Thermal and Plasma-enhanced ALD of TiN on Powders using a Rotary Reactor

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To conformally coat particles using ALD, agitation of the particles and efficient reactant usage are necessary[1]. A rotary reactor was developed to enable both thermal and plasma-enhanced ALD growth on mechanically agitated particles[2]. The proposed pump-type rotary reactor allows the combination of static reactant exposures, working under high vacuum conditions (base pressure < 1 x 10^{-5} mbar) and mechanically agitating various types of particles, ranging from (possibly porous) nanosized powder (average particle size < 100 nm) to small objects (up to several mm). The main chamber is a quartz tube. On both ends of the tube, a vacuum tight connection is formed between the rotating quartz tube and a fixed metal frame. One of these metal frames is connected to a gas inlet system, while the other is connected to a turbomolecular pump and a mass spectrometer for performing gas analysis. The mixing of the particles is based on tumbling of the particles over grooves in the quartz tube. Upstream from the tube furnace and just after the gas inlets, a RF power generator is placed to ionize the reactant gas and enable PE-ALD.

The effectiveness of the PE-ALD powder reactor concept was previously demonstrated by depositing Al_2O_3, TiO_2 and AlN by thermal and plasma-enhanced ALD on a variety of particles[2]. In this work we present a comparison of thermal and plasma-enhanced deposition of TiN on micron sized ZnO powder (BET 3.9 m²/g) using TDMAT (tetrakis dimethylamido titanium) and NH_3 gas or plasma. In-situ mass spectroscopy (MS) bar scan measurements confirmed that thermal and PE-ALD reactions were being performed by detecting the expected $HNMe_2$ (45 amu) reaction product and its cracking products. Differences between the spectrum obtained during the thermal and plasma-enhanced NH_3 pulse revealed slightly different reaction mechanisms for both processes. To determine saturation, the NMe_2 (44 amu) signal was monitored as a function of time. This enabled the precise determination of the necessary pulse times for saturation as a function of powder mass present in the reactor and revealed faster saturation of the plasma-enhanced process. Ex-situ XRF measurements confirmed linearity of both processes by monitoring the amount of deposited TiN versus number of ALD cycles and showed that the PE-ALD process has a higher GPC than the thermal process. XPS measurements revealed that the layers grown with the PE-ALD process have a higher nitrogen content and contain less oxygen impurities than the thermally grown layers. Preliminary resistivity measurements were unable to determine the conductivity of the thermally grown layers because the resistivity was beyond the measuring range of the equipment. The resistivity of the plasma-enhanced deposited layers was within measuring range of the equipment, yielding a measurable conductivity of the layers and proving the PE-ALD grown TiN layers to be more conductive than the thermally grown layers.

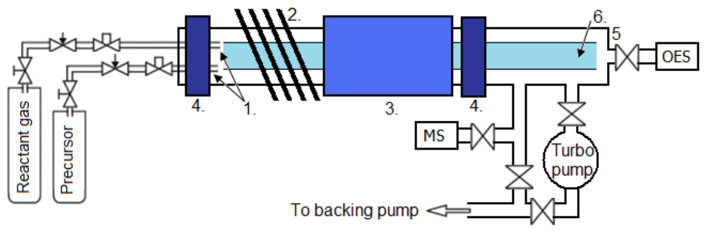

Fig. Left: Rotary reactor showing (1) separate inlets for reactant and precursor gas, (2) RF coil, (3) tube furnace, (4) mechanical rotation system, (5) inlet for the inner dielectric tube and (6) inner dielectric tube containing the objects/powder to be coated. The OES and MS can be connected to the reactor as need be.

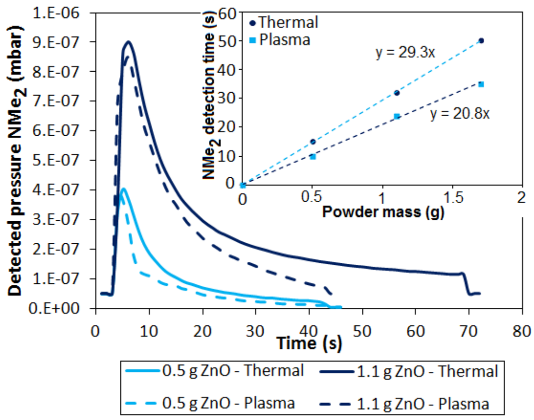

Fig. Right: NMe_2 partial pressure as function of time during the NH_3 pulse of the thermal and PE-ALD process for different amounts of micron sized ZnO powder in the rotary reactor. The detection time increases linearly (see inset) with increasing powder mass to be coated. The PE-ALD process saturates more rapidly than the thermal ALD process.

[1]: King, D. M., Liang, X. H., Weimer, A. W., *Journal of The Electrochemical Society,* **2009**, *25*, 163-190.
[2]: Delphine Longrie et al., *Surface and Coatings Technology*, **2012**, 213, 183-191.