ESRF	**Experiment title:** In situ GISAXS-XRF to probe the chemical selectivity and nucleation of Co and Ni atomic layer deposition	**Experiment number**: 26-02-915
Beamline: BM26	**Date of experiments**: from: 03/11/2021 to: 09/11/2021 from: 22/02/2022 to: 28/02/2022	**Date of report**: April 13, 2022
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Names and affiliations of applicants (* indicates experimentalists): Proposers: FILEZ Matthias[1], DENDOOVEN Jolien[1] (*), DETAVERNIER Christophe[1] (*); Participants: ZHANG Zhiwei[1] (*), POONKOTTIL Nithin[1] (*), MINJAUW Matthias[1] (*), SANTO DOMINGO PENARANDA Juan[1] (*), SOLANO MINUESA Eduardo[2] (*); [1]Ghent University (UGent). Krijgslaan 281/S1. 9000 Gent, Belgium; [2]ALBA,

Report:

The original aim of proposal 26-02-915, submitted in March 2020, was to provide insights in the chemical sensitivity and nucleation during atomic layer deposition (ALD) processes for cobalt and nickel. In the meantime, however, additional experiments have shown that the originally proposed experiments are not of sufficient interest any more; i.e. the Co and Ni precursors are difficult to work with (they rapidly degrade during film processing) and there turned out to be a CVD component in the ALD process, making it difficult to control. In addition, preliminary measurements for Co deposits on Pt carried out at SOLEIL (SiXS beamline) in June 2021 showed that the GISAXS patterns are dominated by scattering from the Pt support layer; no clear features could be attributed to the Co. Therefore, in consultation with the beamline staff, it was decided to focus on another material system, in continuation of earlier work done at DUBBLE (26-02-854) that resulted in a publication in Nanoscale in 2020 [1]. We previously showed that (1) by depositing ultrathin Al_2O_3 layers on Pt nanoparticles (NPs), the thermal stability of the latter against particle sintering can greatly be enhanced [1], and (2) in situ GISAXS measurements during thermal annealing of such overcoat@Pt systems is a great tool to monitor Pt NP coarsening behavior [1,2]. In the two campaigns scheduled for the project 26-02-915, we have focused on MgO overcoats synthesized using different precursors at different deposition temperatures, and applied to Pt NPs on Si with different metal loading. Such MgO overcoats are expected to decorate specific edge or facet sites on the Pt NPs, depending on the precursor and temperature used in ALD. A systematic study of the selectivity of the surface decoration is currently ongoing in the frame of the PhD of Z. Zhang.

Experimental

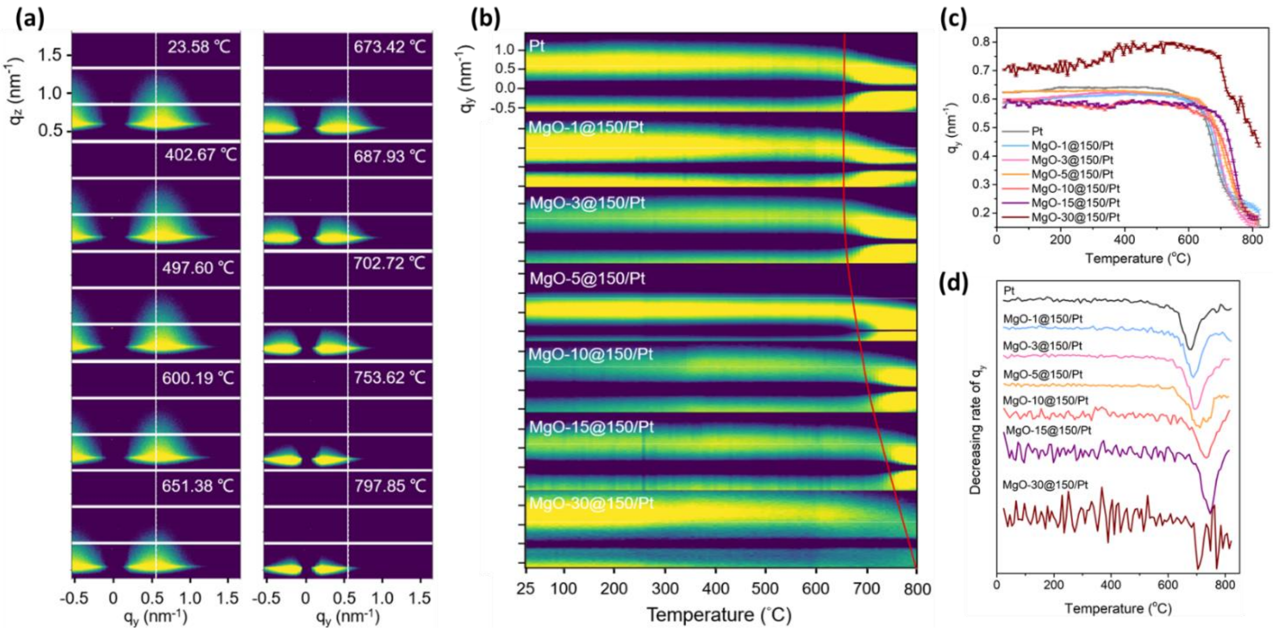
<u>*Sample preparation at UGent.*</u> Several series of MgO@Pt samples were prepared with varying numbers of Pt ALD cycles and MgO ALD cycles. For Pt NP synthesis on Si with native oxide, a static ALD mode was applied at 300°C, with $(Me)_3Pt(MeCp)$ as metal precursor and O_2 as reactant. For MgO, two different precursors were applied ($Mg(EtCp)_2$, $Mg(TMHD)_2$) at different temperatures (150, 200, 250°C), expecting to lead to a different nature of the MgO surface decoration on Pt. The Pt and MgO loading were investigated with XRF and XPS.

<u>*Annealing experiments at DUBBLE.*</u> Annealing experiments were performed in the same custom-built vacuum chamber that was used before [3]. The MgO@Pt NPs were subjected to a temperature programmed annealing in 20% O_2 (He) to 850 °C using a ramp rate of 0.2 °C/s while the NP morphology was monitored with in situ GISAXS (at an incidence angle of 0.4°, beam energy of 12.0 keV, detector-to-sample distance of 4.6 m). In the first campaign, after succesful installation of the setup during the preparation day (Nov 2), no beam was available during Nov 3-5 due to a machine issue, and beam alignment could only be done on Nov 6, leaving us a limited number of shifts for annealing experiments. Therefore, a second beamtime was scheduled for this project in February 2022.

[1] Solano et al. Nanoscale, 2020, 12, 11684-11693. [2] Solano et al. Nanoscale, 2017, 9, 13159-13170. [3] Dendooven et al. Review of Scientific Instruments, 2016, 87, 113905.

Results: *In situ GISAXS during annealing of MgO@Pt NPs by $Mg(EtCp)_2$ precursor*

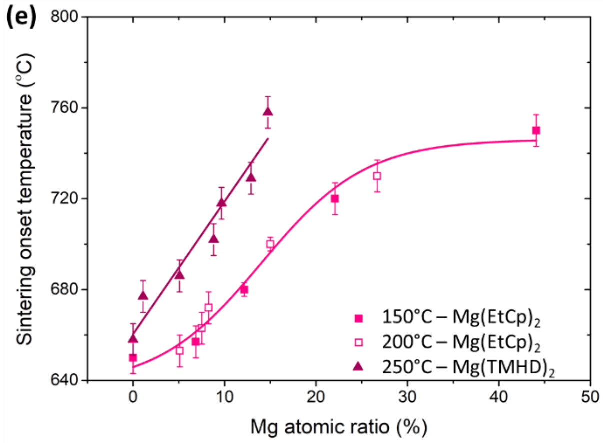
A first set of MgO overcoated Pt samples investigated, comprised those produced with different cycles of the $Mg(EtCp)_2$-based process at a deposition temperature of 150°C. The 2D GISAXS patterns recorded during the annealing of uncoated Pt NPs (25 ALD cycles) are shown in Figure (a) below. The intensity and position of the main scattering feature remain constant until 600 °C, indicative of the absence of NP coarsening below that temperature. From ca. 650 °C, the scattering feature shifts to lower q_y-values and the intensity decreases. Extracted 1D horizontal profiles in the Si Yoneda region are shown in Figure (b), for bare Pt NPs, and for Pt NPs overcoated with MgO. The red line is added as a guide to the eye, indicating the onset of NP coarsening. With increasing number of MgO ALD cycles, the onset for NP coarsening can be postponed to higher annealing temperatures, clearly indicating a stabilizing effect of the MgO coating. By fitting a Gaussian to the scattering peak in the 1D profiles, the q_y-position corresponding to the maximum intensity in the fitted curves can be extracted, yielding a continues dot curve of q_y value against the heating temperature (Figure (c)), the derivative of which is shown in Figure (d). A similar series of experiments was carried out for MgO layers deposited with $Mg(EtCp)_2$ at a temperature of 200°C, showing that a larger number of ALD cycles is needed to improve the thermal stability when MgO is deposited at 200°C vs. 150°C. Experiments were also carried out for varying Pt loading (15, 25 and 50 ALD cycles), and thus smaller vs. larger Pt NPs. A positive effect of the MgO overcoat in delaying the NP coarsening is observed in all cases.



In situ GISAXS during annealing of MgO@Pt NPs by $Mg(TMHD)_2$ precursor

We also recorded the coarsening behaviour for a sample series in which the MgO coating was prepared using a different Mg ALD precursor, being $Mg(tmhd)_2$. Samples were prepared with different number of ALD cycles at 250°C. According to XPS analysis of the MgO loading, a much higher number of ALD cycles is needed with the $Mg(tmhd)_2$-precursor than with the Cp-based precursor for depositing a similar amount of oxide. Analysis of the GISAXS patterns, and comparing samples with a similar MgO loading, shows a larger Pt coarsening inhibition effect for the MgO ALD coatings grown with the $(tmhd)_2$ precursor, pointing towards a different atomic-scale arrangement of the MgO coating on the Pt NPs.

Conclusion We have obtained an interesting and complete data set for the ongoing PhD project of Z. Zhang on stabilizing Pt NP catalysts with atomically tailored surface decoration. Figure (e) summarizes the results and displays the onset temperature for NP coarsening against Mg loading for all experiments performed. Those results will be linked to the ongoing investigations of the selectivity/nature of the MgO overcoat in these different MgO@Pt systems and a manuscript on this work will be prepared.



We are grateful that we could recover the loss of beamtime in November 2021 during a second campaign in February 2022.