISAXS data were acquired during a prolonged pumping step following the reactant pulse. GISAXS was performed at incidence angles of 0.3° and 0.5° using an acquistion time of 20 or 60 s. The high surface sensitivity that is obtained at 0.3° is beneficial during the start of the ALD process, while in the later stages of growth, the incidence angle of 0.5° ensures that the full Pt layer is still penetrated. The amount of deposited Pt atoms was followed in situ by XRF using a measurement time of 20s and an incidence angle of 1.2°.

The Figure shows the 60s GISAXS patterns measured after 24, 40, 56, and 72 ALD cycles for the O_2-based process on a SiO_2 surface at 300 °C. Following an incubation period of ~15 ALD cycles, a clear intensity lobe appears at a q_y position that is indicative of a ca. 6 nm center-to-center distance between the initial Pt nuclei. During the early growth phase, the GISAXS peak shifts towards smaller q_y values pointing to an increase in average spacing, mainly due to diffusion phenomena and coalescence of adjacent Pt particles. The scattering lobes also move towards larger q_z values due to a shift in the prominent Yoneda region from Si to Pt when more and more Pt covers the Si substrate. Further ALD deposition gives rise to intensity modulations along q_z that can be related to a growing average thickness of the Pt clusters or, finally, the coalesced Pt layer. More detailed analysis and interpretation of the scattering patterns to determine the evolution in particle size, shape and spacing as a function of the deposition parameters (substrate, reactant gas and temperature) is ongoing.

Conclusions

We conclude that this first beamtime confirmed the feasibility of our novel approach to employ in situ XRF and GISAXS to study the nucleation and growth during Pt ALD. Analysis of the acquired data sets is ongoing and will enable us to obtain unique insights in the formation, growth and coalescence of Pt islands by ALD.

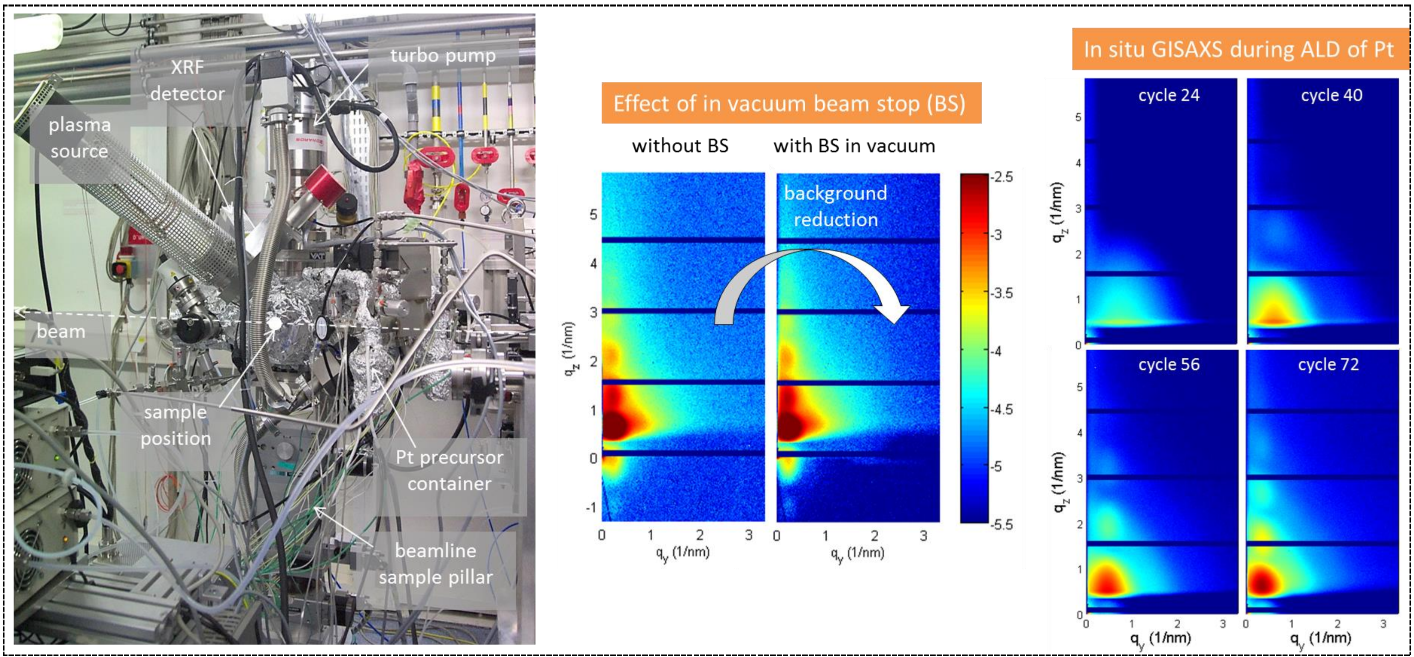

Figure 1: Photograph of the dedicated ALD setup installed at the DUBBLE beamline (left). The use of an in vacuum beam stop leads to a reduction in background scattering originating from the exit Be window (middle). Selection of 2D GISAXS patterns measured during O_2-based Pt ALD on SiO_2 at 300 °C (right).