A rotary reactor for thermal and plasma-enhanced atomic layer deposition on powders and small objects

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1. Introduction

Possible applications for particles have strongly increased during the last decade. Many of these applications require particles to have different surface and bulk properties¹⁻⁵ which can be achieved by e.g. coating the particles with a nanometer thick layer. The key challenge is in coating the individual particles with an ultrathin and conformal coating, which is especially difficult in the case of nanoparticles since they have a very large surface area and the tendency to coalesce.

Fig. 1: ALD cycle for growth of Al_2O_3 using TMA as precursor and H_2O as reactant. One complete ALD cycle consists of a precursor pulse, pump time, a reactant pulse and pump time.

Atomic layer deposition (ALD) is a technique consisting of two sequential, self-limiting gas-phase surface reactions that enables deposition of ultrathin, conformal and uniform thin films⁶⁻⁸. Fig. 1 shows the ALD cycle for growth of Al_2O_3 . During the first step of the ALD cycle, the OH-terminated starting surface is exposed to a pulse of TMA (Trimethylaluminium). These precursor molecules will interact with the OH surface groups when binding to the surface, forming CH_4 as reaction product. These CH_4 molecules and any remaining TMA will be evacuated during the subsequent pump time. The reactant in the case of thermal ALD is H_2O . The H_2O molecules will remove the remaining CH_3 ligands and creating CH_4 as reaction product, form O-bonds between the Al atoms creating the Al_2O_3 layer and terminate the surface with OH-bonds. The remaining H_2O molecules and the formed CH_4 will be evacuated during the subsequent pump time, leaving a new OH-terminated surface for the next precursor pulse to react with. When performing PEALD, an O_2 -plasma replaces the H_2O pulse. The oxygen radicals in the plasma will then remove the remaining CH_3 groups on the Al atom in combustion-type reactions, creating CO_2 and H_2O as reaction products.

To enable the deposition of ALD coatings on large quantities of particles, fluidized bed reactors have been developed and proven for a variety of processes⁹⁻¹³. Since a gas flow is used to levitate the particles, a high gas throughput is required and only fine and light powders can be fluidized. Due to the high pressures inside these reactors, plasma-enhanced ALD (PEALD) will be impossible, limiting them to thermal ALD processes only. Furthermore, additional energy will be necessary (e.g. mixing, vibrations) when coating nanopowders due to their high interparticle forces which causes them to coalesce^{9,14-16}. Finally, the use of a fluidizing gas also renders it impossible to use static reactant exposures to increase the efficiency of the process¹⁷ and minimize the usage of expensive precursors.

Therefore it is important to develop alternative ways of fluidizing nanopowders, particles and granules while enabling static reactant exposures. A method based on a rotating metal cylinder was proposed by McCormick et al.¹⁸⁻²⁰ which traps the powder inside pores of a rotating metal cylinder. The particles are released when reaching the top of the rotation circle, thus being exposed to the reactant gas. While enabling depositions with static exposures, the use of a metal cylinder inside a stainless steel vacuum chamber still renders PEALD using an inductive coupled RF plasma impossible.

2. Objectives

In this paper a design for a rotary ALD reactor²¹⁻²² is presented that enables both thermal and plasma-enhanced ALD on large quantities of agitated particles. The agitation of the particles is achieved mechanically, thus no fluidizing gas is used. This makes it possible to coat particles ranging from nanometer sized powders to centimeter sized objects. The effectiveness of the reactor design will be demonstrated by depositing Al_2O_3 , TiO_2 and AlN by both thermal and plasma-enhanced ALD on ZnO

nanopowder, stainless steel micron sized powder and titanium granules and glass beads. Saturation of the ALD half-reactions will be confirmed using in-situ optical emission spectroscopy (OES) and mass spectroscopy (MS) measurements. The composition and conformality of the deposited films will be verified by ex-situ X-ray fluorescence (XRF), X-ray photo-electron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM) measurements.

3. Methods

3.1. Rotary reactor

The rotary reactor that will be described allows for the combination of static reactant exposures, working under high vacuum conditions (10^{-5} mbar) and mechanically agitating large quantities of particles ranging from (porous) nano sized powders (< 100 nm) to small objects (up to 1 cm). The reactor performs pump-type ALD reactions, so no purging is used. A diagram of the reactor design is shown in Fig. 2. The main chamber is a rotating quartz tube attached at both ends by a vacuum tight connection to a fixed metal frame. One end of the frame is connected to a gas inlet system consisting of a custom-made, multiple-input flange, while the other end is connected to a turbomolecular pump for evacuating the chamber and a mass spectrometer for performing gas analyses.

To enable switching between pulse-type ALD reactions and static reactant exposures, a pneumatic valve can be closed between the reactor chamber and the pumping system. This enables exposure of the particles to a predefined reactant pressure for any length of time while still mechanically agitating them. The particles are contained in the vacuum reactor chamber in an open glass tube which is placed inside the outer quartz tube and coupled to it. The powder is confined to a 15 cm sized zone of the inner tube by indentations narrowing the tube diameter. Along the length of this zone two grooves were made to mix the particles by making them tumble over the grooves.

The temperature of the particles inside the reactor is controlled by a tube furnace positioned around the outer quartz tube. This allows for accurate control of the deposition temperature within a wide range (up to 1000°C). Upstream from the tube furnace a RF power generator (13.56 MHz) is placed to ionize the reactant gas and enable PEALD. The RF generator is composed of an RF coil placed around the outer tube, a power supply and a matching unit. The reaction zone is downstream from the plasma region, making PEALD possible by ensuring the presence of radicals while minimizing the presence of high energy ions, thus avoiding physical bombardment and damage to the surface.

Fig. 2: Diagram of the rotary reactor: (1) inlets for gases, (2) RF coil, (3) tube furnace, (4) mechanical rotation system, (5) inlet for the inner dielectric tube and (6) inner tube containing the particles to be coated.

Fig. 3: SEM images of (A) ZnO powder, (B) stainless steel powder, (C) Ti granule and (D) glass beads.

3.2. Experimental

Al_2O_3 was deposited by thermal ALD with TMA (1.5×10^{-3} mbar) and H_2O (1.5×10^{-3} mbar) as reactants and by PEALD with TMA and an O_2 -plasma (4×10^{-4} mbar, 200 W) as reactants. The reaction zone was heated to 200°C . TiO_2 was deposited by thermal ALD with TDMAT (Tetrakis dimethylamino titanium) and H_2O as reactants. Due to the low vapor pressure of TDMAT, argon was used as a carrier gas to reach a pressure of 1.5×10^{-3} mbar during the TDMAT pulse. The reaction zone was heated to 150°C . AlN was deposited by thermal ALD with TMA and NH_3 as reactants and by PEALD with TMA and an NH_3 -plasma (4×10^{-4} mbar, 200 W) as reactants. The reaction zone was heated to 100°C .

Depositions were performed on different types of powders (shown in Fig. 3): micron sized ZnO powder (BET: $3.9 \text{ m}^2\text{g}^{-1}$) and nano sized ZnO powder (BET: $33.2 \text{ m}^2\text{g}^{-1}$), smooth and spherical micron sized stainless steel powder (from $45 \mu\text{m}$ to $125 \mu\text{m}$), rough and irregular titanium granules (from 0.2 mm to 1.5 mm) and smooth and spherical glass beads (particle diameter 2 mm).

In-situ MS (HAL 7 RC RGA 511#3203, Hiden analytical) measurements were performed using the spectrometer in Multiple Ion Detection mode and Bar Scan mode using the Faraday detector (source voltage 70 V). In-situ OES (Ocean Optics QE65000, int. time 100 ms) measurements were also performed. The composition and conformality of the ALD coatings were verified using EDX (Quanta 200F, FEI), TEM (Tecnai G2, 200 kV), XPS (Surface Science Instruments, monochromatic Al K_{α} radiation) and XRF (Artax, Bruker, silicon drift detector, angle 52°, real time 100 s) using simultaneously Cu K_{α} (angle 15°, 40 kV, 40 mA) and Mo K_{α} radiation (angle 45°, 12 kV, 120 μ A).

4. Results

4.1. Thermal ALD

Three different amounts of ZnO powder area were coated thermally with Al_2O_3 while the formation of the reaction product CH_4 was measured using MS. Tracking the formation of CH_4 as function of time during the reactant (H_2O) pulse makes it possible to determine saturation of the surface reactions. The formation of CH_4 starts simultaneously with the reactant pulse (see Fig. 4), confirming fast reactions between the reactant gas and the powder surface. The CH_4 signal quickly reaches a maximum and will remain constant as long as the maximal amount of surface reactions occur. When the amount of reactive powder surface decreases, the partial pressure of CH_4 will decrease as a result of fewer surface reactions occurring and evacuation of the reaction products through pumping. There is a linear relationship between the necessary pulse time for saturation and the surface area of powder present inside the reactor. The rather long pulse times found experimentally are due to the low pressures used and can be significantly reduced by increasing the reactant pressure. XPS measurements confirmed the composition of the layer, while TEM images (Fig. 5) show that all individual ZnO grains were uniformly coated with a conformal 5 nm (50 ALD cycles, 1 $\text{\AA}$ /cycle) thick amorphous Al_2O_3 layer.

Fig. 4: CH_4 partial pressure as function of time during the H_2O pulse for different amounts of ZnO powder in the reactor and (inset) linear relationship between the CH_4 detection time and the powder surface.

Fig. 5: TEM image of ZnO nano sized powder coated with 5 nm (50 cycles) amorphous Al_2O_3 .

Besides the deposition of conformal and uniform layers, a marked advantage of ALD as a thin film deposition technique is the precise control over the thickness of the grown layers. Every ALD cycle, the same amount of material is deposited (0.5 $\text{\AA}$ /cycle for the TiO_2 process), allowing for a linear relationship between the thickness of the grown layer and the amount of cycles deposited. XRF was used to confirm linearity of the thermal TiO_2 process by coating ZnO nano sized powder with different numbers of ALD and measuring each sample with XRF. Fig. 6 shows the increase in the titanium peak at 4.512 keV in the subsequent XRF spectra, corresponding to larger amounts of titanium on the powder surface. The inset proves the linear relationship between the ratio of the titanium-to-zinc signal and the number of ALD cycles deposited, confirming that the ALD process leads to linear growth.

Fig. 6: Evolution of the titanium XRF-peak (4.512 keV) as function of the number of TiO_2 ALD cycles deposited and (inset) ratio of the Ti-to-Zn XRF-signal as function of the number of TiO_2 ALD cycles on ZnO nanopowder.

4.2. Plasma-enhanced ALD

One advantage of this reactor design is that it is possible to coat particles using PEALD. During plasma processes, OES becomes available as a detection tool in addition to MS. OES measurements can detect the formed reaction products during the plasma pulse of the ALD cycle. For PEALD of Al_2O_3 these reaction products are CO_2 and H_2O and they are visible in the OES spectra as CO^+ , OH^+ and H^+ emissions due to the excitation of CO_2 and H_2O molecules by electron impact. Comparable to MS saturation measurements, the formation of the reaction products CO^+ and H^+ in the OES spectra was monitored for different amounts of powder inside the reactor. These measurements showed that an increase in powder mass inside the reactor leads to a longer detection time for the formed reaction products, confirming that a longer time is needed to saturate the surface reactions. The saturation time is linearly dependent on the powder mass present, as is the case for thermal ALD processes. MS measurements were performed simultaneously and confirm the saturation times found with OES.

The chief advantage of PEALD is that it enables growth under circumstances where thermal ALD is not possible, e.g. at low substrate temperatures. This is illustrated by the deposition of 50 cycles of AlN on ZnO nanopowder using both the thermal and the plasma-enhanced ALD process at 100 °C. This substrate temperature is below the temperature window for the thermal process, thus no thermal growth occurs, while AlN is grown with the PEALD process, as shown in Fig. 7. These depositions were also performed successfully (confirmed by EDX and XPS) on the other particles mentioned.

Fig. 7: EDX measurements of ZnO powder coated with 50 cycles of AlN deposited with the thermal and plasma-enhanced processes.

5. Conclusions

A rotary reactor for thermal and plasma-enhanced ALD on agitated particles has been developed. The mechanical agitation is performed to reduce the necessary exposure time to the precursor gases and to allow coating the individual particles instead of larger agglomerates. The reactor can be used for both pump-type ALD reactions and static exposures, which leads to a more efficient usage of reactant gases. A first advantage of this reactor design is the possibility of performing PEALD, which allows growth of very pure ALD layers under circumstances where thermal ALD is not possible. A second advantage is the large variety of agitated particles that can be coated: from nano sized powders under 100 nm up to particles and small objects up to 1 cm. The performance of this reactor design was illustrated by deposition of Al_2O_3 , TiO_2 and AlN by thermal and plasma-enhanced ALD on a variety of particle substrates: ZnO micron and nano sized powder, smooth stainless steel micron sized powder, rough and irregularly shaped titanium granules and larger glass beads. In-situ OES and MS measurements allowed for the precise determination of the pulse times needed for saturation, while XRF measurements confirmed linearity of the ALD process and deposition of AlN at 100°C illustrated PEALD growth. By successfully depositing different ALD layers on particles varying greatly in size, composition and shape it was demonstrated that the reactor has a wide potential range of applicability. The TEM, XPS, XRF and EDX results on the coated and uncoated particles indicate that the deposited layers that were tested were conformal, uniform and believed to be pinhole free.

6. References

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