ESRF	**Experiment title:** In situ GISAXS towards the controlled synthesis of noble-metal-free Ni-based bimetallic nanoparticles by atomic layer deposition	**Experiment number**: 26-02/854
Beamline: BM26B	**Date of experiment**: (including 2 preparation days) from: 06/02/2018 to: 13/02/2018	**Date of report**: 04/03/2018
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Introduction

Supported bimetallic nanoparticles (BMNPs) often exhibit improved catalytic activity, selectivity and/or durability compared to their monometallic counterparts due to synergistic effects. However, these effects require a precise control on the size, shape and composition of the BMNPs during synthesis. Recently, atomically precise synthesis of supported BMNPs has been achieved by **ALD**, a vapour phase deposition method. In colloboration with DUBBLE, we recently developed a strategy for the preparation of alloys containing a non-noble metal next to Pt[1] (selected as one of the **ESRF Highlights of 2016**). **The present campaign** aimed at extending this **ALD-route to noble-metal-free compounds**, such as Ni-Fe and Ni-Ga. In view of their catalytic importance, a systematic study was carried out to study how the final particle size, shape and distribution can be controlled by varying the ALD and annealing conditions. In addition to experiments related to the proposed research topic of Ni-based BNMPs, two additional research topics have been addressed during this campaign. Firstly, *in situ* GISAXS was performed during annealing of Pt NPs with Al_2O_3 overcoats (remaining experiments of a previous study (26-02-726) that were needed to finalize a manuscript). Secondly, exploring a new topic in view of future synchrotron beam time proposals, we deposited Au NPs via ALD while performing *in situ* GISAXS at the DUBBLE beamline.

Experimental

Our dedicated vacuum chamber, described in ref. 2, was used for the ALD and annealing experiments. The energy of the X-ray beam was set to 12.7 keV (we aimed for 12.0 keV, but we found that the monochromator had an offset of 0.7 keV), and the detector-to-sample distance to 4.2 m. The beam size was 1 x 0.5 mm^2 (H x V) at the sample position. In view of our first objective (Ni-Fe BMNP synthesis), a series of Fe_2O_3/NiO bilayer samples were prepared in our lab at Ghent University (UGent). TBF and $Ni(MeCp)_2$ precursors were used for Fe_2O_3 and NiO ALD, respectively, and O_2 plasma was used as reactant. The deposition temperature was 200°C on Si with native oxide. The thickness and composition [described as Ni wt% = Ni/(Ni + Fe)] of the bilayer samples were determined by XRF measurements at UGent. At DUBBLE, the as-deposited Fe_2O_3/NiO bilayers were subjected to a temperature-programmed reduction (TPR) in H_2 to 700 °C using a ramp rate of 0.2 °C/s while the formation of Ni_xFe_y BMNPs was monitored with *in situ* GISAXS. For the second objective, Pt NPs with distinct size and spacing but same Pt loading were pre-prepared on SiO_2 surfaces. Finally, Au ALD was performed at DUBBLE on Si with native oxide at 120°C using $Au(CH_3)_3P(CH_3)_3$ as the precursor and O_2 plasma or H_2 plasma as the reactant. *In situ* XRF and GISAXS measurements were performed during the ALD process at an incidence angle of 0.5°.

Results

In situ GISAXS during reduction of Ni-Fe bilayers

Bilayer samples with three different compositions, Ni wt% ~ 75, 50 and 35, were prepared by changing the NiO and Fe_2O_3 thicknesses (dNiO and dFe_2O_3, **Fig. 1a**). **Fig. 1c** shows *in situ* XRD data recorded during the TPR of a Fe_2O_3/NiO bilayer with ~ 75 wt% Ni. At 450°C, the diffractions of NiO disappear and Ni_3Fe is formed. A similar experiment for a bilayer consisting of ~ 50 wt% Ni resulted in a NiFe phase, demonstrating that our approach enables tuning of the Ni-Fe alloy composition. Similar samples were then annealed at DUBBLE while recording *in situ* GISAXS patterns using 30 s measurements (α_i = 0.5°). **Fig. 1d** shows the evolution of the scattering features while annealing. Iniatially a very faint scattering lobe is visible, attributed to the rougness of the as-deposited film. At 450 °C, i.e. the onset of alloying as indicated by *in situ* XRD, the scattering lobe clearly shifts to lower q_y values and increases in intensity. These observations indicate that the formation of particles occures upon reduction. In view of catalytic applications, the size

tuning of the Ni_xFe_y BMNPs was investigated by preparing bilayers with different total thicknesses, but with same compositions. SEM and *in situ* GISAXS measurements revealed the formation of smaller particles with decreasing dTotal. *In situ* GISAXS measurements also revealed that the alloying temperature decreases with increasing Ni wt%. We propose that during the annealing the NiO gets reduced to Ni first, which then facilitates the reduction of Fe_2O_3 and eventually the formation of alloyed BMNPs.

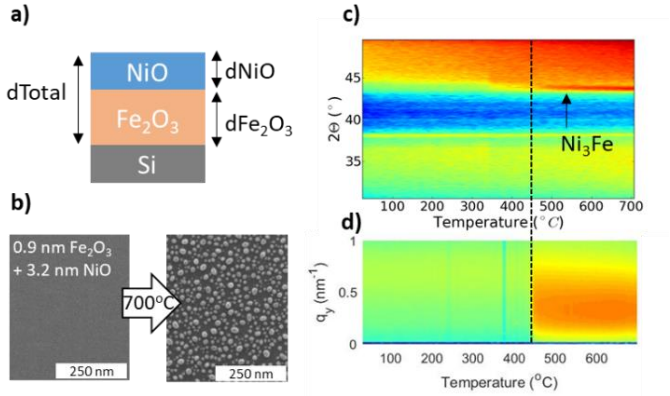

Figure 1. a) Schematic of the as-deposited bilayer Fe_2O_3/NiO sample. (b) SEM images of an as-deposited Fe_2O_3/NiO bilayer (left) and the BMNPs obtained after TPR in 5% H_2/He up to 700°C (right). (c) *In situ* XRD patterns measured during TPR in 5% H_2/He. (d) 2D color maps showing the intensity evolution of the main scattering peak along q_y (1D line profile along the Yoneda peak position).

<u>*In situ* GISAXS during annealing of Pt NPs with Al_2O_3 overcoats:</u>

In situ Pt annealing experiments were performed in order to finish a project with data acquired during a previous campaign (26-02-726) and which we aim to publish in the coming months. Supported Pt NPs with same loading but distinct initial particle size (i.e. Pt-A and Pt-B) were prepared via ALD. In previous campaigns, we investigated the effect of the O_2 partial pressure and the as-deposited morphology on the particle size evolution during annealing up to 1000°C in different partial pressures of O_2 in He.[3] We also investigated how a thin Al_2O_3 overcoat (few Å) via ALD increases the onset temperature for particle coarsening during annealing in 18% O_2/He. Here, we performed additional *in situ* GISAXS experiments to finish this overcoat investigation (Fig. 2): i) annealing of the as-deposited samples (Pt-A and Pt-B); ii) overcoat Pt-A and Pt-B with 10 Å of Al_2O_3 and annealing; and iii) Pt-B annealing up to 600 °C to reach a particle size equivalent to the as deposited Pt-A (Fig. 2 black line (arrow 1)), and then overcoat with 10 Å of Al_2O_3 and anneal up to 1000 °C (Fig. 2 black line (arrow 2)). With this last experiment, we confirmed that the particle size evolution during annealing depends only on the particle size and not on the particle preparation or thermal *history*, since after heating to 600 °C, then overcoat and annealing, the particle size evolution behaves similarly to the as deposited Pt-A with 10 Å of Al_2O_3 overcoat.

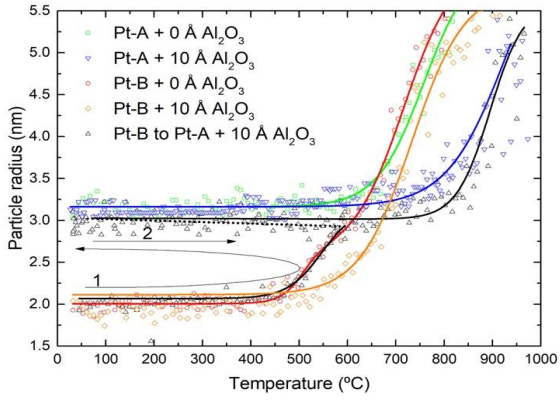

Figure 2. Pt particle size evolution during annealing

<u>*In situ* GISAXS during ALD of Au NPs:</u>

In a published work by Griffiths et al.[4], it is shown that supported Au NPs with a bimodal size distribution can be obtained by using $Au(CH_3)_3P(CH_3)_3$ as precursor and O_2 plasma (O_2^*) as reactant. Recently, we discovered at UGent that the same precursor can also be used in combination with H_2 plasma (H_2^*) to grow Au NPs. *Ex situ* SEM showed that the NP coverage for both processes is quite different (Fig. 3a, 3b), motivating the interest for studying these processes with *in situ* XRF and GISAXS. The Au/O_2^* process results in a combination of larger particles with a large inter-particle distance and smaller particles with a small inter-particle distance. The Au/H_2^* leads to a more uniform particle distribution and a small inter-particle distance. Fig. 3c and Fig. 3d show the *in situ* GISAXS results for the Au/O_2 plasma process and the Au/H_2 plasma process, respectively (cuts along q_y). The q_y-position of the scattering maximum for the Au/O_2^* process appears around 0.25 nm^{-1} and stays at this position for the entire ALD process, consistent with the large spacing of the Au NPs in the SEM images (Fig. 3a). A lobe for the expected smaller particles is not present, probably because scattering mainly occurs between the larger particles with a large inter-particle distance. For the Au/H_2^* process the lobe appears around q_y = 1.0 nm^{-1} and shifts with increasing number of ALD cycles to lower q_y values. This shows that the morphology of the surface changes during the ALD process, starting with particles that have a small inter-particle distance which merge during the process creating larger particles with a larger inter-particle distance.

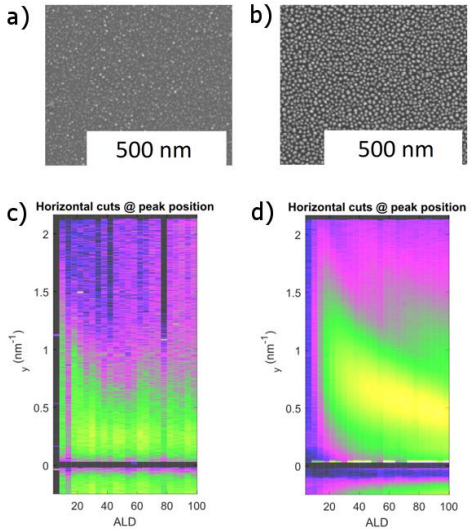

Figure 3. SEM images of Au NPs grown with O_2^*(a)/H_2^*(b) on Si. Intensity evolution of the main GISAXS peak along q_y during ALD with O_2^* (c) and H_2^* (d) on Si.

Conclusions

The campaign has been very successful and resulted in a large amount of data for different ongoing projects in the group: Ni-Fe BMNP formation (manuscript in preparation), in situ Pt annealing with overcoats (to be published soon), and in situ Au ALD (first in situ depositions at the synchrotron yielded promising results).

(1) ACSNano **2016**, 10, 8770 (2) Rev. Sci. Instrum. **2016**, 87, 113905 (3) Nanoscale **2017**, 9, 13159 (4) Chem. Mater. **2016**, 28, 44