In situ GISAXS study of the initial island growth during atomic layer deposition of platinum

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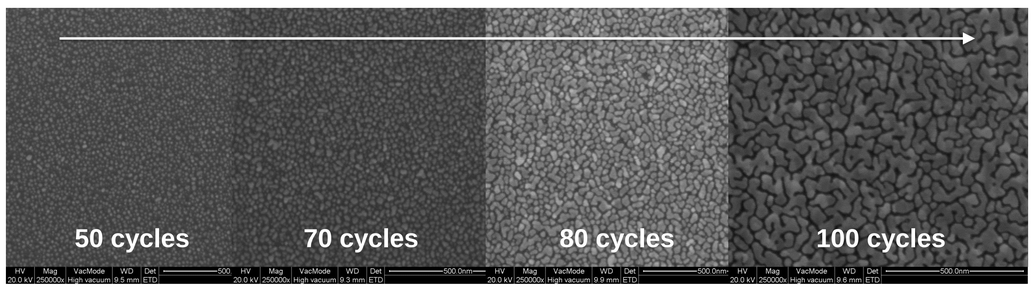
Introduction

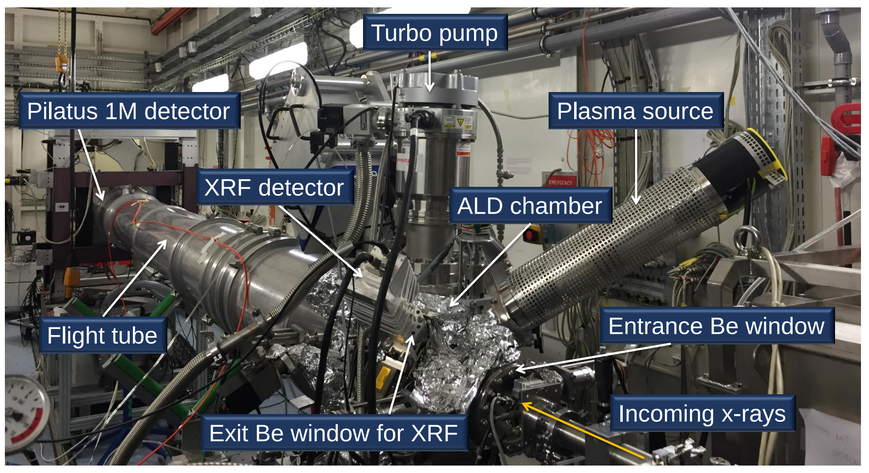
Atomic layer deposition (ALD) is a thin film growth method which enables atomic-level thickness control and excellent conformality on complex 3D substrates. ALD relies on sequential self-terminating reactions between gas phase precursor molecules and a solid surface. Although the technique is traditionally perceived as a layer-by-layer method, processes for noble **metals** are often characterized by **nucleation controlled growth**. After a certain incubation period, growth is initiated in localized islands spread across the surface. This island growth offers intriguing opportunities for the controlled deposition of nanoparticles for applications in catalysis.

This work demonstrates the unique suitability of synchrotron-based **x-ray fluorescence (XRF) and grazing incidence small angle x-ray scattering (GISAXS) for *in situ* monitoring of the nanoscale surface morphology** during ALD of Pt.



Experimental

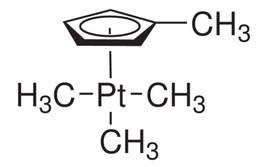
Setup



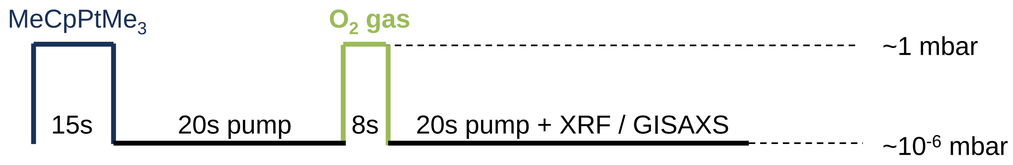
ALD setup for *in situ* XRF and GISAXS measurements installed at the BM26B beamline at the European Synchrotron Radiation Facility [1].

Method

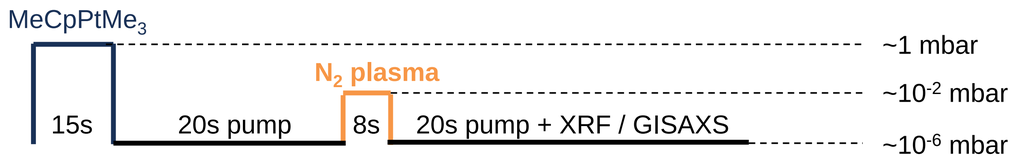
Pt precursor: (methylcyclopentadienyl)trimethylplatinum
Substrate: Si with native SiO_2
Pretreatment: 30s O_2 plasma exposure
Deposition temperature: 300°C



ALD cycle O_2 process:



ALD cycle N_2 plasma process [2]:



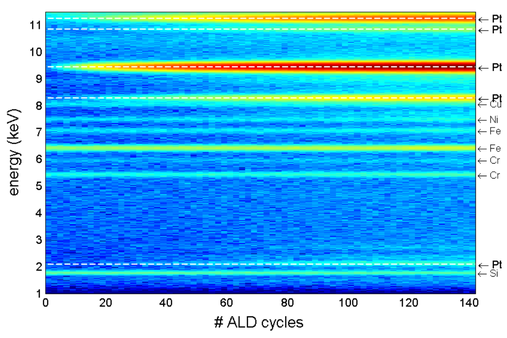
XRF:
- every 2 ALD cycles
- acquisition time 20s
- incidence angle 1.2°
- photon energy 12keV

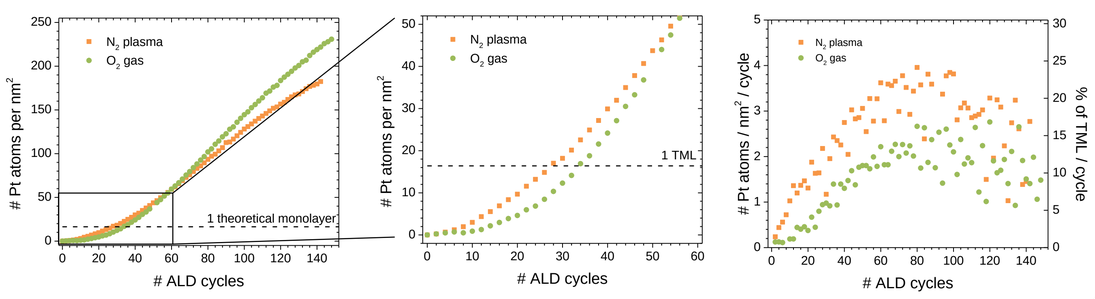
GISAXS:
- every 2 ALD cycles
- acquisition time 20s
- incidence angle 0.5°
- photon energy 12keV

[1] K. Devloo-Casier, K. F. Ludwig, C. Detavernier, J. Dendooven, J. Vac. Sci. Technol. A 32(1), 010801 (2014).
[2] D. Longrie, K. Devloo-Casier, D. Deduytsche, et al. ECS J. Solid State Sci. Technol. 1(6), Q123-129 (2012).

Results - *XRF measurements*

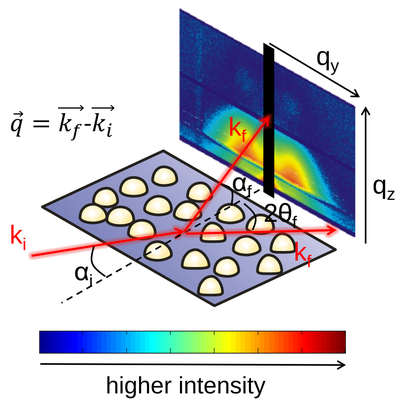
- In situ XRF was used to monitor the amount of Pt atoms deposited.
- During the initial growth stages more Pt atoms are deposited with the N_2 plasma process than with the O_2 gas process.
- After ca. 30 ALD cycles, the number of Pt atoms on the surface reaches a theoretical monolayer.
- The maximum in the growth per cycle is indicative of island growth.

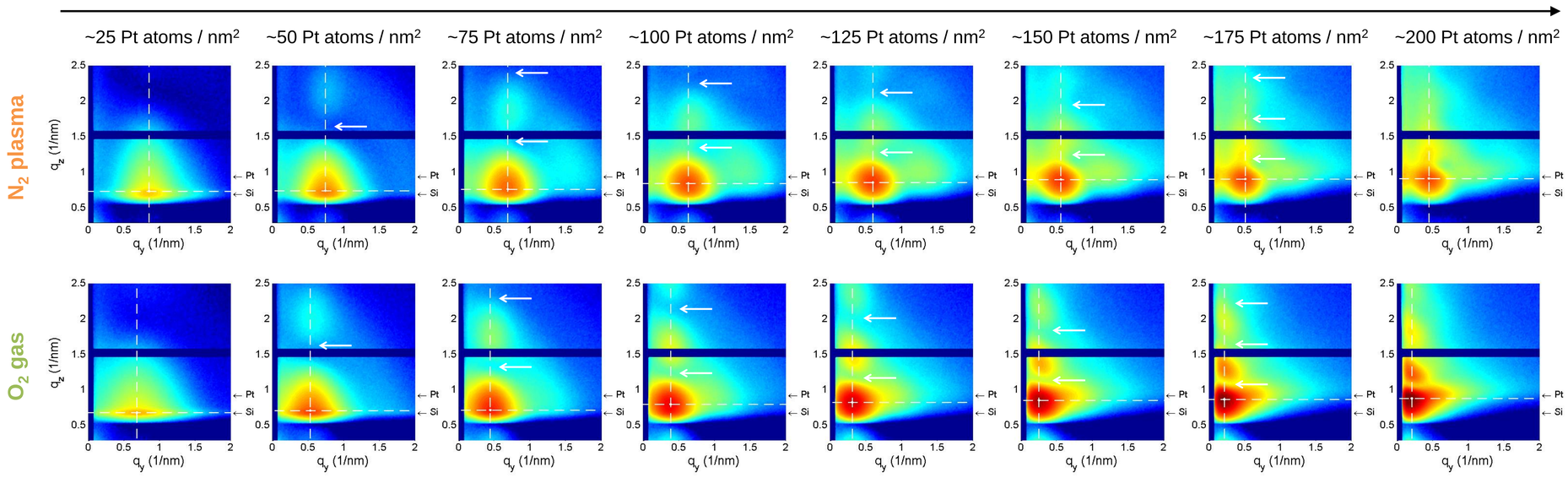




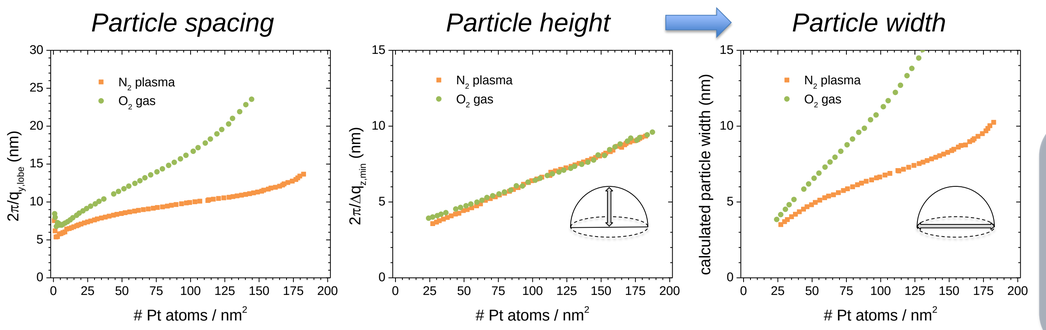
Results - *GISAXS measurements*

A GISAXS experiment consists of measuring the diffuse scattering around the specularly reflected beam at a fixed incident angle.





- The main scattering lobe shifts towards smaller q_y values pointing to an increase in average center-to-center particle spacing. This increase in spacing is much more pronounced for the O_2 gas process compared to the N_2 plasma process.
- The main scattering lobe also moves towards larger q_z values due to an increase in the critical angle of the surface material when more and more Pt covers the Si substrate.
- The intensity modulations along q_z can be related to an increasing thickness of the Pt particles / coalesced Pt layer.
- Assuming a hemi-ellipsoidal shape for the Pt particles, the particle width can be calculated.



- The O_2 gas process results in flattened particles, while the aspect ratio is close to 1 for the N_2 plasma process.
- O_2 induces atom and cluster surface diffusion and promotes the ripening of the Pt particles, meaning that larger clusters grow at the cost of small ones.
- Diffusion phenomena seem to be suppressed during N_2 plasma ALD leading to smoother Pt layers [2].

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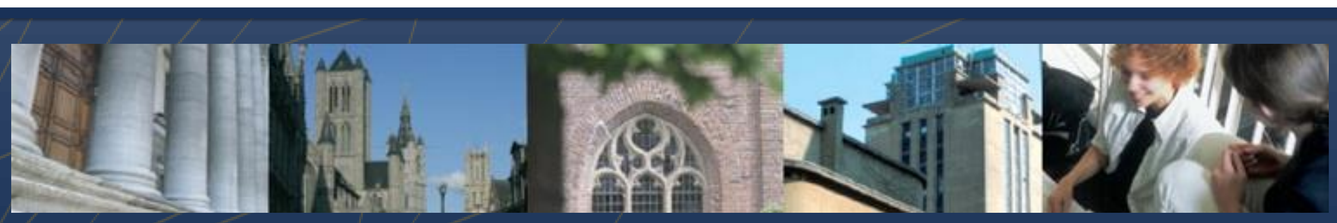

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