## Atomic Layer Deposition of Platinum: GISAXS Study of the Initial Island Growth Mode

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Atomic layer deposition (ALD) is a thin film growth method which enables atomic-level thickness control and excellent conformality on complex 3D substrates. ALD is a cyclic process and relies on sequential self-terminating reactions between gas phase precursor molecules and a solid surface.

Although ALD is traditionally perceived as a layer-by-layer method, for noble metal ALD processes nucleation regularly proceeds through the formation of islands that coalesce in a continuous film after a sufficient number of cycles [1]. By carefully controlling the nucleation stage, ALD can be used for the conformal deposition of nanoparticles, e.g. for catalytic applications [2]. It is therefore important to obtain an in-depth understanding of the nanoscale structure and morphology of the nuclei formed at the start of noble metal ALD processes.

In this work, GISAXS was used to systematically study the initial growth stages of Pt ALD films as a function of underlying substrate, deposition temperature ( $150^{\circ}$ C vs.  $300^{\circ}$ C) and reactant gas. The depositions were done in a home-built ALD setup using (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe<sub>3</sub>) as precursor and O<sub>2</sub> gas, O<sub>2</sub> plasma, N<sub>2</sub> plasma or O<sub>3</sub> as reactant [3]. As substrates SiO<sub>2</sub>, amorphous TiO<sub>2</sub> and polycrystalline TiO<sub>2</sub> were used to investigate how the surface chemistry and crystalline phase affect the formation and growth of Pt islands.

2D GISAXS patterns were recorded with a Pilatus 100K detector at beamline X21 of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The images in Figure 1 were obtained at different stages of the O<sub>3</sub>-based ALD process at 150°C. With progressing growth the scattering lobes increase in intensity and move towards  $q_y \approx 0$ . This indicates an increase in particle size and inter-particle distance: Pt islands grow and coalesce leading to a lower number of particles per unit area.



Figure 1: Island growth during  $O_3$ -based ALD of Pt on a SiO<sub>2</sub> surface: (top) 30 cycles, (middle) 60 cycles, and (bottom) 100 cycles grown at 150°C.

## References

- [1] S. T. Christensen et al., Chem. Mater. 21, 516 (2009).
- [2] J.S. King et al., Nano Lett. 8, 2405 (2008); J. A. Enterkin et al., ACS Catal. 1, 629 (2011).
- [3] T. Aaltonen *et al.*, Chem. Mater. 15, 1924 (2003); H.C.M. Knoops *et al.*, Electrochem. Solid-State Lett. 12, G34 (2009); D. Longrie *et al.*, ECS J. Solid State Sci. Technol. 1, Q123 (2012).