ESRF	**Experiment title:** Unraveling the atomic structure of Pt nanoparticles grown by atomic layer deposition	**Experiment number**: MA-5626
Beamline: ID15A (C02)	**Date of experiment**: from: 4 April 2023 at 08:00 to: 6 April 2023 at 16:00	**Date of report**: 5 July 2023
Shifts: 6	**Local contact(s)**: Stefano Checchia	*Received at ESRF:*

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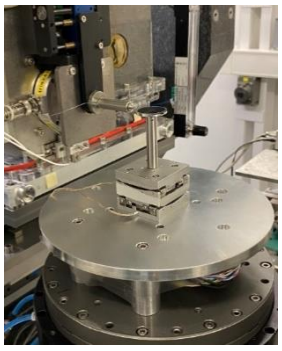
Report:

Atomic layer deposition (ALD) allows to prepare well-defined ensembles of supported nanoparticles with sub-monolayer precision over a wide range of metal loadings (atoms/cm^2), e.g. for their use as model nanocatalysts. GISAXS experiments by our group previously showed that the choice of reactant in the ALD process has a significant impact on the deposited NP size and spacing. However, there is still a lack of information on the sub-3 nm scale where GISAXS becomes insensitive. Hence, little is known on the atomic structure of the NPs, including their crystal structure and shape. To shed light on this 3D structure and on how it impacts surface reactivity in ALD and catalysis, several series of samples were prepared at Ghent University and brought to ID15A for total scattering measurements and subsequent pair distribution function (PDF) analysis.

Experimental considerations

Sample preparation. Five sets of Pt nanoparticle samples have been investigated. The samples were prepared in different ALD processes with trimethyl(methylcyclopentadienyl)platinum(IV) ($MeCpPtMe_3$) as precursor gas, different reactant gases and at different deposition temperatures: (1) O_2 plasma as reactant gas at 300 °C, (2) O_3 as reactant gas at 300 °C, (3) O_3 as reactant gas at 150 °C, (4) N_2 plasma as a reactant gas at 300 °C and (5) O_2 plasma at a reactant gas at 300 °C but the process was stopped in the middle of the final ALD cycle. The samples were deposited on 1 cm x 1 cm or 1cm x 2 cm fused quartz substrates. Within each series, different Pt loadings were covered by varying the number of ALD cycles from 4 to 20 in steps of 2. Some extra samples were brought in case extra measurement time was available. First of all, (6) A series of amorphous silicon (aSi) samples deposited with ion plating on fused quartz substrates, annealed at different temperatures up to 600 °C. Secondly (7) a series of amoprhous Ta_2O_5 samples deposited on fused quartz substrates with different deposition techniques (ALD, ion beam sputtering (IBS) and ion plating). For the measurements, the samples were mounted on a motorized stage with a customized sample holder (see picture on the right).



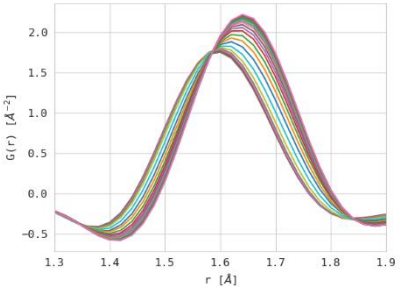
Beamline configuration. Total scattering experiments in grazing incidence geometry are a recent approach to study thin films, and this is especially a novelty in the ALD and catalysis community. The present experiment is a continuation of the experiment MA-4987 performed in October 2021. To focus the beam to a size of 2.5-3 μm (V) by 6 μm (H), the 64 keV beam is attenuated and refractive lenses are positioned in the beam path 3 m before the sample. Slit systems and a pinhole closer to the sample are inserted to reduce background scattering. Sample alignment was done by making use of a CMOS imaging detector while data were acquired with the Pilatus3 X CdTe 2M diffraction detector.

Results

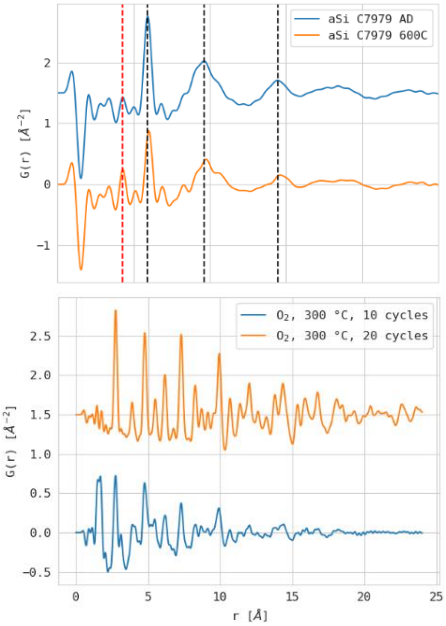
Sample alignment procedure. Because of the experience gained during the PDF campaign of October 2021, we got acquainted with the aligment procedure more quickly. In contrast to the previous PDF campaign, the samples were now mounted on a completely motorized stage with a customized sample holder. This allowed for a faster

alignment. The alignment procedure consisted of three steps. The first step consists of a scan over the height of the sample stage (z-scan). When the sample is aligned flat, this z-scan results in a clear step in the intensity as function of sample hight in the region on the CMOS detector where the direct beam is expected, where the width of the step is defined by the height of the X-ray beam. In the case the sample is tilted, the intensity will show a dip, and the width of the dip can be used to calculate how much the sample tilt must be adjusted. This procedure is repeated until the sample is oriented flat. Next, the tilt of the sample is adjusted again, such that the direct beam disapears on the CMOS camera, and the reflected beam is most intense. This ensures the sample is positioned in total reflection geometry. Next, the CMOS detector is moved away and the beam stop and Pilatus detector are moved into the beam path. Finally, the tilt of the sample is adjusted further so that the scattered X-ray signal from the material that needs to be probed is optimal compared to the signal from the substrate.

Measurements and Data processing. After alignment, several 2D scattering images were recorded. The sample-to-detector distance was determined with a transmission measurement of a CeO_2 calibration sample. During the campaign, preliminary data processing was already carried out. Azimuthal integration of the 2D detector data was performed using the python package PyFAI, resulting in intensity as a function of q and subsequent extraction of the PDF was carried out with PDFgetX3. During the campaign, it became clear that a small deviation of the incidence angle or sample height causes small variations in the sample-to-detector distance. This causes an error in the mapping from the detector image to q-space during the azimuthal integration and peak shifts in the extracted PDF. In order to define a procedure to correct for this error, the bare substrates were measured under different tilt angles, below and above the critical angle of quartz. An example of the peak shift at the Si-O distance in the PDF of quartz, caused by measurements under different incidence angles is shown in the figure on the right. During the beam time, it was discovered that the Pt samples unexpectedly suffered from radiation damage: the Pt signal on the Pilatus detector decreased over time when multiple measurements were carried out on the same position on the sample, meaning that the nanoparticles were being destroyed or removed from the sample by the X-ray beam. Cancellation of the radiation test in the night of 4-5 April, and the fact that the beamline was not occupied on 7 April resulted in extra measurement time and gave us the opportunity to remeasure most of the Pt samples, where now the alignment and the measurement were carried out on different locations on the sample surface by shifting the sample along the y-direction. Shortening the exposure time ensured a limitation of the radiation damage. By the end of the beamtime, high quality data was obtained for all provided samples.



Initial results. For some of the obtained data sets, preliminary data processing was performed. Absorption measurements with photothermal common path interferometry, carried out at Maastricht University, showed differences in optical absorption between aSi samples annealed at different temperatures. Although the Si stays amorphous, this hints at differences in the atomic ordering. In the top figure on the right, small but visible peak shifts in the PDF can be observed. Currently, different possibilities for more detailed analysis (small box modeling, reverse Monte Carlo) are being considered. The bottom figure on the right shows a PDF from Pt samples created with 10 and 20 ALD cycles of the O_2 process at 300 °C. In both cases, a clear Pt signal is visible. This is promising for more detailed analysis in which we aim at investigating the shape of the NPs. Different methods for this analysis are being considered (deep learning, cluster mining etc.). Furthermore, a correction procedure to correct for deviations in the exact sample detector distance due to variations in sample tilt is under development.



Conclusion and outlook

In-depth analysis of the acquired data is still ongoing, but it is already clear from the preliminary results that GI-PDF at ID15A is a powerful technique to study the atomic structure of supported Pt nanoparticles deposited by ALD. Also the extracted PDFs of the measured Ta_2O_5 and a-Si samples show promising features. In future measurements, possible radiation damage of the samples should be checked, and the sample holder should be adapted with two perpendicular grooves and without edges to allow alignment of the slant angle as well.