

ENCAPSULATING PARTICLES WITH NANOSCALE PRECISION USING ATOMIC LAYER DEPOSITION

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INTRODUCTION

In most encapsulation processes, the coating is introduced via the liquid phase: either by dispersing the particles in a liquid, or by spraying a liquid onto the particles. An alternative is to use gas-phase coating. One way of doing this is with chemical vapor deposition (CVD): exposing the substrate to volatile precursors, that react at the surface to form a coating. Typically, two different precursors are being used. Although CVD is mostly used in the semiconductor industry for coating wafers, it is also used for coating particles. The typical coating thickness obtained with CVD is in the μm -range. Following Moore's law, there is an ongoing drive towards semiconductor components miniaturization, which also requires a coating technology that enables thinner films. This explains why atomic layer deposition (ALD) has become more popular in recent years: with this gas-phase coating technique, sub-nanometer precision can be achieved.

The difference in approach between CVD and ALD is that in the latter the gaseous reactants are added alternately. As a consequence, the coating chemistry is split into two half-reactions. Each of these reactions is self-limiting, such that at most a monolayer can be deposited. In this way, we have full control over the coating thickness: the number of times the alternating

feed of the two precursors is repeated determines the thickness of the achieved coating. For example, for an alumina coating, a precursor such as trimethyl-aluminium chemisorbs on a substrate by reacting n ($1 < n < 2$) of its methyl-groups (ligands) with active sites (commonly hydroxyl-groups) at the surface, releasing methane (step 1). In step 2, the remaining ligands react with an oxidizer such as water releasing the other methyl-groups and repopulating the surface with hydroxyl groups (see Fig. 1.a.). After this second step, step 1 can be repeated. The formation of alumina is just one example: dozens of different inorganic materials can be made via ALD (Miikkulainen et al., 2013). Moreover, it is also possible to deposit organic films via an analogous mechanism (see Fig. 1.b); the method is then referred to as molecular layer deposition (MLD).

ALD ON PARTICLES

Most research on ALD is aimed at depositing ultrathin films on wafers and other flat substrates. However, when carried out in a so-called fluidized bed, ALD is an attractive way of providing particles with an ultrathin coating. In a fluidized-bed ALD reactor, the particles are suspended in an upward nitrogen flow. The good mixing of the particles and the gas results in a very uniform coating of the particles. Moreover, this approach has an excellent scale-up potential: at the lab-scale we can coat

batches from less than 1g to more than 100g. However, in an industrial setting it would be rather straightforward to coat batches of several hundreds of kg. The size of the particles to coat is not limited to the μm range: ALD can also be applied to fluidized nanopowders. Nanoparticles – contrary to what is typically observed for micron-sized particles – are fluidized as very dilute agglomerates with distinctive fluidization characteristics. One of our research topics is understanding the fluidization of nanoparticles, and applying it as a tool for ALD on these particles. When working with powders of which the particle size is in the nanorange or just slightly larger (a few μm), the particles often have a strongly cohesive behavior. In those cases, we work with assistance methods such as vibration or microjets to obtain smooth fluidization behavior (van Ommen et al., 2012).

RESULTS & DISCUSSION

In the semiconductor industry, most ALD processes are carried out at vacuum. However, we operate our fluidized bed reactors typically at atmospheric pressure to facilitate scale-up. Normally, ALD processes are carried out between 100°C and 300°C , depending on the chemistry used. However, for several substrate particles – especially for materials of biological origin – this would be too high. Therefore, we recently investigated coating of titania nanoparticles with alumina at room temperature and atmospheric pressure using the coating chemistry given in Fig. 1.a. We found conformal, homogenous coatings (see Fig. 2.a). Moreover, the coating thickness linearly increases with the number of cycles applied (see Fig. 2.b), demonstrating the precise control over the thickness we can achieve (Valdesueiro et al., 2015).

As the precursors used in ALD are typically quite expensive, it is a prerequisite for economical process operation that they are efficiently used. We recently published a paper aimed at understanding and optimizing the precursor utilization efficiency using a multiscale modelling approach (Grillo et al., 2015). We showed that fluidized-bed ALD on high surface area powders is a forgiving process that can be

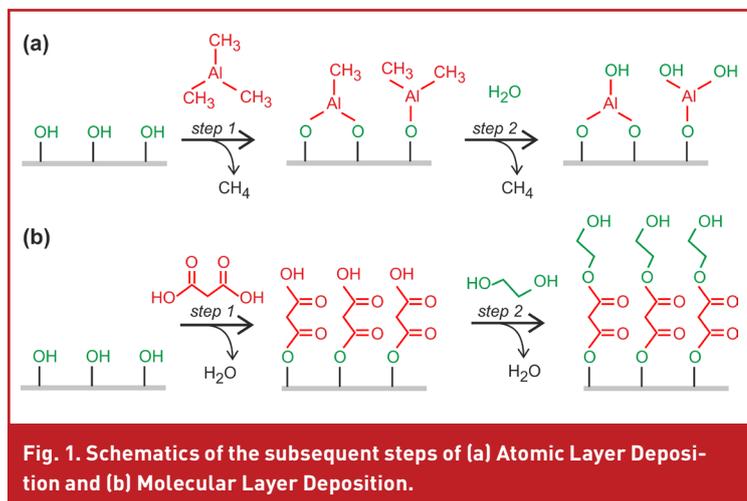


Fig. 1. Schematics of the subsequent steps of (a) Atomic Layer Deposition and (b) Molecular Layer Deposition.

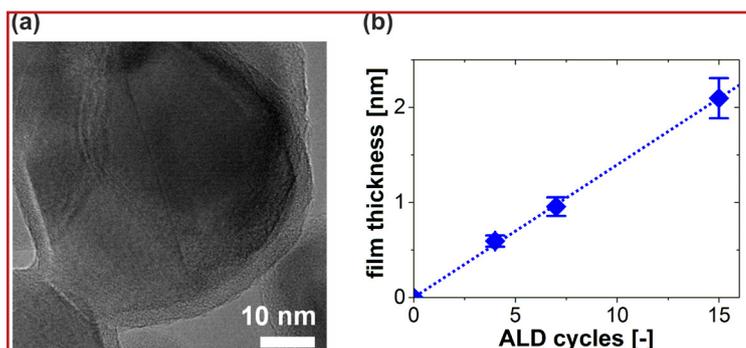


Fig. 2. Alumina coating of titania nanoparticles: (a) TEM picture of a particle coated with 15 ALD cycles; (b) film thickness as a function of the number of cycles.

carried out with virtually no precursor wasting. For nanoparticles, the precursor will have to diffuse into the nanoparticle agglomerations. However, still more than 99% precursor efficiency can be achieved. In the case of porous micron-sized particles, typically used as carrier particles in the manufacturing of supported catalysts, this will be somewhat lower (~95%), but for the encapsulation of non-porous particles with a diameter in the micron-size range very high efficiencies of virtually 100% can be achieved. Another attractive feature of encapsulating micron-sized particles with this approach is that just very small amounts of coating material have to be used: on a 10 μm particle, an alumina coating of 10 nm is just 0.6 vol% of the total particle. However, already such a thin film allows the formation of an extremely high barrier coating: it can reduce the water vapor transmission of a polymer substrate with more than a factor 100.

Like most conventional ALD reactors, fluidized-bed ALD reactors are operated in a temporal mode: the pulses of the different gaseous reactants are delivered subsequently in time. An alternative is to separate the administering of the reactants in space. We recently developed a spatial ALD reactor for particles. In this device, the particles are blown through the reactor with nitrogen as a carrier gas at atmospheric pressure: they are pneumatically transported. This pneumatic transport line consists of three parts: first the particles are heated, then reactant A is added and reacts with the particles, and subsequently reactant B is added and reacts with the particles. Our current test setup is laid-out for just a single ALD cycle. However, it is easy to devise equipment with multiple injection points for both precursors,

such that multiple ALD cycles can be carried out. Currently, we are able to produce coated nanoparticles via ALD at a production rate of about 1 g/min (van Ommen et al., 2015).

However, the experience with pneumatic transport from other fields opens up promising scale-up prospects for continuous particle ALD.

CONCLUDING REMARKS

ALD is an attractive technique to efficiently encapsulate particles via a gas-phase process. Since the obtained coating has a very high quality, excellent encapsulation results can be obtained with films of just a few nm. With ALD, many different inorganic coatings can be deposited, such as oxides, nitrides and pure metals. Its organic counterpart MLD, which received less research attention up to now, can also be very relevant for encapsulation. We have demonstrated that ALD of alumina can be carried out at atmospheric pressure and room temperature, opening the door for coating sensitive substrates, and for carrying out the coating at large scale. The coating can be carried out either on batches of particles in a fluidized bed, or on continuously transported particles with a pneumatic transport reactor.

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