

In situ study of noble metal atomic layer deposition processes using grazing incidence small angle X-ray scattering

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Metal nanocatalysts typically consist of noble metal nanoparticles (NPs) anchored on a metal oxide support, where the NP surface exposes active sites to catalyse target chemical reactions. The catalyst's economic viability demands high activity, high selectivity, and high stability. It is well established that the performance of catalytic NPs is closely related to their size, shape and interparticle distance. Synthesis methods that can tailor the structural properties of noble metal NPs are therefore attractive to elucidate performance-structure relationships. In this regard, there is an increasing interest in *Atomic Layer Deposition* (ALD), a vapour-phase deposition method which proved its efficiency in dispersing noble metal NPs on complex high surface area supports with atomic-scale control over the metal loading (atoms per cm²) and nanoparticle size [1]. However, an improved understanding of how the deposition parameters influence the formation and growth of the noble metal NPs is required to fully exploit the tuning potential of ALD.

We designed a high-vacuum setup for thermal and plasma-enhanced ALD that is compatible with synchrotron-based in situ X-ray fluorescence (XRF) and grazing incidence small-angle X-ray scattering (GISAXS) monitoring [2]. Using this setup, we resolved the dynamics of Pt and Pd NP formation and growth on planar SiO₂ and Al₂O₃ surfaces [3-5]. In situ XRF was used to quantify the evolution of metal loading with the number of ALD cycles, while analysis of the key scattering features allowed us to correlate the amount of deposited material with the evolution of structural parameters such as cluster shape, average size and areal density.

In a first study we focused on the growth of Pt deposits on SiO₂ with the thermal ALD process comprising sequential MeCpPtMe₃ and O₂ exposures at 300°C [3]. The results indicated a nucleation stage, followed by a diffusion-mediated particle growth regime during which the size and spacing of the Pt NPs is largely determined by adsorption of migrating Pt species on the surface and diffusion-driven particle coalescence. Interestingly, diffusion phenomena and ripening of the Pt NPs during ALD could be suppressed by using N₂ plasma as a reactant instead of O₂ in the ALD cycle. By combining O₂-based and N₂ plasma-based ALD processes, we developed a tuning strategy that offers independent control over the Pt NP size and areal density [4].

Secondly, we studied the initial nucleation of Pd NPs deposited at 150°C on oxide substrates (SiO₂ or Al₂O₃) by combining Pd(hfac)₂ and H₂ plasma in an ALD sequence [5]. The results confirmed a long nucleation process and revealed a relatively low NP areal density, in line with the occurrence of surface poisoning during the initial ALD cycles [6]. The reaction of the Pd precursor with the oxide surface leaves site blocking surface species behind, thereby inhibiting the nucleation. To enhance the nucleation, we explored two potential methods to 'clean' the surface: (1) introducing trimethylaluminum (TMA) exposures during the initial ALD cycles, and (2) introducing an O₂ plasma exposure, either before or after the H₂ plasma step, throughout the ALD process. Both these approaches had a significant impact on the evolution of NP size and spacing, and the insights obtained were used to develop a strategy that enables precise control of the Pd NP dimensions and coverage [5].

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