	Experiment title: Atomic layer deposition of Pt nanoparticles: tracking the evolution in shape and surface facet structure with in situ GISAXS	**Experiment number**: 26-02-953
Beamline: BM26	**Date of experiment**: from: 25/09/2022 to: 03/10/2022	**Date of report**: May 15, 2023
Shifts: 15	**Local contact(s)**: ROSENTHAL Martin	*Received at ESRF:*

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Report:

Introduction

The state-of-the-art insights into the morphological evolution of metal nanoparticle (NP) populations on metal oxides during atomic layer deposition (ALD) cover the NP size and coverage,[1] but currently lack information on the crystallography and NP shape. To overcome this, the approach of proposal 26-02-953 was to deposit Pt NPs on single cristal oxide substrates, aiming for epitaxial stabilization of the NPs. The well-defined orientation of the NPs was expected to give rise to clear scattering streaks in GISAXS,[2] allowing to model facetted NP shapes. Prior to the planned *in situ* measurements, a series of *ex situ* GISAXS measurements under different conditions (incidence angle, sample direction) were done to verify if a specific crystallographic orientation and shape of the NPs is detectable in GISAXS. The results of these experiments are reported here.

Experimental section

Sample preparation at UGent. Several series of Pt NPs on single crystal MgO(001) (10 mm×10 mm/15 mm×15mm) were prepared with varying numbers of Pt ALD cycles (20, 30, 40, 50, 60). $MeCpPtMe_3$ was used as the metal precursor for Pt ALD, and O_2 was the coreactant. Depositions were performed at 300 ºC on cleaned MgO. Our custom-made vacuum chamber[3] was used for all ALD depositions. In addition to as-deposited samples, samples post-annealed in He and in 20% O_2/He mixture up to 900°C were also brought to the beamline.

Measurements at DUBBLE. The energy of the X-ray beam was set to 12 keV and the detector-to-sample distance was set to 4.7 m. The beam size was 800 × 750 microns (H × V) at the sample position. The samples were measured twice, i.e. with a different orientation of the sample with respect to the beam. One configuration named “straight” meant that one side of the square sample (corresponding to the [100] direction) was put along the beam direction. Another “diagonal” configuration was that the diagonal of the square sample (corresponding to the [110] direction) was along the beam. GISAXS measurements were performed at incidence angles of 0.3º and 0.5º, respectively.

Results

SAMPLES	Pt20	Pt30	Pt40	Pt50	Pt60
As-deposited (AD)	✓	✓	✓	✓	✓
900°C, 20% O_2 annealed	✓	✓	✓	✓	✓
900°C, He annealed	✓	✓	✓	✓	✓

Five groups of Pt samples with different Pt loading were successfully measured (see Table). The as-deposited Pt/MgO(001) samples from low to high loading were measured to see the effect of NP size. As shown in Figure 1, the main scattering feature originating from the Pt NPs increases in intensity and shifts to lower q_y values with increasing Pt loading. This is in line with our previous investigation of Pt ALD on SiO_2.[3] However, the scattering streaks expected for highly oriented and facetted NPs were not observed, suggesting that the ALD process did not establish an epitaxial growth of Pt NPs on MgO(001).

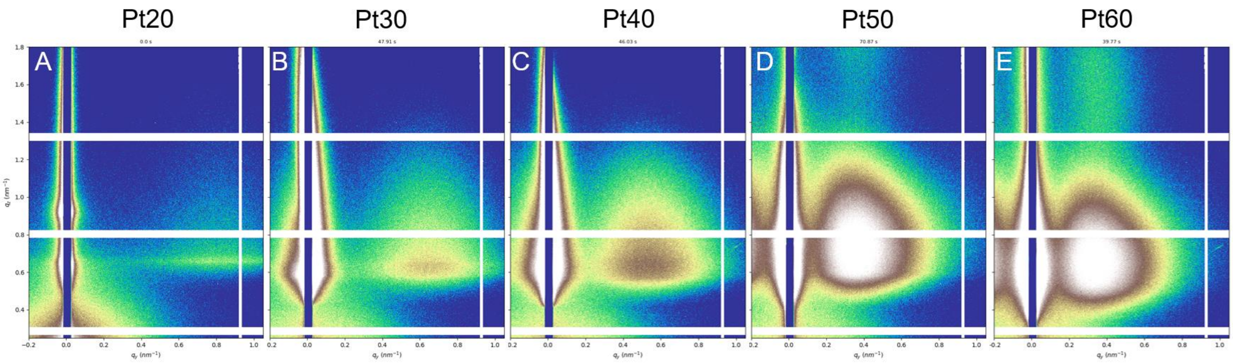

***Fig. 1**: Ex situ GISAXS data for 20 (A), 30 (B), 40 (C), 50 (D) and 60 (E) Pt ALD cycles on MgO(001).*

Based on preliminary results of lab pole figure XRD, post-annealing enhances the preferential orientation of the NPs, surprisingly, with the <111> plane parallel to the substrate surface. Therefore, also post-annealed samples were investigated via *ex situ* GISAXS at DUBBLE. As shown in Figure 2, as a consequence of the annealing, the scattering feature appears at much lower q_y values, close to the rod-shaped beamstop. This result is again in line with our previous work: the thermal treatment induces coarsening of the NPs, increasing their size and interparticle distance, and leading to a shift of the scattering peak to lower q_y values.[4] Unfortunately, also in this case, no additional scattering streaks originating from oriented NP facets could be observed.

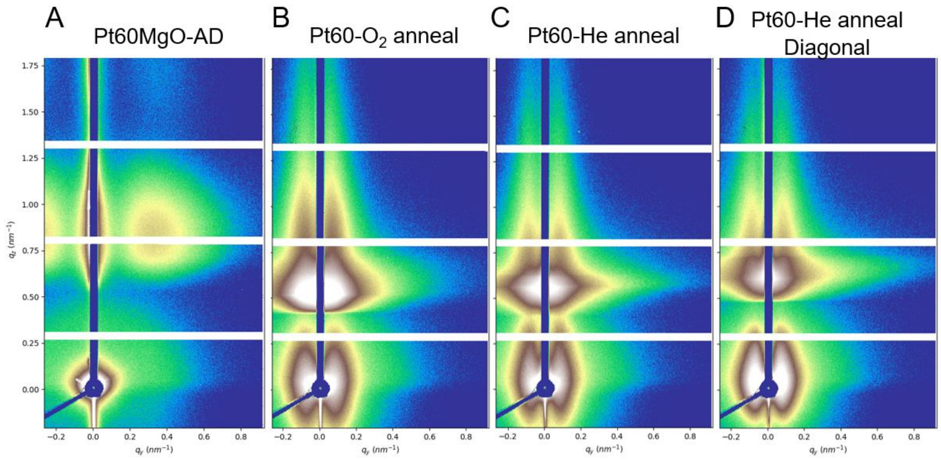

***Fig. 2**: Ex situ GISAXS data for 60 Pt ALD cycles on MgO(001) (A) followed by annealing in O_2 (B) and He (C,D).*

Conclusion

Even if preliminary pole figure XRD measurements showed promising texture, the *ex situ* GISAXS images did not show scattering streaks indicative of highly oriented and facetted NPs hampering the detailed shape analysis that we aimed for. In view of these results, it was decided to not carry out the *in situ* GISAXS investigations during Pt ALD on MgO(001), planned for the second part of the beamtime. However, we did make full use of the beamtime: in situ GISAXS measurements during Photo-ALD of Pt on SiO_2 substrates were performed instead, allowing us to finish a project with data acquired during a previous campaign at DUBBLE (A26-2-938) and which we aim to publish in the coming months. Thus, even if the originally proposed project could not be fully achieved, the campaign provided (1) useful information for follow-up work concerning Pt ALD on single crystal oxides, and (2) necessary data to complete our work on Photo-ALD of Pt (see experimental report of (A26-2-938)).

References

[1] Dendooven et al. Nat. Comm, 2017, 8, 1074. [2] Revenant et al. Phys. Rev. B 79, 235424, 2009. [3] Dendooven et al. Phys. Chem. Chem. Phys., 2020, 22, 24917. [4] Solano et al. Nanoscale, 2020, 12, 11684-11693.