ESRF	**Experiment title:** Study of the nucleation rate and morphology during photo-assisted atomic layer deposition of metals	**Experiment number**: A26-2-938
Beamline: BM26	**Date of experiment**: from: 08/06/2022 to: 13/06/2022	**Date of report**: 21/09/2022 *(revised 22/05/2023)* *Received at ESRF:*
Shifts: 15	**Local contact(s)**: ROSENTHAL Martin	

Names and affiliations of applicants (* indicates experimentalists):

DENDOOVEN Jolien*[1] (main proposer), DETAVERNIER Christophe[1] (co-proposer), MINJAUW Matthias*[1], SANTO DOMINGO PENARANDA Juan*[1], ZHANG Zhiwei*[1], SOLANO MINUESA Eduardo*[2], MIKKULAINEN Ville*[3] (co-proposer)

1 CoCooN research group – Department of Solid State Sciences, Ghent University, Krijgslaan 281, building S1, 9000 Gent, Belgium.

2 ALBA Synchrotron Light Souce – NCD-SWEET Beamline, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallès, Spain.

3 School of Chemical Engineering, Aalto University, Kemistintie 1, 02150 Espoo, Finland.

Introduction

Area-selective deposition has sparked special interest, in recent years, within the Atomic Layer Deposition (ALD) community. Patterning is currently done through photolithography with good results, but it is a complex process with multiple steps. Therefore, efforts are constantly being made to find simpler ways to deposit layers in designated areas of patterned substrates. There are reports on precursors that show inherent selectivity towards specific surfaces. Additionally, self-assembled monolayers are often used to inhibit growth on certain surfaces. However, **bottom-up** approaches to laterally confine ALD growth on a non-patterned substrate are scarce. The present campaign aimed at expanding the understanding of **photo-assisted** ALD of metals as a way to achieve selective deposition in the irradiated area of a homogeneous substrate. During Pt depositions, a systematic study via in-situ XRF was performed in order to track the growth kinetics. Secondly, in-situ GISAXS measurements were used to track the nucleation and island growth of Pt. By combining the two techniques, we aimed to shed light on the effect of the photon's during Pt ALD.

Experimental

Our custom-made vacuum chamber was used for all ALD depositions [1]. The energy of the X-ray beam was set to 12 keV and the detector-to-sample distance to 4.7 m. The beam size was 800 x 750 μm^2 (H x V) at the sample position. Depositions were performed in a temperature range between 175-300ºC on Si substrates with native oxide. To prepare the sample surface before deposition, O_3 treatments were performed. During the ALD depositions, the sample was illuminated. A fused silica window was attached to the reactor for this purpose. During the ALD depositions, in-situ XRF and in-situ GISAXS measurements were performed on the samples, at an incidence angle of 0.5º and 1.2º, respectively. The former was used to track the Pt loading on the samples, while the latter served to monitor the particle size and spacing.

Results

In-situ XRF study

The optimal temperature for thermal ALD of Pt is 300°C with a drastic decrease in growth at lower temperatures. First, we aim to show that photo-ALD allows to enhance the growth of Pt at temperatures below 300°C. Figures (a) and (b) show the growth curves obtained at 200 and 175°C, respectively. After 120 ALD cycles at 200ºC, the Pt loading obtained with the thermal process is about 51% of the loading obtained with photo-ALD. At

175ºC, the thermal growth of Pt is virtually zero, while the photo-ALD nucleation delay is still rather small. Hence, at this temperature, the growth of Pt would be selective in the irradiated areas of the substrate.

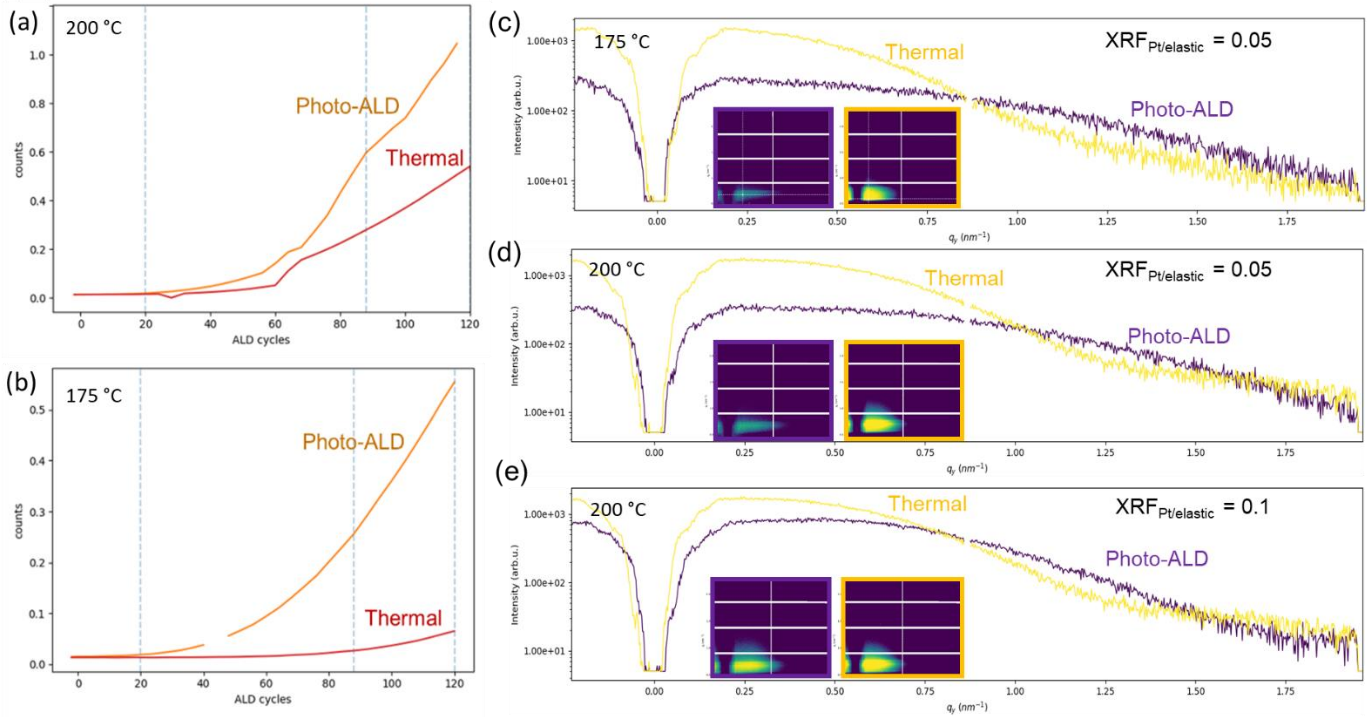

Figure (a-b) *In-situ XRF data showing the Pt counts normalized to the elastic peak as a function of the number of ALD cycles. Comparison of thermal and Photo-ALD at 200°C* ***(a)*** *and 175°C* ***(b)****.* ***(c-e)*** *In-situ GISAXS data showing the patterns and horizontal cuts at the Yoneda wing for thermal vs. Photo-ALD at 175°C* ***(c)*** *and 200°C* ***(d-e)****, at the same Pt loading.*

<u>In-situ GISAXS measurements</u>

To obtain a better understanding of the nucleation stages during photo-ALD *vs.* thermal ALD, the in-situ recorded GISAXS patterns for the same metal loading, obtained from the in-situ XRF data, are compared. This comparison allows to understand how the same amount of Pt atoms is arranged on the surface for both processes. Figures (e-g) show three comparisons of in-situ GISAXS images with corresponding horizontal cuts under identical Pt loading ($XRF_{Pt/elastic}$ = 0.05/0.1). In all plots, a similar trend is observed. The purple curves, corresponding to the photo-ALD process, show a lower intensity at low q_y values but they exceed the yellow curves, corresponding to the thermal ALD process, at higher q_y values. This points at a smaller particle width for the Photo-ALD deposited nuclei at the same Pt loading. Consequently, the areal density of the nuclei deposited with Photo-ALD must be larger. This result is indicative of a photo-enhanced generation of nucleation sites during the Pt ALD. These insights are critical towards an improved understanding of the effect of the photons on the nucleation.

As a remark, the 2D GISAXS patterns, shown as inset, show a smeared out Yoneda region, visible as a bright horizontal band instead of a sharp line in the pattern. Towards the end of our campaign, we figured out that this was the result of clamping the samples on the heated stage. This will be avoided in future work.

Conclusions

The results obtained during the campaign allow us to understand better the photo-ALD process of Pt. Key information about the optimal process conditions to achieve selectivity, as well as insights in the effect of the light in the process have been obtained. Some nucleation differences have been found by combining in-situ XRF and GISAXS. Complementary studies of the surface chemistry are ongoing at Ghent University, after which the work will be submitted for publication.

References

[1] Dendooven et al. Rev. Sci. Instrum. 2016, 87, 113905.