ESRF	**Experiment title:** Plasma-enhanced atomic layer deposition of gold metal studied by *in situ* GISAXS	**Experiment number**: 26-02-895
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Introduction

During the last decade, ALD has emerged as an effective method to deposit noble metal nanoparticles (NPs) with a precise control of the particle morphology (size and areal density), which has promising potential applications in heterogeneous catalysis (Pt, Pd) and plasmonics (Au, Ag). Here, our home built ALD system enabling *in situ* monitoring of the NP morphology and loading by GISAXS and XRF measurements has been exploited to study the NP nucleation and formation during ALD growth of Au. In collaboration with Prof. S. Barry at Carleton University, we recently developed a PE-ALD process for the deposition of metallic Au, using $Me_3Au(PMe_3)$ as the precursor in combination with H_2 plasma as the reactant. The goal of this synchrotron campaign was to get a better understanding of the island growth mode during this new ALD process.

Experimental

GISAXS patterns were recorded using the Pilatus 1M detector of the beamline, using an acquisition time of 30s. The X-ray energy was set to 11.98 kev. The distance between sample and detector was 3.9 m, while the incident angle was 0.5°. XRF spectra were simultaneously recorded using a Vortex detector. Au NPs were deposited on SiO_2 (LPCVD oxide and thermal oxide) and Si (HF dipped) substrates at 110°C by alternating exposure to $Me_3Au(PMe_3)$ as precursor and H_2 plasma as reactant. Argon is used as the carrier gas for the precursor. Low pressure ($6x10^{-3}$ mbar) pulses were employed for the precursor exposures.

Results

In situ study of Au NPs on three different silicon substrates

Based on some intial experiments in our lab, we found that the nucleation behaviour of the Au process on Si-H and SiO_2 substrates differs significantly from each other, see SEM images in Figure 1. We expect that OH groups on the substrate can influence the nucleation on the substrate. Therefore, we studied the nucleation behaviour *in situ* using XRF and GISAXS on three different substrates that each have a different amount of OH groups on the surface: Si-H (0 OH/nm^2), thermal SiO_2 (1 OH/nm^2) and LPCVD SiO_2 (5 OH/nm^2). The Au loading, derived from the *in situ* XRF measurements, versus ALD cycles graph shows reduced growth on the H-terminated Si. The GISAXS patterns recorded *in situ* for the 3 processes reveal a clear difference in the morphological evolution of the Au NPs (Figure 1), where we estimate the center-to-center distance (D) between neighboring NPs as $2\pi/q_{y,max}$, with $q_{y,max}$ the q_y–position of the main scattering peak. It is clear that the spacing between the Au NPs on Si-H vs. SiO_2 is very different, as expected from the SEM images. Due to the fewer OH groups on the initial surface, the particles are spaced further apart. The difference in spacing between the two SiO_2 surfaces (1 and 5 OH groups per nm^2, respectively) is however not that obvious. A

possible explanation is that, for this range of OH densities, the nucleation density is governed by the size of the Au precursor rather than the OH density.

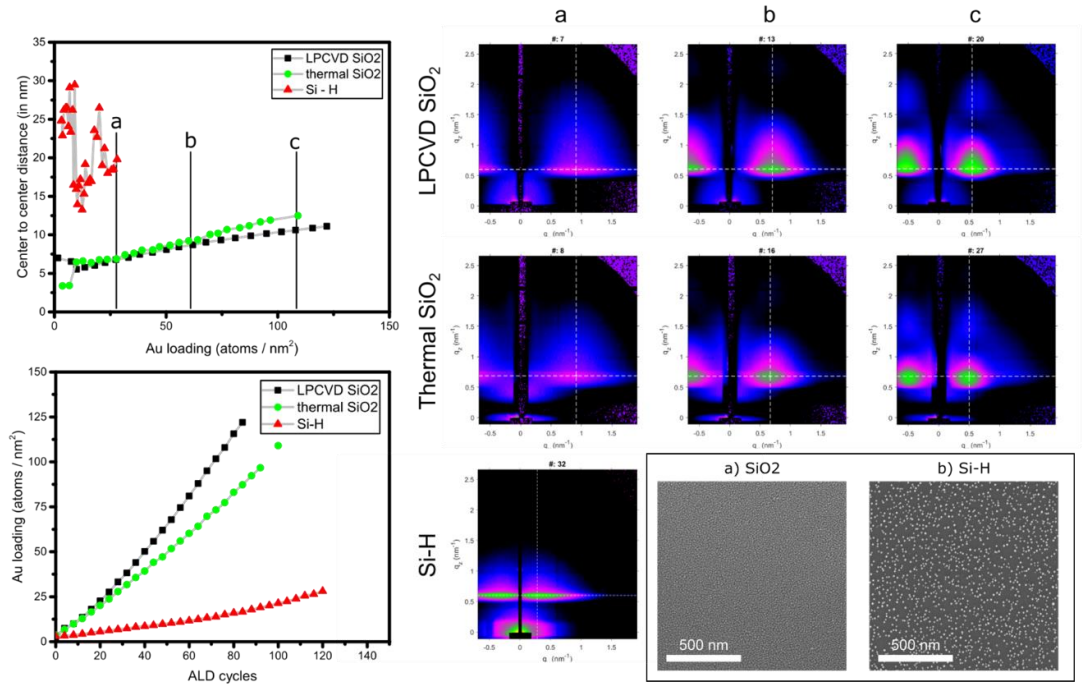

Figure 1: *Bottom – right: SEM images of Au NPs on SiO_2 vs Si-H. Bottom – left: Au loading agains ALD cycles. Top – left: center-to-center distance against Au loading. Top – right: selected GISAXS patterns.*

In situ study of Au NPs deposited on Ru seed layers

Because metal-on-metal nucleation is typically very different from metal-on-dielectric nucleation, we also investigated Au ALD on Ru seed layers. A first experiment used a sputtered Ru layer, but as this layer also gave rise to a pronounced GISAXS pattern, it proved to be difficult to distinguish the pattern caused by the Au NP's from that of the seed layer. In another experiment, we deposited a Ru seed layer via ALD, without breaking the vacuum between the Ru deposition and the Au deposition. The ultrathin Ru seed layer appeared smooth in GISAXS, while the *in situ* deposition avoids oxidation of the Ru layer. On the other hand, the *in situ* GISAXS data showed that the Au ALD process clearly resulted in Au NPs instead of a continuous Au layer (scattering patterns not shown here).

Annealing of Au NPs in oxidizing and reducing atmospheres

Finally, we annealed different coupons of the same sample in different atmospheres to investigate the coarsening behavior and thermal stability of the Au NPs on the surface. The coupons were annealed to 900°C at a rate of 0.2°C/s. The starting GISAXS pattern and SEM image of the sample before annealing can be seen in Figure 2. The final surface looks very different for all annealing conditions, as can be seen by the SEM image and the GISAXS pattern before and after each anneal. Using a reducing atmosphere (5% H_2 in He) caused the largest change in the particle size and spacing. For the oxidizing and inert atmospheres, the increase in particle size and spacing is less pronounced. The reason for this distinct difference is not yet clear to us.

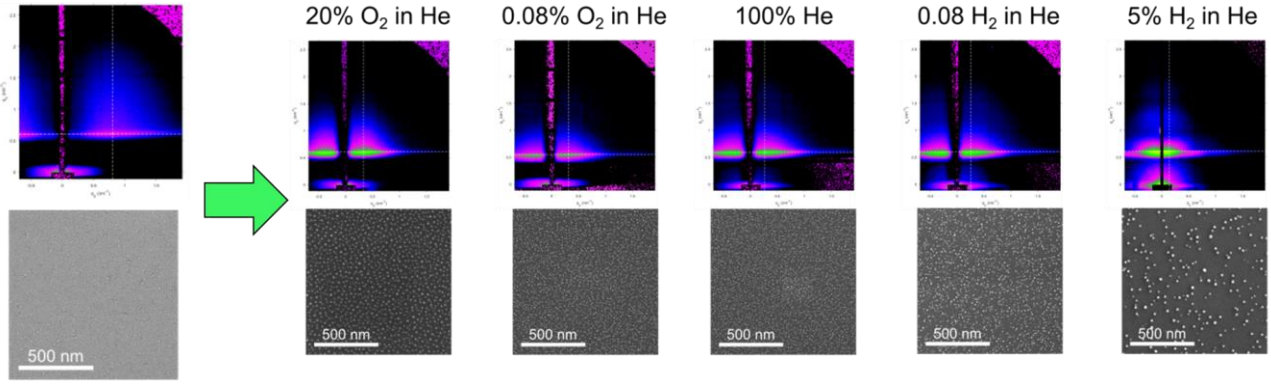

Figure 2*: SEM images and GISAXS patterns for the starting sample and after annealing under different atmospheres. The surface has changed under all annealing conditions. However, the largest difference occurs for the 5% H_2 in He atmosphere.*

Conclusion

The synchrotron campaign allowed us to study the nucleation during Au ALD. Simulations to complement the quick GISAXS analysis shown here are ongoing, and the work is in progress of being written down in a publication.