

Gas-Phase Deposition of Thin Aluminium Oxide Films at Ambient Conditions

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Proefschrift

ter verkrijging van de graad van doctor aan de Technische Universiteit Delft, op gezag van Rector Magnificus prof. ir. K.C.A.M. Luyben, voorzitter van het College van Promoties, in het openbaar te verdedigen op

> woensdag 4 november 2015 om 12:30 uur

> > door

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The research reported in this thesis was conducted in the Product and Process Engineering section of the Chemical Engineering department, Faculty of Applied Sciences (TNW) of the Delft University of Technology and received funding from the European Union Seventh Framework Program FP7/2007-2013 under grant agreement no. 26722, and from Royal DSM.

ISBN: 978-94-6186-564-9 Copyright © 2015 by David Valdesueiro Printed in The Netherlands by CPI Wöhrmann Print Service

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To my parents

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Summary

Particles are widely used in the chemical industry as raw material and end product. In many applications of particles, it is advantageous to give them a coating that can either protect the particle from outside influences or give it an additional function. Technologies to provide micron-sized particles with relatively thick coatings (in the order of μ m) are readily available. However, for many applications it would be attractive to apply coatings to fine particles (of the order of 50 μ m or smaller) and to make these coatings thinner (<< 1 μ m). This opens possibilities for new properties. In addition, a lower amount of the compound would be needed to coat the material of interest. This thesis focuses on a technique for depositing ultrathin and conformal films, with control down to nanometre scale, with high a utilisation of the precursors: atomic layer deposition (ALD) applied to fine particles.

ALD is a gas-phase coating technique that relies on two self-terminating reactions, that form a coating cycle, after which a fraction of a monolayer of compound is deposited on the substrate. This cycle can be repeated a desired number of times to deposit thicker layers. Amongst the wide variety of compounds that have been deposited with ALD, alumina (Al_2O_3) has been the favourite one to study, due to the ideal layer-by-layer growth mode that is observed when used trimethyl aluminium (TMA) and water as precursors, and its broad applicability in different fields.

Thin Al_2O_3 ALD films have been used, for example, in the fabrication of semiconductor devices, in the production of catalysts and the passivation of the cathode of the Li-ion batteries. Besides these applications, other materials such as polymers or biological products could benefit from the deposition of ultrathin alumina films. However, alumina has been typically deposited at relatively high temperatures (~170 °C) and low pressures (< 1 mbar), inhibiting its application to heat-sensitive materials. This is our main motivation to investigate the deposition of alumina films at room temperature and atmospheric pressure. Working at ambient conditions would, in first place, permit the coating of heat sensitive materials, and, in second place, facilitate the coating process and improve the scaling-up prospects, since less complex equipment would be required.

Atomic layer deposition provides accurate control over the film thickness based on the selfterminating nature of the ALD reactions. That means that deposition only takes place as long as there are surface species available for reaction. The combination of the operating temperature and pressure, and the purging of the reactor with nitrogen after each reaction, ensure the removal of unreacted precursor molecules from the surface of the substrate. However, the physisorption of these unreacted molecules is the main challenge that we face when depositing alumina at 25 °C and 1 bar, since the normal boiling temperature of TMA and water is 125 and 100 °C, respectively. In Al₂O₃ ALD processes at 170 °C and < 1 mbar, where no physisorption occurs, the thickness of the deposited films depends solely on the number of coating cycles, since once the active sites on the surface are depleted, no more reaction takes place, regardless of the amount of precursors fed to the reactor in excess. In contrast, at ambient conditions, the thickness of the alumina film will depend on the number of cycles and on the dosing time of the precursors due to the accumulation of the unreacted precursor molecules that are fed in excess.

In this work, we aimed at controlling the physisorption of the precursors at ambient conditions by adjusting the dosing time of the precursors to the reactor. By feeding the amount of precursor molecules needed to saturate the active sites present on the surface of the substrate (TiO₂ nanoparticles in our case), we obtained similar growths as in pure ALD, i.e., 0.1-0.2 nm per cycle, even if the reactions are not self-limiting. Complementarily, having a faster growth of the alumina film could be done by dosing both precursors in excess due to the physisorption of unreacted molecules.

These findings were applied in the remainder of the thesis to deposit alumina, at ambient conditions, on three different substrates: polymeric powder coating paint, lead-selenide quatum dot (PbSe QD) films, and silicon carbide (SiC) particles. Two of these materials, the powder coating and the QD films, are heat sensitive, thus working at room temperature was essential.

 Al_2O_3 films were used to tune the surface appearance of a powder coating (i.e., dry paint without any solvent). The polymeric core particles were coated with alumina films of different thicknesses. The alumina layers partially confined the core material when it softened above the glass transition temperature. As the softened core did not flow during the curing of the paint, it created roughness of the surface, and therefore, a matte surface appearance. The mechanical properties of the matte powder coating were similar to the ones of the originally glossy one. Thin alumina films were used to tune the final appearance of the powder coating paint without the use of foreign particles that would produce the same effect.

Additionally, films of PbSe QD crystals, which are nanosized crystals with very interesting properties for semiconductor applications, were passivated using alumina. QDs films have very promising applications, e.g., as high-efficiency photovoltaic material. However, they are air and heat sensitive and irreversibly oxidize after a short exposure to air, losing their good properties. Previous work showed the passivation of the QDs with alumina at temperatures between 25 and 90 °C, and pressures smaller than 1 mbar. In this work, alumina was deposited at 25 °C and 1 bar to efficiently passivate the QDs. At ambient conditions, a fast deposition of alumina took place as a consequence of different groups that can react with TMA, such as hydroxyl and amine groups. Coating with alumina at ambient conditions can be easily coupled with the fabrication of the QD films, which also is done at room temperature and atmospheric pressure.

The final application we considered is the production of radioactive tracer particles. For fluidized bed studies, we would like to label SiC particles with a minimum change to their other physical properties. SiC particles have a rather inert surface towards radioactive ions, so we used the Al_2O_3 coating to enhance the labelling efficiency of this material and produce a tracer. Typically, a completely different material is used for the tracer particles, such as γ - Al_2O_3 . However, this would produce a mismatch in properties such as size, shape and density between the tracer and the material of study. In this work, alumina films were deposited on

SiC particle to mimic the affinity of the γ -Al₂O₃ particles towards the radioactive ions, and produce a SiC-based tracer. Since the labelling efficiency depends on the alumina film thickness, TMA and water were fed in large excess, achieving a growth per cycle of alumina of about 10 nm. The resulting core-shell particles, with an alumina coating of about 400 nm, had only a slightly lower relative activity as the γ -Al₂O₃ particle. Nevertheless, this SiC-based tracer was used in a particle tracking experiment, having enough activity to be detected by the sensors and reconstruct its trajectory during fluidization.

One might argue whether the studied deposition process at atmospheric pressure and room temperature is still true ALD, since the reactions are not self-terminating and we deposit several layers of alumina in each cycle. Nevertheless, it gives the possibility of depositing alumina on heat sensitive materials, with good tunability and control over the films thickness, at operating conditions that would simplify the scaled-up of this technology. The findings in this thesis could be expanded to other applications, such as the coating of biological compounds, that would require low-temperature processing, or the deposition of other compounds at ambient conditions, i.e., zinc oxide (ZnO). This is further discussed in the outlook of this thesis.

Samenvatting

Deeltjes worden op grote schaal toegepast in de chemische industrie als basismateriaal en als eindproduct. Bij vele toepassingen van deeltjes is het aantrekkelijk om een coating aan te brengen als een beschermende of functionele laag. Technieken om microdeeltjes te voorzien van een relatief dikke laag (in de orde van micrometers) zijn reeds beschikbaar. Echter, voor veel toepassingen is het aantrekkelijk een dunne laag (<< 1 μ m) aan te brengen op fijne deeltjes (50 μ m of kleiner) om op deze manier nieuwe eigenschappen van de deeltjes mogelijk maken. Bijkomend voordeel van de dunne laag is dat er minder materiaal nodig is om de coating aan te brengen op het gewenste materiaal. Dit proefschrift richt zich op een techniek voor de depositie van ultradunne en conforme lagen, met nanometer-precisie en met zeer efficiënt gebruik van de precursors: atoomlaagdepositie (ALD) op kleine deeltjes.

ALD is een coatingtechniek in de gasfase, gebaseerd op twee zelf-terminerende reacties die elke cyclus een fractie van een monolaag vormen op het substraat. De dikte van de laag wordt bepaald door het aantal cycli. Van alle materialen die gebruikt worden voor ALD, is alumina (Al₂O₃) een populair materiaal om te bestuderen, vanwege de ideale laag-per-laag-groei die wordt waargenomen bij het gebruik van trimethylaluminium (TMA) en water als precursors, en de vele mogelijke toepassingen in verschillende vakgebieden.

Dunne Al₂O₃-ALD-films worden onder andere gebruikt bij de fabricatie van halfgeleiders, in de productie van katalysatoren en bij de passivering van de kathode van Lithium-ion-accu's. Daarnaast zou de depositie van ultradunne alumina films gebruikt kunnen worden voor andere materialen zoals polymeren en biologische producten. Echter, alumina depositie gebeurt over het algemeen bij hoge temperaturen (~170 °C) en lage drukken (< 1 mbar), waardoor deze techniek niet toegepast kan worden op warmtegevoelige materialen. Dit is de belangrijkste motivatie om de depositie van alumina bij kamertemperatuur en atmosferische druk te onderzoeken. Op deze manier kan de ultradunne alumina laag aangebracht worden op warmtegevoelige materialen; daarnaast wordt het proces vereenvoudigd en toepasbaar voor grootschalig gebruik.

ALD biedt nauwkeurig controle over de filmdikte, gebaseerd op het zelf-terminerende karakter van de ALD reacties. Dat betekent dat de depositie slechts plaats vindt waar substraatoppervlak beschikbaar is voor de reactie. De combinatie van de temperatuur, de druk en de zuivering van de reactor met stikstof na iedere reactie, zorgt voor de verwijdering van het overschot aan precursors van het substraat oppervlak. Echter, de fysisorptie van deze niet-gereageerde precursor moleculen is de voornaamste uitdaging die we ondervinden bij alumina-depositie bij 25 °C en 1 bar, aangezien de kookpunten van TMA en water onder deze condities respectievelijk 125 °C en 100 °C zijn.

Bij het ALD proces van Al_2O_3 bij 170 °C en < 1 mbar, waar geen fysisorptie plaatsvindt, hangt de dikte van de aangebrachte laag enkel af van het aantal coating cycli, aangezien de reactie stopt zodra alle reactieve plekken op het oppervlak bezet zijn, ondanks de hoeveelheid aanwezige precursors. Bij standaardomstandigheden, kamertemperatuur en atmosferische druk, daarentegen, hangt de dikte van de laag af van het aantal cycli en de doseringstijd van de precursor, wegens accumulatie van de overmaat aan precursors in de reactor.

In dit onderzoek streven we naar controle over de fysisorptie bij standaardomstandigheden door de doseringstijd van de precursor in de reactor aan te passen. Door de benodigde hoeveelheid precursors toe te voegen om alle reactieve plekken op het substraat (in dit geval TiO₂ nanodeeltjes) te verzadigen, verkrijgen we vergelijkbare groei als in pure ALD (0.1-0.2 nm per cyclus), ondanks het ontbreken van de zelf-terminerende reactie. Daarnaast kan snellere groei van de alumina film verkregen worden door beide precursors in overmaat te doseren, dankzij de fysisorptie van de niet-gereageerde moleculen.

In het vervolg van dit proefschrift zijn bovenstaande bevindingen toegepast om, onder standaardomstandigheden, een alumina-coating aan te brengen op drie verschillende substraten: een polymere poedercoating-verf, lagen van lood-selenide quantum dots (PbSe QD) en silicium carbide (SiC) deeltjes. Twee van deze materialen, de poedercoating verf en de QD-film, zijn warmtegevoelig waardoor het essentieel is deze experimenten bij kamertemperatuur uit te voeren.

Al₂O₃ films zijn gebruikt om de afwerking van een aangebrachte poedercoating-verflaag (verf zonder oplosmiddel) te variëren. De polymere kerndeeltjes zijn gecoat met alumina lagen van verschillende diktes. De alumina lagen bedekten het kernmateriaal gedeeltelijk wanneer deze boven hun glas transitie temperatuur zachter werden. Doordat de zachtere kern niet vloeide tijdens het harden van de verf, werd een ruw oppervlak gecreëerd met als resultaat een matte afwerking. De mechanische eigenschappen van de matte poedercoating verf waren vergelijkbaar met de originele glanzende verf. Dunne alumina lagen zijn gebruikt om de uiteindelijke afwerking van de poedercoating verf te variëren zonder het gebruik van externe materialen die hetzelfde effect creëren.

Hierna zijn films van PbSe QD-kristallen gepassiveerd met behulp van alumina. PbSe QD kristallen zijn nanokristallen met zeer interessante eigenschappen voor toepassingen binnen de halfgeleiders en fotovoltaïsche materialen. Deze laatste zijn echter luchten warmtegevoelig en oxideren irreversibel na een korte blootstelling aan lucht, waarbij de goede eigenschappen verloren gaan. Eerder werk heeft de passivering van quantum dots met alumina laten zien bij temperaturen tussen de 25 en 90 °C en drukken lager dan 1 mbar. In deze thesis is alumina aangebracht bij 25 °C en 1 bar om quantum dots efficiënt te passiveren. Bij deze standaardomstandigheden vond een snelle depositie plaats van alumina als gevolg van functionele groepen op de quantum dots, zoals hydroxyl en amine groepen, die kunnen aanbrengen reageren met TMA. Het van een coating met alumina bii standaardomstandigheden kan gemakkelijk gekoppeld worden aan het productieproces van quantum dot films, diat ook uitgevoerd worden bij kamertemperatuur en atmosferische druk.

De laatste toepassing die we hebben bestudeerd, is de productie van radioactieve marker deeltjes. Voor gefluïdiseerd-bed-studies wilden we SiC deeltjes labelen met een minieme verandering aan hun fysische eigenschappen. SiC deeltjes hebben een vrijwel inert oppervlak voor radioactieve ionen. We gebruikten de Al₂O₃ coating om de labeling-efficiëntie van dit materiaal te vergroten en markers te produceren. Echter, dit zou leiden tot een discrepantie in

de eigenschappen wat betreft de grootte, vorm en dichtheid tussen de marker en het bestudeerde materiaal. In deze studie zijn alumina films aangebracht op SiC deeltjes om de affiniteit van γ -Al₂O₃ deeltjes voor radioactieve ionen te imiteren en markers te produceren gebaseerd op SiC. Aangezien de labeling-efficiëntie afhangt van de dikte van de alumina film, zijn water en TMA in overmaat toegevoegd zodat een groei van ongeveer 10 nm per cyclus plaatsvindt. De gevormde deeltjes, met een alumina schil van ongeveer 400 nm, blijken slechts een iets lagere relatieve activiteit te hebben dan de γ -Al₂O₃ deeltjes. Deze SiC marker is gebruikt in een deeltjes-tracking- experiment, aangezien deze marker genoeg activiteit bezit om gedetecteerd te worden door de sensoren en een traject te reconstrueren tijdens het fluïdiseren.

Men kan betwisten of het bestudeerde depositie-proces bij atmosferische druk en kamertemperatuur nog steeds ALD is, aangezien de reacties niet zelf-terminerend zijn en we iedere cyclus verschillende lagen alumina aanbrengen. Desondanks biedt deze methode de mogelijkheid alumina aan te brengen op warmtegevoelige materialen, met een nauwkeurige controle over de filmdikte en technieken die het proces op grote schaal zullen versimpelen. De bevindingen van deze thesis kunnen uitgebreid worden tot andere toepassingen als coatings, bijvoorbeeld zinkoxide (ZnO), voor biomaterialen bij standaardomstandigheden. Dit wordt verder besproken in het laatste hoofdstuk van dit proefschrift.

Chapter 1

Introduction

1.1 Research Field

1.1.1 Particle Technology

Powders play an important role in the process industry, as it is estimated that 75% of the raw materials and 50% of the end products are found as particulate matter [1]. Thus, the production and handling, the characterization of the physical and chemical properties, and the development of applications of particles represent an important research field. The particle size is one of the properties that define the behaviour of powders, and therefore, their application. Particles in the millimetre range are typically found in food and pharmaceutical products, detergents and building materials. Finer particles - in the micron and submicron range - are used for catalysis, aerosols or electronics [2].

In the past two decades, nanoparticles (NPs) received increasing attention because of the special properties associated to their size ($d_p < 100$ nm), such as the large values of the specific surface area, and the quantum confinement effects [3]. Therefore, NPs are widely researched for the production of drugs, solar cells and catalysts amongst other fields [4-6]. In several of those applications, the performance of nanoparticles can be enhanced by depositing a compound that brings additional functionalities, such as protection or activation. For example, a thin film of about 2 nm of aluminium oxide (Al₂O₃) was deposited on the cathode material of Li-ion batteries (LiMnO₂ nanoparticles) to prevent its dissolution in the electrolyte, and thus, reduce the aging of the battery [7-9]. Another example is the activation of a photocatalyst, i.e., TiO₂ P25 nanoparticles, by depositing a small amount of platinum clusters on its surface. The resulting material was five times more active than the bare uncoated TiO₂ nanoparticles [10, 11]. These two examples show that even small modifications on the surface can have a significant influence on the performance of a material.

In this thesis, we explore the field of particle coating and how we can, by depositing small amounts of material, tailor the properties and add new functionalities to different type of particles. We now introduce and briefly review relevant theory about this topic.

1.1.2 Coating techniques for particles

A wide range of techniques are used to coat particles, depending on the size of the solids and the desired thickness and nature of the film (Fig. 1 left). Liquid-based techniques, such as spray drying or fluid bed coating, are used in food and pharmaceutical industry to deposit films from micrometre to millimetre scale. For example, the fluid bed coating technique was used to spray a solution composed of a mixture of polymers to encapsulate micro-crystalline cellulose ($d_p \sim 1200 \ \mu m$) [12]. This process was performed at 70 °C, avoiding the degradation of the core and shell materials. However, it requires a drying stage to evaporate the solvent. This involves longer process times, the generation of larger amounts of waste, and a higher energy consumption. Thinner coatings can be deposited with chemical vapour deposition (CVD). This is a gas-phase technique based on the reaction of two precursors, that are fed to the reactor simultaneously, on the substrate. The CVD process combines a relatively rapid growth of layers with a precise control of the film thickness, down to hundreds of nanometres [13]. As an example, 75 μm tungsten particles where coated, in a fluidized bed, with a film of SiO₂, with a thickness of few hundreds of nanometres. The coating process was carried out at

650 °C, with a deposition rate of 1 - 16 nm/min. Around 1970's, atomic layer deposition (ALD), formerly known as atomic layer epitaxy or molecular layering [14, 15], was developed based on the CVD process. ALD comprises the reaction of two gas precursors that are fed in a consecutive manner to the reactor, as opposed to CVD. In this way, the two reactions, one per precursor, only take place on the surface of the substrates. These two reactions form one ALD cycle to deposit less than a full monolayer of compound, due to the concentration of active sites on the surface, and the steric hindrance between precursor molecules [16, 17]. This cycle is repeated a desired number of times to deposit thicker films (Fig. 1 right). In this manner, ALD provides atomic control over the thickness of the films, that can be as thin as few nanometres [16].

1.1.3 Atomic Layer Deposition

The high precision and controllability of the film growth of ALD is based on the selfterminating nature of the chemical reactions. That means that the precursors molecules only react as long as there are unreacted active sites or functional groups available on the surface. Once all the surface species have reacted, the so-called saturation regime, no more reaction will take place independently of how much precursor is dosed in excess. To ensure the selftermination of the reactions, the operating temperature and pressure, and the purging step with nitrogen, contribute to remove the unreacted molecules and prevent their absorption to the substrate surface.



Fig. 1. (left) Map of several coating techniques for particles, based on the particle size and the film thickness. (**right**) Reaction mechanism of ALD, based on two cyclic reactions.

The growth per cycle (GPC), which refers to the increase in the film thickness in each cycle, is used to characterize the coating process. Besides the concentration of active sites and the size of the precursor molecules, other parameters influence the GPC of a film, such as the operating temperature and pressure, the flow of purging gas, and dosage of the precursors. The removal of unreacted molecules is severely diminished at temperatures and pressures at which the precursor cannot evaporate, such as room temperature and atmospheric pressure. At these conditions, the unreacted molecules would accumulate on the surface of the substrate, taking part in the upcoming coating reactions. After each reaction, nitrogen is flowed through the reactor for purging, which is favoured at high temperatures and low pressures. At 25 °C and 1 bar, it is possible that nitrogen is not sufficient to remove the unreacted molecules, which would unavoidably accumulate on the surface [18, 19]. Consequently, the flow of precursors would define the GPC, as the excess molecules after the surface has been saturated

with precursor would accumulate. That results in the deposition of several layers of compound in each cycle [20]. This process coating does not fit as ALD, since the reactions are not self-limiting, nor as CVD, since the precursors are fed in separate steps. The term *parasitic CVD-growth* is used to define this deposition [21, 22]. We refer to it simply as gas-phase coating technique. In the bright side, working at ambient conditions allow the coating of heat sensitive materials, and the hindered removal of unreacted precursor could be used to deposit thicker films faster.

The versatility of ALD was shown by Miikkulainen *et al.* [23] as a periodic table with all the compounds that had been deposited until 2013 (Fig. 2), including pure elements, oxides, nitrides, etcetera. To carry out an ALD process, we just need two precursors that can be easily taken into the gas phase, and which combined reaction results in the desired coating material. Usually, the first precursor is the source of metal, often an organometallic compound, while the second one would determine whether the deposited compound is a pure element, an oxide or a nitride, by using as co-reactant water, oxygen or ammonia, respectively [23]. The deposition of aluminium oxide using trimethylaluminium (TMA) and water is the most studied ALD system, since (i) the deposition of alumina shows the typical layer-by-layer growth mechanism of ALD, (ii) it can be carried out at a wide range of temperatures and pressures given the high reactivity of TMA molecules, and (iii) it has been applied to a wide range of applications [7, 24-29].



Fig. 2. Periodic table of ALD, adapted from Miikkulainen et al. [23]

ALD was initially developed and applied on flat substrates for semiconductor applications [30]. Later, it expanded to substrates with irregular geometries [18, 31] and particles [32, 33]. Amongst the several reactor configurations available for ALD of particles [34], a fluidized bed reactor (FBR) was used in the work described in this thesis [35].

1.1.4 Fluidization of Particles

Fluidizing particles are characterized by a good gas-solid mixing that translates in efficient mass and heat transfer [36]. Additionally, fluidized bed reactors can process large amounts of particles, and are, in general, well scalable. Fluidized beds are widely used in industry for gasification and combustion of biomass, and chemical looping combustion [36-38]. However, the fluidization behaviour of powders depends on the size and density of the particles, as described in the Geldart diagram (Fig. 3 left) [39]. The suspended state of the fluidizing particles is achieved when the drag force exerted by the fluidizing gas equals the forces that oppose the fluidization of the particles, i.e., gravity and interparticle forces (Fig. 3 right). There are usually four contributions to the interparticle forces: van der Waals, capillary, electrostatic forces and hydrogen bonding [40, 41], from which the capillary force can be neglected if no liquid is present.



Fig. 3. (left) Geldart diagram of the fluidization properties of particles based on the particle size and the difference between the particle and fluidizing gas densities. (**right**) Values of the interparticle forces with the particle size.

In the fluidization of fine cohesive powder, with a particle diameter $< 50 \mu$ m, the interparticle forces predominate over the gravitational and drag forces, causing the agglomeration of the particles (Fig. 3 right). The formation of the agglomerates results in a poor fluidization behaviour, characterized by channels, dead zones and plugs that reduce the mixing, and disturb the circulation patterns of the particles [42]. Nevertheless, uniform fluidization of fine particles can be attained by using fluidization assistance methods. This consists of an external supply of energy that contributes to the breakage of the agglomerates, and improves the quality of the fluidization. Some of these assistance methods are mechanical vibration, both in vertical and horizontal directions, stirring, microjets and ultrasounds amongst others [43-48].

The agglomeration of cohesive particles could be seen as detrimental for the coating process, since the inner particles of the agglomerates would not be exposed to the precursor molecules. However, nanoparticle agglomerates are open structures with a size of about 300 μ m and a void fraction of about 99% [49]. Additionally, the fluidization of nanoparticle agglomerates is dynamic, meaning that the agglomerates break and recombine continuously as result of the agglomerate-agglomerate and agglomerate-wall collisions [35]. Thus, the high porosity and dynamic behaviour of these agglomerates ensure that the surface of the primary particles is exposed to the coating precursors [50]. The good processing properties of fluidized bed reactors, and the versatility and precise control over the film thickness of ALD reactions, convert this technology in an interesting field, not only for research purposes, but also for industrial production.

1.2 Objectives of this Study

This PhD project was defined as a product-driven and process-development project, in collaboration with DSM Coating Resins (Zwolle, The Netherlands). The objective of this project is to develop the deposition of alumina at atmospheric pressure and room temperature on particles, in a ALD-like process, and demonstrate its application to improve the performance of several materials.

Alumina ALD films have been applied as passivating material, and in the production of membranes and catalysts amongst others [26, 27, 51], in both flat substrates and particles. Al₂O₃ has been deposited, using ALD, at different operating conditions, such as 170 °C and < 1mbar, at 170 °C and 1 bar, and at 33 °C and < 1 mbar [7, 18, 52]. However, it was never investigated the deposition of alumina at atmospheric pressure and room temperature. In the case of particles, the vast majority of the work was reported at 170 °C and < 1mbar. At these conditions, (i) it will not be possible to coat heat sensitive materials, such as polymers and biological compounds, and (ii), operating at low pressures would require certain equipment and an exquisite process control at both lab and industrial scales. This was the reason to investigate the deposition of alumina at ambient conditions.

The main challenge that we face at ambient conditions is the physisorption of unreacted precursors molecules on the surface of the particles. As a consequence of the accumulation, several layers of alumina would be deposited in each cycle, in a parasitic CVD-type of process. Given that molecules accumulate at ambient conditions, we think that the dosage of precursors will be crucial. Then, we could play with the dosing time of reactants to only saturate the surface by feeding the same amount of precursor as the number of active sites, or to overexpose the substrate to the precursors, and deposit several layers per cycle. This can be used to deposit thicker films faster. Below, we list several sub-objectives in the form of questions that were addressed during the completion of this research.

- (i) Are the coating reactions self-terminating at room temperature and atmospheric pressure, as in ALD processes?
- (ii) Can we deposit ultrathin alumina films at ambient conditions? Are these alumina films uniform and conformal? How good is the control over the film thickness at ambient conditions?
- (iii) What are the properties of the alumina films? Are there pores or unreacted molecules entrapped in the alumina films?
- (iv) Could we benefit from accumulation of molecules to purposely deposit thicker alumina films faster?
- (v) Can we deposit Al_2O_3 films on heat sensitive materials without degrading them?

As discussed earlier, the agglomeration of fine particles represents a challenge for the coating process [42]. Thus, we could investigate how to interfere on the agglomerate formation in two different manners. First, by influencing directly the interparticle attractive forces and prevent the agglomeration [41, 53, 54]. And second, by supplying external energy in the form of fluidization assistance methods to induce the breakage of the agglomerates [43]. In this

respect, there are still missing studies on the contribution of different interparticle forces to the agglomeration, such as the electrostatic force and hydrogen bonding, and a comparison of different assistance methods regarding energy consumption, influence on the fluidization quality, etcetera. These studies would be very useful, but that obtained less emphasis in this thesis. Nevertheless, we discuss some of these issues in the outlook of this thesis (chapter VI).

1.3 Outline

This thesis comprises four papers published in or submitted to peer-reviewed journals, and a final chapter with the outlook of this work. A brief summary of the chapters is given below.

In chapter II, we studied the deposition of alumina films at atmospheric pressure and room temperature on fluidizing TiO_2 nanoparticles [20]. For that, we first fed enough precursor to saturate the particles, and then we fed large excess of precursors, to compare the film thickness and the GPC. We show that it is possible to deposit ultrathin films alumina at ambient conditions, while maintaining accurate control over the film thickness.

In chapters III, IV and V we deposited alumina films on materials for three different applications: to modify the surface appearance of a paint, to stabilize quantum dot (QD) films for production of solar cells, and to enhance the labelling efficiency of a SiC-based (silicon carbide) tracer. We now explain the main issues that are addressed in each of these chapters.

In chapter III, we deposited thin layers of aluminium oxide to alter notably the finish properties of an industrial powder coating paint, and characterized the alumina-coated particles and the powder coated panels, which is the final product. In agreement with literature, we observed that alumina only formed complete films after several cycles [55, 56]. The partial confinement of the polymeric core particles by the alumina films above the glass transition temperature reflected on the appearance of the final paint. We found that an equivalent alumina film of 6 nm was able to tune the surface finish of the painted panel from gloss to matte. This study aimed at depositing alumina films on a heat-sensitive industrial material that would give a tailored property, such as converting a gloss paint into a matte one, by using exactly the same material with a slight modification on the surface of the primary solids.

In chapter IV, we deposited aluminium oxide on PbSe QD films, which are heat and air sensitive. QD crystals oxidize and degrade irreversibly after short exposure to air. ALD of alumina, performed at a range of temperatures of 27-100 °C and < 1 mbar, was used to effectively passivated the QD films and prevent their degradation [57, 58]. The main research question in this chapter was whether we could benefit from the physisorption of precursors at ambient conditions to obtain full passivation of the QD films after a low number of cycles. The results showed a fast deposition of alumina from the first cycle as the combination of several mechanism, i.e., presence of solvent molecules, reactivity of TMA with both amine and hydroxyl groups, and the excess of precursors fed to the reactor. The alumina infilled and overcoated the QD films, giving full passivation after a relatively low number of cycles. This process could be combined with the fabrication process of the QD films by dip-coating, which also is done at ambient conditions.

In chapter V, we deposited alumina films on silicon carbide (SiC) particles to increase its affinity towards ¹⁸F radioactive ions, aiming at enhancing the labelling efficiency. SiC

particles are fluidized to harvest solar energy in concentrated solar plants [59, 60]. Hydrodynamics studies of these systems are needed to assess the efficiency of this technology, evaluated with the circulation frequency of the particles near the wall of the column, where they get heated. Positron emission particle tracking (PEPT) is a tool to track a radioactive tracer particle in a multiphase system, such as a fluidized bed, and reconstruct its trajectory. Thus, the tracer must resemble the material of study. As the surface of the SiC particles is inert, it has low affinity with the ¹⁸F ions and cannot be used as tracer. Therefore, we deposited alumina films on SiC particles to improve the affinity and the labelling efficiency. In this chapter we propose a general method to produce tracers for particle tracking applications from originally inert particles by depositing films of aluminium oxide, which shows a good affinity towards the radioactive ions of ¹⁸F.

This thesis was aimed as proof of principle on how thin films of alumina, deposited at ambient conditions, improved the performance or properties of different materials. Thus, this work could be further optimized, regarding the dosing of the precursors, number of cycles and purging time, for instance. Additionally, there are studies that could be done to investigate the fluidization of cohesive particles, or to expand the deposition at ambient conditions to other compounds and substrates. These issues and other remaining open questions from this work are discussed in the outlook of this thesis (chapter VI).

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Chapter 2

Gas-phase deposition of ultrathin Al₂O₃ films on nanoparticles at ambient conditions

We have deposited aluminium oxide films by atomic layer deposition on titanium oxide nanoparticles in a fluidized bed reactor at 27 ± 3 °C and atmospheric pressure. Working at room temperature allows the coating of heat-sensitive materials, while working at atmospheric pressure would simplify the scale-up of this process. We performed 4, 7 and 15 cycles by dosing a predefined amount of precursors, *i.e.*, trimethylaluminium and water. We obtained a growth per cycle of 0.14–0.15 nm determined by transmission electron microscopy (TEM), similar to atomic layer deposition (ALD) experiments at a few millibars and ~180 °C. We also increased the amount of precursors dosed by a factor of 2, 4 and 6 compared to the base case, maintaining the same purging time. The growth per cycle (GPC) increased, although not linearly, with the dosing time. In addition, we performed an experiment at 170 °C and 1 bar using the dosing times increased by factor 6, and obtained a growth per cycle of 0.16 nm. These results were verified with elemental analysis, which showed a good agreement with the results from TEM pictures. Thermal gravimetric analysis (TGA) showed a negligible amount of unreacted molecules inside the alumina films. Overall, the dosage of the precursors is crucial to control precisely the growth of the alumina films at atmospheric pressure and room temperature. Dosing excess precursor induces a chemical vapour deposition type of growth due to the physisorption of molecules on the particles, but this can be avoided by working at high temperatures.

Published as: D. Valdesueiro, G.M.H. Meesters, M.T. Kreutzer and J.R. van Ommen. *Gas-Phase Deposition of Ultrathin Aluminium Oxide Films on Nanoparticles at Ambient Conditions*. Materials, 2015. 8(3): p. 1249-1263, doi:10.3390/ma8031249.

2.1 Introduction

The production of core-shell nanoparticles using atomic layer deposition (ALD) in a fluidized bed reactor (FBR) is an attractive technology because of the good mixing between gas and solids, and the possibility to process large amounts of solids up to industrial scale [1–4]. For instance, aluminium oxide (Al₂O₃) coating obtained by ALD on particles in a FBR was applied as a passivating barrier against oxidation, as a gas barrier on sensors, and in the production of catalysts, amongst other applications [5-10]. Nanoparticles are widely used in diverse fields such as catalysis, medicine, energy conversion and storage [11–14]. In addition to the large specific surface area, surface modification can introduce additional functionalities to improve these nanomaterials. Atomic layer deposition, which was developed for the semiconductor industry [15,16], appears as an enabling coating technique to either protect or activate the surface of substrates with a precise control over the amount of material deposited [11,17–21]. The ALD layer-by-layer growth mechanism relies on two alternating gas phase reactions with a purging step in between, using an inert gas to remove the unreacted molecules of precursor. These reactions can be repeated a certain number of times to deposit conformal and pin-hole free thin films with a precision down to atomic scale. In addition, the absence of solvent in ALD processes reduces the waste generated when considering industrial scale production [3]. These features establish the ALD in a FBR as a suitable technique to produce core-shell nanoparticles with tailored functionalities.

The deposition of Al₂O₃ is typically done at low pressure (~1 mbar or lower) and elevated temperatures (~180 °C) to enable the evaporation of the excess molecules of precursors, and in this manner ensure atomic growth of the films by an efficient removal of the excess precursors [22]. The physisorption of unreacted molecules at ambient conditions would result in undesired parasitic CVD-type (chemical vapour deposition) of reactions [23,24]. ALD of alumina has been studied at different reactor temperatures ranging from 33 °C to ~180 °C, and pressures, from 10^{-5} bar to 1 bar, over a diverse variety of powders. To our knowledge, alumina ALD at both low temperature and atmospheric pressure has not yet been investigated, neither on flat substrates nor on particles. The growth per cycle (GPC) is used to characterize the coating experiments [25,26]. ALD at pressures of a few millibars and ~180 °C provides alumina layers with a growth between 0.1 and 0.2 nm per cycle [27-32]. At atmospheric pressure and 160 °C Al₂O₃, ALD revealed the possibility of depositing few-nanometre films with slightly larger growth per cycle [33]. Alumina ALD performed at 10⁻⁵ bar and 33 °C gave a GPC of 0.3 nm [34,35]. With regards to flat substrates, more studies were reported either at room temperature and low pressure [36-38], or at atmospheric pressure and a temperature above 100 °C [39,40] showing an influence of these variables on the GPC, which is higher than at lower pressure and higher temperature. These conditions can be improved in two different ways. First, working at room temperature opens the possibility to apply ALD on heat-sensitive materials [41]. Secondly, using atmospheric pressure would facilitate the scaleup towards the industrial production by easing the handling of the powder and reducing the complexity of the equipment required. For these reasons, we study the deposition of alumina on nanoparticles at room temperature and atmospheric pressure.

This experimental paper describes the aluminium oxide ALD in a FBR at 1 bar and 27 ± 3 °C, using TiO₂ P25 nanoparticles as the support. The objective of the paper is to understand whether conformal alumina films can be deposited at ambient conditions, supressing the physisorption of the excess precursor molecules by a careful dosage of the precursors. For that, we performed three sets of experiments. In the first one, we examined whether we can achieve a growth per cycle that is similar to that reported in the literature at lower pressure and higher

temperature. In the second set, we determined if the precursor would physisorb on the surface of the particles if the dosing of precursor is extended, at constant concentration, thus increasing the excess of precursor relative to the amount of reactive sites inside the reactor. In the third set, we investigated the GPC of the alumina films at 1 bar and 170 °C when both precursors are fed in excess. In this work, we consider the dosed amount of the precursors as a crucial factor to avoid the CVD-type growth expected at ambient conditions, particularly in the case of water [39,42,43]. These molecules would react in the subsequent reaction, resulting in thicker and non-uniform alumina films. We try to avoid the accumulation of unreacted molecules with an accurate delivery of the precursors. That would allow the deposition of ultrathin films at room conditions, while maintaining the control over the properties of the films.

2.2 Experimental Section

2.2.1 Experimental Setup

Experiments are carried out in a fluidized bed reactor similar to the one described by Beetstra et al. [33], which is composed by a vertical glass column of 26 mm internal diameter and 500 mm height, placed on a single motor Paja PTL 40/40-24 vertical vibration table to assist the fluidization [2]. The vibration table is operated at 35 Hz, and provides a vibration amplitude of 2 mm to the column. An infrared lamp placed parallel to the column, and a type-K thermocouple inserted in the column, are used to control the bed temperature. The gas is introduced to the column through a stainless steel SIKA-R 20 AX distributor plate of sintered particles with a pore size of 37 µm, to achieve a homogenous flow of gas through the full cross-section of the column. An identical distributor plate is placed on top of the column to prevent nanoparticles from leaving the column. Although the pore size of the distributor plates is several orders of magnitude larger than the particle size, the risk of losing particles is small since they do not fluidize as individual particles, but as agglomerates of 200-300 µm [2]. These agglomerates, which have a void fraction of 98%-99% [44], demonstrate a dynamic behavior during fluidization [45]. This means that the agglomerates break and recombine constantly as a consequence of the collisions between solids. The dynamic behavior and large porosity of the agglomerates ensure that the precursor molecules reach the whole surface area of the individual particles, even though they exist as agglomerates.

Aeroxide P25 titanium oxide (TiO₂) particles from Evonik Industries (Hanau, Germany) are used as the substrate for the coating experiments. This powder has a Sauter mean diameter $(d_{3,2})$ of 32.7 nm (Supplementary Information 2.A), a specific surface area of 52.4 m²/g, and a surface concentration of hydroxyl groups of 5.0 OH/nm² [46]. Semiconductor grade TMA (trimethylaluminium) was provided by Akzo Nobel HPMO (Amersfoort, The Netherlands) in a 600 mL WW-600 stainless steel bubbler, which is kept at 30 °C during the coating experiments. The second precursor, demineralized water, is kept in a similar bubbler. Pressurized nitrogen grade 5.0 is provided to the column as the carrier gas; no pump is present after the column. The column is always kept at atmospheric pressure. During start-up of an experiment, we first used nitrogen to drive away the air before starting the coating. The off-gas of the fluidized bed was led through a rack of five washing bubblers filled with Kaydol oil to remove possible traces of unreacted precursors and the products of the reactions. The precursor bubblers, the fluidized bed reactor and the washing bubblers are placed inside a nitrogen-blanketing cabinet as a TMA safety measure. The cabinet is operated at an O_2 concentration below 6%. For each experiment, 2.00 g of TiO₂ powder were placed inside the column. A flow of 0.4 L/min of nitrogen, which corresponds to a superficial gas velocity of 1.26 cm/s, was applied to fluidize the powder.

2.2.2 Design of the Experiments

To calculate the precursor dosing times, we estimated the total amount of active sites in the bed of particles, *i.e.*, hydroxyl groups. This amount is calculated with the surface area of the TiO₂ (52.4 m^2/g), the mass of powder placed inside the column (2.00 g), and the surface concentration of hydroxyl groups (5.0 OH/nm²) [46]. For 2.00 g of powder, we have an initial amount of 8.7×10^{-4} mol of OH. To calculate the amount of TMA dosed to the reactor, we assumed that at 30 °C, which is the TMA bubbler temperature, TMA forms dimers [47-50]. We estimated that the saturation of the nitrogen bubbles with TMA inside the bubbler, using the model proposed by Mayer et al. [51], is about 50% when the bubbler is filled with TMA up to the secure level. In addition, we assumed that the entire particle surface area is exposed to TMA in the gas phase (*i.e.*, no "dead zones") because fluidized bed reactors provide intense contact [52,53]. between precursors and solids Based on these assumptions, and using the vapour pressure of TMA and the ideal gas law, we obtained a flow of TMA to the reactor of 4.8×10^{-4} mol/min, which translates into an ideal dosing time of 1.7 min for TMA. To account for the assumptions used in the theoretical estimation, and ensure that the surface of the powder inside the column is fully saturated, we doubled the resulting dosage time for TMA and water. As a result, a significant fraction of the TMA leaves the reactor without reacting. This inefficient use of TMA is an acceptable penalty for the objective of this paper, *i.e.*, to find out how much excess of precursor can be tolerated close to physisorbing conditions.

From the calculation above, we obtained a final dosing time of 3.5 min for TMA, and 2.5 min for water. After dosing each precursor to the reactor, we purge the system with N₂ for 10 min (which corresponds to 13 residence times), establishing a feeding sequence of TMA–N₂– H₂O–N₂. With these dosing times (3.5–10–2.5–10 min), which we will consider as the base case situation, we performed 4, 7, and 15 cycles. In the second set of experiments, we studied the deposition of alumina when increasing the dosing times of precursors and keeping the same purging time of nitrogen. For this study, we perform 7 cycles at three different dosing times: 2 times (7–10–5–10 min), 4 times (14–10–10–10 min), and 6 times (21–10–15–10 min) larger than in the base case study. In addition, we performed 5 cycles at 1 bar and 170 °C with dosing times of 21–10–15–10 min, to investigate whether we can avoid the physisorption of the molecules in excess and gain the self-limitation of the ALD reactions, by increasing the reactor temperature.

2.2.3 Characterization of the Coating

To characterize the deposition process, we determined the thickness of the alumina film by both TEM and elemental analysis, and divided it by the number of cycles to calculate the growth per cycle. For these measurements, we used TEM (transmission electron microscopy) with EDX (energy dispersive X-ray spectroscopy), done with a Tecnai TF20 (FEI, Hillsboro, OR, USA), which provides direct observation of the thickness of the coating δ_{TEM} . Elemental

analysis was carried out using ICP-OES (Induced Couple Plasma Optical Emission Spectroscopy, performed with a PerkinElmer Optima 5300, PerkinElmer, Waltham, MA, USA), which provides the mass fraction of aluminium in the coated sample x_{Al} . To determine x_{Al} in the samples, we first destructed an amount of 50 mg of the coated powder in a solution prepared with 1.5 mL 65% HNO₃ + 4.5 mL 30% HCl + 1 mL 40% HF using the microwave. After destruction, the samples were diluted to 50 mL with MQ (milli-Q) water. The samples were then analyzed with ICP-OES to determine the mass fraction of aluminium in the samples. With this value, we calculated, using Equation (2.1), the corresponding volume of aluminium oxide in each particle $V_{Al_2O_3}^{1P}$, assuming spherical TiO₂ particles with a diameter $d_{3,2}$ and density ρ_{TiO_2} , using the molecular mass of alumina $M_{Al_2O_3}$ and aluminium M_{Al} , a factor of $\frac{1}{2}$ because there are 2 moles of Al in one mole of Al₂O₃, and a density of the film of aluminium oxide $\rho_{Al_2O_3}$ of 2500 kg/m³, equal to the value reported by Groner *et al.* [36] for Al₂O₃ ALD at room temperature. We presume that the density of alumina deposited by ALD on particles would be smaller than the one deposited on flat substrates, due to the discontinuities between the facets of the particles.

$$V_{\rm Al_2O_3}^{\rm 1P} = \frac{x_{\rm Al}}{1 - \frac{M_{\rm Al_2O_3}}{2 \cdot M_{\rm Al}} \cdot x_{\rm Al}} \cdot \frac{M_{\rm Al_2O_3}}{2 \cdot M_{\rm Al}} \cdot \frac{\rho_{\rm TiO_2}}{\rho_{\rm Al_2O_3}} \cdot \frac{\pi}{6} \cdot d_{3,2}^3$$
(2.1)

Then, we used Equation (2) to calculate the thickness of the film δ_{ICP} based on the volume of alumina per particle determined with Equation (1). Assuming spherical particles, we calculated the thickness of the alumina film as the difference of the volume between the coreshell particle, and the uncoated TiO₂ P25 particle. Using Equations (1) and (2), we account for the curvature of the particles to estimate the thickness of the alumina film δ_{ICP} :

$$\delta_{\rm ICP} = \frac{\sqrt[3]{\frac{6}{\pi} \cdot V_{\rm Al_2O_3}^{1P} + d_{3,2}^3} - d_{3,2}}{2}$$
(2.2)

In the calculation of the film thickness, we used average values for particle size, mass fraction of aluminium and density of the aluminium oxide; however, that implies an inaccuracy due to the experimental error. To account for that, we performed the propagation of the uncertainty (Supplementary Information 2.B), using a Sauter mean diameter $d_{3,2}$ of 32.7 ± 3.3 nm (Supplementary Information 2.A). The errors correspond to 10% of the measurement of the diameter $\Delta d_{3,2}$, 3% of the mass fraction value from ICP-OES Δx_{Al} , and 200 kg/m³ for the density of alumina $\Delta \rho_{Al2O3}$, to obtain the interval of confidence for the film thickness δ_{ICP} .

2.3 **Results and Discussion**

This section is divided in four parts: (i) experiments performed with the base case dosing times of the precursors; (ii) experiments done to study the self-limitation of the reactions when feeding excess of precursors at 1 bar and 27 °C; and (iii) at 1 bar and 170 °C, and (iv) a study of density of the alumina films using BET (Brunauer-Emmett-Teller) N₂-adsorption and thermal gravimetric analysis (TGA) (Mettler Toledo TGA/SDTA 851 e, Greifensee, Switzerland).
2.3.1 Base Case Coating Experiments

We performed 4, 7, and 15 ALD cycles with a dosage sequence of 3.5-10-2.5-10 min, of TMA, nitrogen, water, and nitrogen, respectively, using a flow of 0.4 L/min of N₂. We measured the film thickness of a significant number of points and particles (Supplementary Information 2.C and 2.D) for a proper analysis of the coated samples. Measuring the film thickness after 4 cycles is complex since each cycle deposits about 30% of a monolayer as consequence of the steric hindrance between the alkyl ligands, and the density of active sites on the surface of the particles [54]. Such thin films of around 0.6 nm could be deceiving if the particles are not properly focused in the TEM images. In addition, we calculated the growth per cycle after dividing the thickness by the number of ALD cycles, plotted the histograms, and calculated the mean value and the standard deviation of all the measurements. With this characterization we evaluated the thickness of the film, the deposition rate, and conformality of the alumina films.



Figure 2.1. TEM images of the alumina film on TiO_2 nanoparticles for a dosing sequence of 3.5–10–2.5–10 min after (a) 4 ALD cycles; (b) 7 ALD cycles; and (c) 15 ALD cycles. (d) Distribution of the growth per cycle from the TEM pictures after 4 ALD cycles; (e) after 7 ALD cycles; and (f) after 15 ALD cycles. The mean growth per cycle and the standard deviation values are given in each histogram.

Figure 2.1a–c shows TEM pictures, and the distribution of the growth per cycle (Figure 2.1d–f) for the 4, 7, and 15 ALD-cycle experiments, respectively. The values of the growth per cycle are similar to the results reported for ALD experiments at a few millibars and ~180 °C, *i.e.*, 0.1–0.2 nm. Although the histograms show some spread, from the TEM images we can see that the alumina coating on each particle is rather uniform and conformal. Figure 2.2a suggests a linear correlation between the number of cycles and the film thickness from TEM with a GPC of about 0.14–0.15 nm (Figure 2.2a), although it would require more data points to draw solid conclusions about linearity.

To support the results from the TEM images, we performed ICP-OES (Supplementary Information 2.E) on the samples to calculate the thickness of the alumina films with Equations (2.1) and (2.2), using a density of alumina of 2500 kg/m³ (Figure 2.2b). First, we observe that x_{Al} for the samples coated with 4 and 7 cycles (Supplementary Information 2.E) are similar, while there is a clear difference in the film thickness observed from TEM pictures (Figure 2.1). We have not found a plausible explanation for the comparable values from ICP (Figure 2.2b). Besides these values for the 7-cycle experiment, which seem lower than expected, the other two values are in good agreement with those from the TEM (Supplementary Information 2.E). The error bars in Figure 2.2b represent the error in the measurements obtained from the propagation of the uncertainty (Supplementary Information 2.B).



Figure 2.2. (a) Thickness of the alumina film, determined from TEM images, for the different number of cycles for a dosing sequence of 3.5-10-2.5-10 min. The error bars represent the 10% error assumed in the image analysis; (b) Comparison of the film thickness from TEM images and ICP-OES measurements for a density of alumina of 2500 kg/m³. The horizontal error bars represent the 10% error in the image analysis, while the vertical error bars show the error made in the calculation of the thickness, which accounts for the size of TiO₂ particle, the experimental error of the ICP-OES device (3%) and the density of the alumina. The red line represents ideal agreement between the results.

In this study, we used relatively long pulsing and purging times to provide precursor molecules to the total surface area of powder, and to make sure that all non-absorbed reactants were removed. Nevertheless, if one is not carrying out a research study, but rather an industrial process, the initial load of powder inside the reactor may be increased and purging times reduced to find a proper compromise between production rate, reactant removal and operating costs.

2.3.2 Coating with Excess of Precursors at Ambient Conditions

After obtaining a reasonable value for the GPC in line with ALD literature, 0.14–0.15 nm, we studied what occurs when we feed an excess of precursor by increasing the dosage by a factor of 2, 4, and 6, compared to the base case dosing times (Figure 2.1b,e), and performed 7 cycles.

Figure 2.3 shows the TEM pictures of the coating experiments with a dosage of TMA of 7 min (Figure 2.3a), 14 min (Figure 2.3b), and 21 min (Figure 2.3c) per cycle. The pulsing time

of water was also increased accordingly for each of the experiments. Figure 2.3d–f gives the distribution of the growth per cycle for each of the experiments. The mean value and standard deviation, calculated from over 125 measurements (Supplementary Information 2.D), is shown in each histogram (Figure 2.3d–f). Although the films look uniform in the TEM pictures we assessed (Figure 2.3a–c), we observed a noticeable spread in the histograms compared to Figure 2.1. Nevertheless, if we calculate the normalized standard deviation (*i.e.*, standard deviation divided by the mean) for the growth per cycle, we observe similar relative spread of the data. The larger deposition rates obtained from Figure 2.3 compared to the base case study indicate the presence of a CVD type of growth, especially in the sample where TMA was fed for 21 min (Figure 2.3c,f). This suggests that part of the excess molecules adsorbs to the surface of the particles, and reacts during the subsequent reaction, which is a consequence of operating below the boiling temperature of TMA (~128 °C) and water. Figure 2.4a shows the increase of the growth per cycle with the dosing time of TMA.



Figure 2.3. TEM image of the alumina film on TiO_2 nanoparticles after 7 cycles when the dosing time of TMA per cycle is (a) 7 min; (b) 14 min; and (c) 21 min. The distribution of the GPC obtained from TEM images for a dosing time of TMA of (d) 7 min; (e) 14 min; and (f) 21 min. The mean and standard deviation values are shown in each histogram. The results in this figure can be compared with the ones of 7 cycles, with a dosing time of 3.5 min for TMA (Figure 2.1b,e), considered as the base case study.

We also calculated the thickness of the alumina films and the growth per cycle using the mass fraction of aluminium x_{Al} from the ICP measurements. We observed a discrepancy between the measurements for the longest dosing time; this might be explained by the fact that CVD at these conditions leads to a different alumina density than the assumed 2500 kg/m³.

Although there seems to be a notable CVD-component present at these long pulse times—so we can no longer call the coating truly ALD—it is still possible to get conformal films of a reasonably controlled thickness. Nevertheless, the CVD component that occurs at ambient conditions can be avoided by increasing the reactor temperature.



Figure 2.4. (a) GPC of the alumina film after 7 cycles with different dosing times of TMA per cycle (3.5, 7, 14, and 21 min). The red open circle represents an experiment carried out at 170 °C with a dosing time of TMA of 21 min. The error bars represent the error made in the image analysis of the TEM pictures, which is estimated to be around 10%. (b) Comparison of the GPC from TEM measurements and calculation from ICP-OES measurements for a density of alumina of 2500 kg/m³. The red open circle represents an experiment carried out at 170 °C with a dosing time of TMA of 21 min, for a density of the alumina of 3000 kg/m³. The red open circle represents an experiment carried out at 170 °C with a dosing time of TMA of 21 min, for a density of the alumina of 3000 kg/m³. The horizontal error bars represent the 10% error in the image analysis, while the vertical error bars show the error made in the calculation of the thickness, which accounts for the size of TiO₂ particle, the experimental error of the ICP-OES device (3%), and the density of the alumina. The red line represents the ideal agreement between the results.

2.3.3 Coating with Excess of Precursors at 1 bar and 170 °C

To evaluate the influence of the reactor temperature on the physisorption of the precursor molecules in excess, we performed a coating experiment at higher temperature, *i.e.*, 170 °C. For that, we used the dosing times where we observed the strongest CVD component, *i.e.*, 21–10–15–10 min, and performed 5 cycles at 1 bar and 170 °C. We measured the thickness of the alumina films of about 20 particles using TEM (Figure 2.5a and Supplementary Information 2.D), and plotted a histogram of these values (Figure 2.5b). We measured a mass fraction of aluminum x_{Al} in the sample of 0.044 with ICP-OES, which translated into a film thickness of 0.66 nm and a GPC of 0.13 nm (Figure 2.4a, red-open circular symbol). To calculate these values we used an alumina density of 3000 kg/m³, typical for Al₂O₃ ALD at 177 °C [36]. The results of film thickness and GPC obtained from elemental analysis agree with the values from the TEM images (Figure 2.5), and in general, with the GPC reported for similar ALD experiments at <1 mbar and ~180 °C, *i.e.*, 0.1–0.2 nm. The decrease in the GPC from 0.51 nm at room temperature to 0.16 nm at 170 °C (Figure 2.4a) indicates that the ALD reactions at these conditions, *i.e.*, 1 bar and 170 °C, are self-limiting even when both precursors are fed in large excess.

This work, as a first attempt to describe the ALD coating at room conditions, opens up the possibility for further research, such as that on the purging time. Being able to deposit controlled thin films at these conditions widens the potential use of alumina ALD to other heat sensitive materials, facilitating the coating process of particles at larger scales.



Figure 2.5. (a) TEM image of the alumina film on TiO_2 nanoparticles after 5 ALD cycles for a dosing sequence of 21–10–15–10 min at 1 bar and 170 °C; (b) The distribution of the GPC obtained from TEM images for a dosing sequence of time of 21–10–15–10 min at 1 bar and 170 °C. The mean and standard deviation values are shown in the histogram.

2.3.4 Alumina Film Density

Measuring the density of thin films on nanoparticles is not trivial with flat-substrate techniques such as ellipsometry. The low value of the density can indicate the presence of micropores or unreacted molecules in the film, although the results from Figures 2b and 4b show a good agreement with the value of 2500 kg/m³ [36]. We performed N₂-adsorption measurements using BET, and TGA as further analysis of the alumina films. We measured the surface area of three samples: P25 TiO₂, the sample coated with 15 cycles and base case dosing times, and the sample coated with 7 cycles and a dosage of precursors six times larger than the base case study. The three samples showed similar adsorption and desorption isotherms (Supplementary Information 2.F), indicating that either there are no pores in the films, or that the pores have a small volume since there is no significant hysteresis in the isotherms. The surface area of the coated samples decreases compared to the uncoated nanoparticles (Supplementary Information 2.F), although this is explained by (i) the increase on the particle size due to the alumina coating, and (ii) by the decrease of the density of the core-shell particle, since the alumina film has a lower density than the P25 TiO₂. These two factors do not provide evidence of pore formation in the alumina coating. Moreover, no pores are visible in the TEM images (Figure 2.2, Figure 2.4 and Supplementary Information 2.C and 2.D), although that depends on the focus of the microscope. Both measurements suggest that the obtained films are not porous.

As an alternative explanation, the presence of unreacted water molecules or methyl groups inside the alumina coating could decrease the value of the film density. We performed TGA on the uncoated TiO₂ and the samples coated with 4, 7 and 15 cycles to measure the mass loss when heating the samples from room temperature to 600 °C in air atmosphere. In this range of temperatures, we would observe first the evaporation of water molecules—both physisorbed and entrapped in the coating—and at higher temperatures the combustion of methyl groups. We found a total weight loss of <3.5%, which was mostly produced below 200 °C (Supplementary Information 2.G). This is attributed to water evaporation, part of it physisorbed molecules assumed from the analysis of the uncoated TiO₂ sample, and part of it entrapped molecules within the coating. We compared the amount of water entrapped in the

coating, with the amount of water dosed to the reactor, obtaining that the percentage of entrapped water is <0.1% (Supplementary Information 2.G). This suggests that the accumulation of unreacted water is negligible. The combustion of the unreacted methyl groups, which occurs above 400 °C, would produce an exothermic peak in the heat flow during the TGA and an increase in the SDTA (differential thermal analysis), which relates to the temperature of the sample and the chamber (Supplementary Information 2.G). At temperatures between 400 and 600 °C the mass loss recorded is <0.5% and the temperature difference between the sample and chamber is <0.5 °C for all the cases. We calculated the number of methyl groups of which combustion relates to this increase of temperature, resulting in <0.001% of the total amount of methyl groups being fed to the reactor during the whole experiment. This shows that there is not a substantial amount of unreacted water molecules or methyl groups to alter the properties of the alumina films. The low density of alumina we found—in agreement with the reported value for ALD at room temperature [36]—seems to be caused neither by porosity nor by the presence of unreacted species.

2.4 Conclusions

We demonstrated that ultrathin films of aluminium oxide can be deposited on particles using ALD at 27 °C and 1 bar in a well-mixed reactor, a fluidized bed. For that, we established that controlling the amount of precursor dosed to the reactor is crucial. For a set of experiments of 4, 7 and 15 cycles, we obtained a GPC of 0.14 nm for the defined dosing times. This result is comparable to the GPC of the experiments at ~170 °C and <1 mbar. We also calculated the thickness of the alumina films based on the elemental composition of aluminium in the samples, achieving a good agreement with the measured values from the TEM pictures. We increased the amount of the precursors by a factor of 2, 4 and 6 at constant flow, feed concentration and purging time, and performed 7 cycles. We observed that the thickness of the alumina films increased with the dosage of the precursors. A tentative explanation is that the unreacted molecules, which were fed in excess, accumulated on the surface of the particles, resulting in parasitic CVD reactions and higher GPC. In addition, we performed a coating experiment at 170 °C overdosing both precursors by a factor of 6 compared to the base case study, and obtained a GPC of 0.16 nm. This result agrees with the range of values of GPC reported for typical Al₂O₃ ALD reactions. We conclude that at room temperature and atmospheric pressure, this ALD process ceases to be self-limiting, but allows precise deposition of thin and uniform films by controlling the dosage of precursors. The obtained films are non-porous and do not contain noticeable amounts of unreacted species.

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2.A Particle Size Distribution of TiO₂ from TEM Images

We obtained the PSD (particle size distribution) of the TiO₂ P25 particles from the measurements of the diameter of 25 TEM pictures. We determined the distribution for each particle diameter, and plotted the PSD (Figures 2.A.1 and 2.A.2). From it, we calculated the Sauter mean diameter $(d_{3,2})$ using the equation below. The Sauter diameter accounts for the ration volume to surface area of the particles. The calculation of the alumina film thickness (section 2.B) is based on the surface area of the particle size in order to calculate the film thickness. We also calculated the number-averaged diameter $(d_{1,0})$ from the transmission electron microscopy (TEM) measurement, observing the difference with the $d_{3,2}$. We consider that we do an error of 10% on the measurements of particle diameter from the TEM images ($\Delta d_{3,2} = 3$ nm).

$$d_{3,2} = \frac{\sum n \cdot d_P^3}{\sum n \cdot d_P^2}$$
$$d_{1,0} = \frac{\sum d_P}{n}$$

Figure 2.A.1. PSD of the P25 TiO₂ from TEM images. We measure the diameter in the TEM pictures, and from them we calculated the $d_{3,2}$ and plotted the distributions. We obtained an average $d_{3,2} = 32.7$ nm.

Table 2.A.1. Determination	of the PSD	of TiO2 P25 fr	om TEM images
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Sample	N TEM Pictures	N Particles	N Points	<i>d</i> _{1,0} [nm]	<i>d</i> _{3,2} [nm]
TiO ₂ P25	25	>300	533	26.2	32.7

2.B Al₂O₃ Film Thickness Calculation

This calculation is based on the measurements of the mass fraction of aluminium (x_{Al}) on the coated samples, obtain from the ICP-OES. From this value, we calculate the volume of aluminium oxide per particle (V_{Al2O3}^{1P}) related to the mass fraction of aluminium. Finally, we calculate the thickness of the alumina film (δ_{ICP}) considering spherical particles. To account for the systematic error of the measurements of the particle size $(\Delta d_{3,2})$ and aluminium mass fraction (Δx_{Al}) , we perform the propagation of the uncertainty to calculate the error originated from the calculation of the film thickness $(\Delta \delta_{ICP})$.

2.B.1 Equation of the Volume of Alumina

$$\begin{split} W_{Al2O3}^{TOTAL} \left[m^{3} \right] \\ &= x_{Al} \left[\frac{kg \ aluminium}{kg \ sample} \right] \cdot m_{sample} \left[kg sample \right] \cdot \frac{M_{Al2O3} \left[\frac{kg \ Al_{2}O_{3}}{kmol \ Al_{2}O_{3}} \right]}{M_{Al} \left[\frac{kg \ Al}{kmol \ Al_{2}O_{3}} \right]} \\ & \cdot 0.5 \left[\frac{kmol \ Al_{2}O_{3}}{kmol \ Al} \right] \cdot \frac{1}{\rho_{Al2O3}} \left[\frac{m_{Al2O3}^{3}}{kg_{Al2O3}} \right] \end{split}$$

$$N_{P} = \frac{m_{TiO2}^{TOTAL}}{m_{TiO2}^{1p}} = \frac{m_{sample} - m_{Al2O3}}{\frac{\pi}{6} \cdot d_{3,2}^{3} \cdot \rho_{TiO2}} = \frac{m_{sample} - x_{Al} \cdot m_{sample} \cdot \frac{M_{Al2O3}}{M_{Al}} \cdot 0.5}{\frac{\pi}{6} \cdot d_{3,2}^{3} \cdot \rho_{TiO2}}$$

$$V_{Al2O3}^{1P}[m^{3}] = \frac{V_{Al2O3}^{TOTAL}}{N_{P}} = \frac{x_{Al} \cdot m_{sample} \cdot \frac{M_{Al2O3}}{M_{Al}} \cdot 0.5 \cdot \frac{1}{\rho_{Al2O3}}}{\frac{m_{sample} - x_{Al} \cdot m_{sample} \cdot \frac{M_{Al2O3}}{M_{Al}} \cdot 0.5}{\frac{\pi}{6} \cdot d_{3,2}^{3} \cdot \rho_{TiO2}}$$
$$= \frac{x_{Al} \cdot \frac{M_{Al2O3}}{M_{Al}} \cdot 0.5 \cdot \frac{\rho_{TiO2}}{\rho_{Al2O3}} \cdot \frac{\pi}{6} \cdot d_{3,2}^{3}}{1 - X_{Al} \cdot \frac{M_{Al2O3}}{M_{Al}} \cdot 0.5}$$

Then the volume of aluminium oxide per particle can be calculated with this equation:

$$V_{Al2O3}^{1P} = \frac{x_{Al} \cdot \frac{M_{Al2O3}}{M_{Al}} \cdot 0.5 \cdot \frac{\rho_{TiO2}}{\rho_{Al2O3}} \cdot \frac{\pi}{6} \cdot d_{3,2}^3}{1 - x_{Al} \cdot \frac{M_{Al2O3}}{M_{Al}} \cdot 0.5}$$

2.B.2 Calculation of the Thickness of the Aluminium Oxide Film

$$V_{Al2O3}^{1P} = V_{Core-Shell}^{1P} - V_{TiO2}^{1P} = \frac{\pi}{6} \cdot \left(d_{3,2} + 2 \cdot \delta_{ICP}\right)^3 - \frac{\pi}{6} \cdot d_{3,2}^3$$
$$\delta_{ICP} = \frac{\left[\left(V_{Al2O3}^{1P} + \frac{\pi}{6} \cdot d_{3,2}^3\right) \cdot \frac{6}{\pi}\right]^{\frac{1}{3}} - d_{3,2}}{2}$$
$$\delta_{ICP} = \frac{\left(\frac{A \cdot x_{Al}}{1 - A \cdot X_{Al}} \cdot \frac{\rho_{TiO2}}{\rho_{Al2O3}} \cdot d_{3,2}^3 + d_{3,2}^3\right)^{\frac{1}{3}} - d_{3,2}}{2}$$

where:

$$A = \frac{M_{Al2O3}}{M_{Al}} \cdot 0.5$$

2.B.3 Error Propagation Equation

2.C TEM for Base Case Dosing Times after 4, 7, and 15 Cycles

Figure 2.C.1 TEM images of the base case experiments with (a) four; (b) seven; and (c) 15 cycles.

Table 2.C.1. Determination of alumina film thickness from TEM images, with the standard deviation of the measurements.

Sample	N Pictures [-]	N Particles [-]	N Points [-]	δ_{TEM} [nm]	GPC [nm]
4 cycles	17	20	73	0.6 ± 0.1	0.15 ± 0.02
7 cycles	14	49	148	1.0 ± 0.2	0.14 ± 0.02
15 cycles	14	52	163	2.1 ± 0.6	0.14 ± 0.04

2.D TEM after 7 Cycles, Feeding the Precursors in Excess

Figure 2.D.1. TEM images of the experiments where the precursors were dosing with twice, four and six times the dosing times of the base case study. (a) $2 \times t_{\text{base}}$; (b) $4 \times t_{\text{base}}$; (c) $6 \times t_{\text{base}}$.

Table 2.D.1. Determination of alumina film thickness from TEM images, with the tandard deviation of the measurements. Temperature is 27 °C unless indicated otherwise.

Sample	N Pictures [-]	N Particles [-]	N Points [-]	δ_{TEM} [nm]	GPC [nm]
t base case	14	49	148	1.0 ± 0.2	0.14 ± 0.02
$2 \times t_{\text{base case}}$	11	35	131	1.5 ± 0.3	0.22 ± 0.04
$4 \times t_{base case}$	9	25	126	1.8 ± 0.4	0.26 ± 0.06
$6 \times t_{\text{base case}}$	10	28	113	3.6 ± 1.3	0.51 ± 0.19
170 °C–6 \times t _{base}	15	23	96	0.8 ± 0.1	0.16 ± 0.02

2.E ICP-OES Measurements

Table 2.E.1. Film thickness calculated from the ICP-OES measurements, and comparison with the results from the TEM measurements. The interval of confidence represents the error in the measurements as shown.

Sample	<i>x_{Al}</i> [-]	V_{Al203}^{1P} [m ³]	δ _{ICP} [nm]	δ _{TEM} [nm]
4 cycles	0.036 ± 0.001	2.44×10^{-24}	0.64 ± 0.08	0.59 ± 0.06
7 cycles	0.035 ± 0.001	$2.37 imes 10^{-24}$	0.62 ± 0.08	0.96 ± 0.10
15 cycles	0.105 ± 0.003	$8.32 imes 10^{-24}$	2.02 ± 0.26	2.10 ± 0.21
$2 \times t_{\text{base case}}$	0.086 ± 0.003	$6.48 imes 10^{-24}$	1.61 ± 0.21	1.51 ± 0.15
$4 \times t_{\text{base case}}$	0.100 ± 0.003	$7.79 imes 10^{-24}$	1.90 ± 0.24	1.84 ± 0.18
$6 \times t_{\text{base case}}$	0.131 ± 0.004	$1.10 imes 10^{-24}$	2.58 ± 0.33	3.60 ± 0.36
$170 \text{ °C}6 \times t_{\text{base}}$	0.044 ± 0.001	$2.30 imes 10^{-24}$	0.66 ± 0.08	0.78 ± 0.08

2.F BET Measurements of the Porosity

Figure 2.F.1. BET isotherms for the uncoated TiO_2 (left), sample coated with 15 cycles (middle), and sample coated with a dosage of precursors six times larger than the base case study (right).

Table 2.F.1. Comparison of the surface area measured with BET and calculated.

Samples	δ _{<i>TEM</i>} [nm]	$SA_{BET} [m^2/g]$	$\rho_{eq} [kg/m^3]$	$SA_{calc} [m^2/g]$
Un-coated TiO2	-	52.4 ± 0.1	-	-
15 cycles	2.1 ± 0.7	39.9 ± 0.1	3683 ± 141	44.1 ± 4.6
$6 \times t_{dosing}$	3.7 ± 1.5	38.2 ± 0.1	3422 ± 213	43.7 ± 5.6

We use the values of the particle size measured ($d_{3,2} = 33 \pm 3$ nm), density of TiO₂ ($\rho_{TiO2} = 4200 \text{ kg/m}^3$) and density of the alumina film ($\rho_{Al2O3} = 2500 \text{ kg/m}^3$) to compare the measured surface area (SA_{BET}) with the calculated value (SA_{calc}). We calculated the interval of confidence of the measurement by calculating the propagation of the uncertainty. These are the equations used:

$$SA_{calc} = \frac{6}{(d_{3,2} + 2 \cdot \delta_{TEM}) \cdot \rho_{eq}}$$

$$\rho_{eq} = \frac{V_P}{V_{TOTAL}} \cdot \rho_{TiO2} + \frac{V_{Al2O3}}{V_{TOTAL}} \cdot \rho_{Al2O3}$$

$$= \frac{d_{3,2}^3}{(d_{3,2} + 2 \cdot \delta_{TEM})^3} \cdot \rho_{TiO2} + \frac{(d_{3,2} + 2 \cdot \delta_{TEM})^3 - d_{3,2}^3}{(d_{3,2} + 2 \cdot \delta_{TEM})^3} \cdot \rho_{Al2O3}$$

$$\Delta \rho_{eq} = \sqrt{\left(\frac{\partial \rho_{eq}}{\partial d_{3,2}} \cdot \Delta d_{3,2}\right)^2 + \left(\frac{\partial \rho_{eq}}{\partial \delta_{TEM}} \cdot \Delta \delta_{TEM}\right)^2}$$

$$\Delta SA_{calc} = \sqrt{\left(\frac{\partial SA_{calc}}{\partial d_{3,2}} \cdot \Delta d_{3,2}\right)^2 + \left(\frac{\partial SA_{calc}}{\partial \delta_{TEM}} \cdot \Delta \delta_{TEM}\right)^2 + \left(\frac{\partial SA_{calc}}{\partial \rho_{eq}} \cdot \Delta \rho_{eq}\right)^2}$$

			ALD cycles	P25 TiO ₂	4	7	15
Ξ	1.00-	· · · · · · · · · · · · · · · · · · ·	mass initial [mg]	7.00	5.20	8.60	9.50
ass	0.99-		mass end [mg]	6.88	5.02	8.30	9.15
ů s	0.98-		∆mass [mg]	0.12	0.18	0.30	0.35
los	0.97-	TIO	N H ₂ O loss [mol]	0	$3.4 imes 10^{-6}$	$1.0 imes 10^{-5}$	$1.3 imes 10^{-5}$
Ë	0.06		N H ₂ O dosed [mol]	0	0.007	0.012	0.025
Ŷ	0.90-		H ₂ O desorbed [%]	0	0.05	0.09	0.05
	0.95- (200 - 200 - 400 = 600	∆mass >400 °C [mg]	0.01	0.01	0.03	0.05
		T [°C]	∆mass >400 °C [%]	0.1	0.3	0.3	0.5

2.G Thermo Gravimetric Analysis

Figure 2.G.1. (left) Mass loss profile for the uncoated TiO_2 and the samples coated with four, seven and 15 cycles; (right) Calculation of the percentage of the water molecules fed to the system compared to the amount of water released during the TGA analysis.

Figure 2.G.2. (left) Mass loss profile for the uncoated TiO_2 and the samples coated with an excess of precursors of two and six times that of the base case study; (**right**) Calculation of the percentage of the water molecules fed to the system compared to the amount of water released during the TGA analysis.

Figure 2.G.3. Differential Thermal Analysis (SDTA) from the TGA, for the base case study (**left**); and when the precursors where fed in excess (**right**).

Chapter 3

Tuning roughness and gloss of powder coating paint by encapsulating the particles with Al₂O₃ films

We report a method to change of the surface finish of a standard polyester-based powder coating paint, from gloss to matt, by depositing ultrathin films of Al₂O₃ on the powder coating particles, using trimethylaluminium and water as precursors. We performed this coating in a fluidized bed reactor at 1bar and 27 °C, using a gas-phase coating process of alternating exposure of the particles to the two precursors, similar to atomic layer deposition (ALD). We varied the number of coating cycles (1, 2, 3, 5, 7 and 9 cycles) to obtain film thicknesses ranging from 1 to 30 nm, determined by elemental analysis of the coated samples. The average growth per cycle of the process is 3.5 nm, significantly larger than the growth per cycle for pure self-limiting ALD process. When the average alumina shell was thicker than 6 nm, the shell prevented the flow of the core, that did soften above its glass transition temperature. With the particles morphology intact, this resulted in a rough and matte finish coating after curing. The surface roughness, with a value around 9 µm determined by surface profilometry, is associated to the alumina coated particles as observed from SEM and EDX analysis. In addition, the matte finish coating showed good mechanical resistance. Using this technique, we avoid the use of a foreign particles to produce matte coatings with similar properties as the gloss paints.

Submitted as: D. Valdesueiro, H. Hettinga, J.P. Drijfhout, P. Lips, G.M.H. Meesters, M.T. Kreutzer and J.R. van Ommen. *Tuning roughness and gloss of powder coating paint by encapsulating the coating particles with thin* Al_2O_3 *films.*

3.1 Introduction

Powder coatings have important advantages over liquid-based paints: ease of application, high utilization by electrostatic spraying, being environmentally friendly since they do not contain solvents, and showing excellent performance once applied. These strong points are also known as the *Four E's*, standing for ecology, excellence of finish, economy and energy [1-3]. These properties allow powder coatings to be used in a wide variety of applications, i.e. automotive, architectural, electronics and furniture amongst others [3]. A powder coating is composed by a resin, a catalyst, a cross-linker, pigments and additives such as flow modifiers and degassing agents, which define the properties of the final powder coating, including the surface finish: gloss or matte.

Glossy coatings reflect all the incident light in a mirror-like fashion, whereas a matte finish scatters part of the light, lessening the glossiness. The difference in gloss or matte appearance relies on the surface texture, whether it is highly smooth or rough. Certain indoor applications require gloss finish paints, while for industrial and agricultural purposes, a matte paint is preferred to hide surface irregularities and damages. The transition from a gloss to a matte finish is possible by partially blocking the activity of the catalyst [4], varying the size of the powder coating, adding inert fillers, playing with the humidity of the environment or tuning the conditions during the electro spraying [5]. In this work, we use a different approach to change the surface finish of a powder coating paint, from gloss to matte, by modifying the surface of the powder coating particles.

For that, we deposited ultrathin films of aluminium oxide (Al_2O_3) using a gas-phase technique similar to atomic layer deposition (ALD) on the primary particles of a standard powder coating, produced by DSM, which is characterized by a fast and low-temperature cure, good flow and flexibility, and a gloss surface finish once it cures, ideal for architectural applications [6]. By using the same particles as the original powder coating, but with modified surface, we prevent issues such as lack of homogeneity or of adhesion induced by the polydispersity in the size of the powder and the adhesion of a foreign material to the powder coating paint. We investigated how aluminium oxide films will modify the flowing behaviour of the powder coating particles above the glass transition temperature, and whether that would induce a textured-surface paint.

ALD allows the deposition of inorganic films in a layer-by-layer growth manner based on two consecutive self-terminating reactions, with a purging step using an inert gas after each reaction [7, 8]. The self-terminating feature of the ALD reactions ensures that the precursor molecules will only react where there is an active site available, preventing the growth of several layers of compound in each cycle [9, 10]. Al₂O₃ ALD, using trimethylaluminium (TMA) and water as precursors, is commonly carried out at ~170 °C and a few millibars of pressure, achieving a growth per cycle (GPC) of 0.1-0.2 nm [11, 12]. The growth of the alumina at these conditions is independent of the dosing time of the precursors due to the selfterminating property of the ALD reactions. Since our material cannot be heated to such temperatures, we deposited alumina films using TMA and water at ambient conditions, i.e. 27 \pm 3 °C and 1 bar. Working at these conditions may involve the accumulation of the unreacted species that are dosed in excess above the saturation regime, inducing a chemical vapour deposition (CVD) type of reaction [13, 14]. That results in the deposition of multiple atomic layers of alumina during each cycle, and therefore, a higher GPC than in a typical ALD process, depending on the amount of precursors dosed to the reactor [15]. The experiments in this work were carried out in a fluidized bed reactor, which provides good mixing between gas and solids, and allows processing large amounts of particles [16-20]. In these experiments, we fed an excess of both precursors to induce the accumulation of molecules on the substrates, and in this manner grow thicker alumina films faster.

Alumina deposited with ALD was applied as passivating materials, in the production of membranes and catalysts amongst others [21-28]. In this work, we altered the surface finish of a powder coating paint by depositing small amounts of Al_2O_3 on the surface of the powder coating particles. The alumina films act as physical barrier to confine the softened powder coating paint above the glass transition temperature, and prevent it from mixing homogeneously with other powder coating particles until reaching the curing temperature, at which the resin cross-links and the softened material becomes a crosslinked paint. We investigated the influence of the thickness of the Al_2O_3 films on the flowability of the coated particles, and how this translated into different textures of the final paint. This experimental paper is a proof of concept for the applicability of an emerging technology such as ALD in a fluidized bed reactor to modify the surface appearance of an industrial product, i.e. standard powder coating, while maintaining the same mechanical properties.

3.2 Experimental

3.2.1 Experimental setup and compounds

Al₂O₃ coating experiments were performed in a fluidized bed reactor similar to the one described previously [15, 29], composed by a vertical glass column with a diameter of 26 mm and 500 mm in length which was located in a vertical vibration table to assist the fluidization [17]. Semiconductor grade TMA was provided by Akzo Nobel HPMO in a 600 mL WW-600 stainless steel bubbler, which is kept at 30 °C during operation. Water, the second precursor, is kept in a similar bubbler, while nitrogen grade 5.0 is used as carrier and purging gas. In each experiment we coated 110 g of white standard powder coating particles with glossy finish, provided by DSM Coating Resins (Zwolle, The Netherlands). The powder coating particles, with an Sauter mean diameter of 33 μ m, is composed by five components: resin, i.e. Uralac® P 3210, crosslinker, white pigment, i.e. titanium oxide, flow control agent and degassing agent (more detail in [6] and *Supplementary information 3.A*). In order to fluidize the particles, we used a flow of 0.4 L/min of nitrogen, which corresponds to a superficial gas velocity of 1.26 cm/s.

3.2.2 Coating experiments

We used 8–10–4–10 min for the dosing sequence TMA–N₂–H₂O–N₂. To estimate these dosing times, we calculated the maximum amount of aluminium atoms and methyl groups that can be allocated on the surface of a powder coating particle to obtain fully coverage. These values are 4 and 5 species per nm² of Al and CH₃, respectively [30, 31]. Using the Sauter mean diameter ($d_{3,2}$) of 33 µm and a particle density of 1500 kg/m³ (*Supplementary information 3.A*), and assuming that the particles are spherical, we calculated a specific surface area of the powder of 0.12 m²/g, and a total surface area of inside the column of 13 m², for the 110 g of powder used in each experiment. We used the vapour pressure of the precursors inside the bubblers and the ideal gas law to calculate the amount of precursor molecules fed to the reactor, assuming that the TMA is a dimer at 30 °C [32, 33], and that the saturation of the nitrogen bubbles inside the TMA bubbler is about 50% [34]. We obtained

theoretical dosing times of 0.25 and 0.24 min for TMA and water to saturate the surface of the particles with precursor molecules. In order to obtain thicker alumina films, we overdosed both precursors, fixing the dosing times in 8 and 4 min for TMA and water. At ambient conditions, the molecules of water would physisorb onto the substrate [35-37], being involved in the following reaction with TMA molecules, also dosed in excess. We used a purging time of 10 min, approximately 13 times the residence time in the reactor. With these times, we performed six deposition experiments with different number of cycles, i.e. 1, 2, 3, 5, 7 and 9.

3.2.3 Characterization of the coated particles and panels

To investigate the influence of the alumina film thickness on the surface finish of the cured powder coating. To characterize this process, we first looked at individual powder coating particles. We estimated the film thickness and the growth per cycle from the fraction of aluminium on the samples measured by elemental analysis using ICP-OES (induced couple plasma – optical emission spectroscopy) as shown elsewhere [15]. Further, we performed DSC (differential scanning calorimetry) to study whether the alumina films influenced the thermal properties of the coated particles, such as the glass transition temperature. Finally, we studied the completeness of the alumina films and its barrier performance with a hot stage microscope and the pill flow test, which compares the flowability of the coated powder down an inclined panel while heating the samples in an oven from room to the curing temperature.

Subsequently, we studied the influence of the alumina films on the appearance of the paints by spraying the coated samples onto panels, using a corona-discharge gun, and curing them in an oven at 160 °C during 10 minutes. We found that the aluminium oxide films reduced the charge acquired by the powder, which did not adhere properly to the panels during spraying. To counteract the poor adhesion, we mixed the white Al_2O_3 -coated powder (TiO₂ pigment) with brown uncoated powder (prepared using a mixture of pigments and BaSO₄ as filler) in order to improve the adhesion and give contrast to the panels, and facilitate the characterization of the panels. The other compounds of both powders are the same. Before spraying the panels, we prepared mixtures of the Al_2O_3 -coated white and uncoated brown powders using a 1:1 mass ratio.

We studied the topography of the panels by visual observation, and SEM (scanning electron microscope) coupled with EDX (energy dispersive X-rays) to have a closer look at the surface of the panels. In addition, we measured the roughness with surface pofilometry and the gloss of the paints with a haze-gloss meter, and evaluated the mechanical resistance upon the impact of a steel ball in the reverse side of the panels. More details of the characterization techniques are given in *Supplementary information 3.B*.

3.3 Results and discussion

3.3.1 Characterization of the coated particles

We performed a series of six experiments to apply alumina film, with different thicknesses, on uncoated white powder coating particles, and estimated the film thickness using the fraction of aluminium obtained from elemental analysis with ICP. The uncoated powder coating particles contained a mass fraction of aluminium of 0.0064, coming from the white pigment (*Supplementary information 3.C*). From the fraction of aluminium on the coated

samples, we calculated the corresponding volume of aluminium oxide (V_{Al2O3}). From this value we calculated an equivalent film thickness of alumina (δ_{eq}) assuming that the particles are spherical, and that the coatings are uniform. We refer to this value as "equivalent film thickness" since the coating process requires a certain number of cycles to form a uniform and conformal alumina film [31, 38], that is, there is not yet a complete film after few coating cycles. With an increasing number of cycles, we found an increase in the content of aluminium on the coated samples (i.e., in the deposited volume of aluminium oxide); see Fig. 3.1. We calculated the GPC from the slope of the linear fit shown by the red-dotted line. The uncertainty in the calculation of the film thickness is represented by the error bars in Fig. 3.1 (more details can be found in *Supplementary Information 3.C*). We obtained a GPC of 3.5 nm, much larger than the typically values for Al₂O₃ ALD, i.e. 0.1-0.2 nm. This is explained by the accumulation of the overdosed precursor molecules at ambient conditions, which would react in the subsequent reaction. Obtaining such high GPC benefited our process, since we were able to deposit thick alumina films faster, although we can no longer refer to this coating process as atomic layer deposition. Nevertheless, we maintain a rather good control over the film thickness, as shown in Fig. 3.1.

Fig. 3.1 Volume of aluminium oxide deposited on the particles (primary Y axis) and the equivalent film thickness (secondary Y axis) assuming spherical particles, and uniform and complete alumina films. The increase of the film thickness can be approximated with a linear trend, where the slope represents a GPC of 3.5 nm. The error bars represent the uncertainty in the calculation of the film thickness.

To study whether (i) the aluminium oxide films would act as an insulating layer, changing the thermal properties of the powder such as the glass transition temperature (T_g) , or (ii) the alumina would only act as a physical barrier, preventing the softened resin from flowing freely, we performed DSC to determine the thermal properties and used a hot stage microscope to observe the particles above their glass transition temperature. We combined the results from both techniques to identify the influence of the alumina films on the powder coating particles.

The DSC measurements in Fig. 3.2 show the heating phase, with positive normalized heat flows, and the cooling phase, with negative normalized heat flows. During the heating we see the glass transition as the step function at around 50 °C. The powder coating is amorphous, so we refer as *softening* of the particles above the glass transition instead of melting, which only applies for crystalline materials and would be seen as an endothermic peak with a constant

baseline. To compare all the samples, we normalized the heat flow measured by the DSC device with the amount of powder used in each measurement, which ranged between 10 and 20 mg. We used a multi-step program in the DSC, composed by: (i) equilibration of the sample at 25 °C for 5 min, (ii) cooling down from 25 to 0 °C, (iii) isothermal period at 0 °C for 5 min, heating ramp from 0 to 130 °C, (iv) isothermal period at 130 °C for 5 min, (v) cooling down from 130 to 0 °C, (vi) isothermal period at 0 °C for 5 min, (vii) heating up from 0 to 170 °C, (viii) isothermal stage at 170 °C for 10 min, (ix) cooling down from 170 to 0 °C. All the heating and cooling steps were carried out with a rate of 10 °C/min. Steps (i) and (ii) were carried out so all the samples have the same thermal starting point. Steps (iii) to (vi) were carried out to have "enthalpic relaxation" of the powder, which typically occurs to amorphous resins during the glass transition [39]. Finally, steps (vii) to (ix) were done to determine the glass transition of the particles. Within this approach, we heated the samples above the glass transition temperature during step (iii), but below the curing temperature, then we did not induce any irreversible change on the powder coating particles. Fig. 3.2 only shows steps (vii), (viii) and (ix) of the full procedure. The full DSC profile is given in Supplementary information 3.D.

With DSC, we first evaluated whether the fluidization process would induce any change in the heat properties of the powder, by measuring the DSC profile of a sample that was fluidized for 3 hours at the coating temperature, i.e. 27 °C, and compared it with the profile of the unprocessed powder (Fig. 3.2a). We observed that both uncoated and fluidized samples have the same glass transition temperature and heat flow profile. Thus we conclude that the fluidization process does not alter the thermal properties of the powder. In Fig. 3.2b we compared the normalized heat flow profiles from DSC for the uncoated and coated samples. We can observe that the glass transition is not affected by the alumina films. Therefore, we conclude that the alumina films did not act as thermal insulator for the powder, since the glass transition of all the samples occurred at the same temperature. Then, we investigated the effect of the alumina films as a physical barrier.

Fig. 3.2. (a) DSC profiles of the untreated and fluidized powder. (b) DSC profiles of the powder of the untreated sample and the samples coated with 1, 2, 3, 5, 7 and 9 cycles.

A hot stage mounted on a light microscope was used to determine the confinement efficiency of the alumina films by observing whether the softened powder, above its glass transition temperature, would flow freely or remain enclosed. For that we placed a few particles of the samples on a quartz plate which was placed on top the hot stage, with all the system on the microscope stage. We heated the samples from 25 to 70 °C to study the behaviour of the particles above the T_g with a heating rate of 10 °C/min, similar to the one used in the DSC. In Fig. 3.3 we compared the uncoated, 1-cycle, 2-cycle, 3-cycle and 9-cycle samples.

Fig. 3.3 Hot stage microscope images of the uncoated powder (**a-c**) and the samples coated with 1 (**d-f**), 2 (**g-i**), 3 (**j-l**) and 9 (**m-o**) cycles, and three temperatures, i.e. 30, 50 and 70 °C.

By studying the uncoated sample under the hot stage microscope (Fig. 3.3a-c), we found that the softening of the powder coating particles started at about 45 °C, slightly lower than the 50 °C observed in the DSC curves. In the hot stage microscope, there were loses of heat to the surrounding air since the sample is in contact with the environment, while in DSC the samples are placed inside an isothermal chamber. That could cause the difference in the measured

softening temperatures in the DSC and the hot stage microscope. Despite that, we used the hot stage microscope to compare all the samples, which would experience the same heating process using the same equipment. In order to have a better view of the particles, we illuminated the samples with a LED light source. This gave extra information by providing a 3D visualization of the particles if we compare them with the pictures taken using the built-in light of the microscope (*Supplementary information 3.E*). The bluish colour seen in Fig. 3.3 is produced by the LED light source. By using the light source from the microscope in transmission mode, we counted the fraction of the particles that were contained above the glass transition temperature (*Supplementary information 3.E*).

The images of the uncoated (Fig. 3.3a-c) and 1-cycle (Fig. 3.3d-f) powder coating particles, showed a similar behaviour of the particles upon heating. In both samples, the softened particles flowed at the same temperature. However, a fraction of the sample with 2 cycles (Fig. 3.3g-i) was contained within the alumina film, similar to what was observed with the 3 cycles sample (Fig. 3.3j-1). The particles of the sample with 9 cycles preserved their shape, indicating that the alumina coating was able to enclose the softened powder coating paint (Fig. 3.3m-o). We took images with the transmission light source of the microscope (Supplementary information 3.E), and found that all the particles of the uncoated and 1-cycle samples observed under the microscope flowed out once softened, and eventually coalesced. By investigating about 130 particles per sample, we determined that for the 2-cycle sample, 5% of the particles were retained, while for the 3-cycle sample it was 41%, and for the 5-cycle sample it was 62% of the particles which remained encapsulated. All the particles from the samples with 7 and 9 cycles were completely encapsulated, observing no deformation in any of the particles. The combination of the DSC results, which showed that the glass transition temperature is not altered by the alumina films, and the one from the hot stage microscope, which showed that there is a key number of cycles above which the particles remained encapsulated. We conclude that the alumina films do not act as a thermal insulating layer, but as a physical barrier preventing the particles from flowing out of the alumina shell.

From the hot stage microscopy, we found that there is a critical number of cycles after which the alumina film is sufficiently thick and completely closed to contain the softened particles. We propose two hypotheses: (i) the alumina films are free of defects, and the stress caused inside the shell by expansion upon softening is higher than the stress that the deposited alumina shell can endure; and (ii) that a certain number of coating cycles are required to form a complete alumina film, based on the nucleation of the alumina ALD during the initial cycles when using polymeric particles as substrate [38, 40].

To calculate the resistance of the alumina films upon an increase of the internal pressure p (eq. 1), we modelled the core-shell particles as a "thin-walled spherical vessel" [41]. For this model to be valid, the ratio of the film thickness and the particle diameter should be small (< 0.1), which is the case for our particles. By using this approach, we calculated the tensile stress on the alumina coating (σ_c^{Al2O3}) caused by the expansion of the core (Eq. 2), and compared it to the critical tensile stress before cracks appear in the alumina coating ($\sigma_{critical}^{Al2O3}$), calculated using (Eq. 3). A detailed explanation of these calculations can be found in *Supplementary information 3.F*.

$$p = \frac{(\alpha_V - 3 \cdot \alpha_L) \cdot \Delta T}{\frac{3}{4} \cdot \frac{d_{3,2}}{E \cdot \delta} \cdot (1 - v) + \beta}$$
(eq. 3.1)

$$\sigma_c^{Al2O3} = \frac{p \cdot d_{3,2}}{4 \cdot \delta} \tag{eq. 3.2}$$

$$\sigma_{critical}^{Al2O3} = E \cdot \varepsilon_{critical} \tag{eq. 3.3}$$

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Here, $d_{3,2}$ is the Sauter mean diameter of the particles, α_v is the volumetric coefficient of thermal expansion of the core material, α_L is the linear coefficient of thermal expansion of the alumina shell, ΔT is the difference in temperature between the final T_f and initial T_i state, i.e. 70 and 25 °C, *E* and *v* are the Young modulus and Poisson's ratio of the aluminium oxide film, β is the compressibility factor of the core material (Table 1), and δ is the alumina film thickness. The values of the coefficient of thermal expansion α_V and the compressibility factor β were taken from literature for a similar resin, since we could not determine these two parameters for our material with a good accuracy. We performed a sensitivity analysis of these two variables and observed that they do not have a strong impact on the value of σ_c^{Al2O3} .

Table. 3.1.	Values used in the calculati	on of the tensile stress	$s \sigma_c^{Al2O3}$.
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Variable	$lpha_V$	α_L	β	Ε	υ	
Units	[1/°C]	[1/°C]	1/MPa	GPa	-	
Value	$100 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	$9.2 \cdot 10^{-4}$	170	0.24	
Reference	[42]	[43]	[44]	[45]	[45]	

To calculate the critical tensile stress of the alumina film $\sigma_{critical}^{Al2O3}$, we used (Eq. 3), where *E* is the Young modulus of the alumina, and $\varepsilon_{critical}$ is the critical strain of alumina films deposited by ALD under a tensile stress. The values of the critical strain before cracking depends on the film thickness, as shown by Jen *et al* [46]. We used the values of the equivalent film thickness determined by elemental analysis (Fig. 3.1) to calculate both tensile stresses (σ_c^{Al2O3} and $\sigma_{critical}^{Al2O3}$).

In Fig. 3.4 we can see that for the film thickness deposited in these coating experiments, the aluminium oxide films would break under a much larger tensile stress than the one produced by the expansion of the softened resin. The model predicts that the alumina films would resist the internal pressure in all the cases, while experimental evidences show that the softened powder flowed out the alumina shell for the samples with less than 7 coating cycles. Based on modelling results of Fig. 3.4, we conclude that the onset of flowing is not caused by breaking of the shell. Rather, samples with a small number of cycles start flowing because a closed rigid film has not formed yet, allowing fluid to escape as soon as it softens.

This analysis agrees with the nucleation theory of alumina ALD on polymeric substrates [38, 40]. During the first coating cycles, nuclei of alumina penetrate through the surface of the polymers before making a conformal coating (Fig. 3.5). Several factors promote the formation of alumina nuclei below the substrate surface, such as the solubility of TMA on hydrophobic surfaces as in the case of polymeric substrates, the rough surface of the resin particles, and the free volume near the surface of these materials due to the lack of lattice structure and crystallinity, which is seen as a porosity that can be accessed by the precursors. Although the nucleation phenomena is qualitatively understood, there is no rule-of-thumb for the number of cycles needed to deposit fully conformal films, since this depends on the polymer nature,

preparation method, polymer history, etc. Based on the experiments, it appears that 7 coating cycles are needed to obtain a conformal and complete aluminium oxide film for our material (Fig. 3.3 and *Supplementary information 3.E and 3.F*).

Fig. 3.4. Tensile stress (σ_c^{Al2O3}) exerted on the alumina-coated samples (blue symbols) and critical tensile stress ($\sigma_{critical}^{Al2O3}$) of the alumina before breaking (open symbols) for the different film thickness. The error bars represent the uncertainty in the calculation of the tensile stresses.

Fig. 3.5. Nucleation mechanism of the deposited alumina. (a) Surface of the untreated polymer particle. (b) Surface of the polymer particle during the first cycles, in which the green spheres represent the alumina molecules.

In addition, we performed the pill flow test to study the degree of confinement of the coated particles. With this test we analyse the flowability of a pill of powder coating paint down an inclined panel upon heating between room temperature and the curing temperature of the paint (Fig. 3.6a and b). We observe that even after 1 alumina coating cycle, there is a reduction of the length of the trail compared to the uncoated sample, and kept decreasing when increasing the number of cycles. Interestingly, we found that the sample coated with 9 cycles showed a displacement down the inclined panel, while it remained totally encapsulated in the hot stage microscope. In the preparation of the experiment, a pressure of 5000 psi is applied to the powder to compact the pill; it is possible that part of the alumina film broke because of the compression, creating a way out for the softened core and letting it flow down the panel.

The results from the pill flow test are in agreement with the DSC and hot stage microscopy, showing that the alumina film acts as a physical barrier, preventing the softened particles from flowing freely. We further investigated the impact of the alumina film in the appearance of the final product, the powder coating paint.

Fig. 3.6. Pill Flow test panel before (a) and after (b) introducing it in the oven at 160 $^{\circ}$ C for 10min, which is the curing procedure for this powder. The pills correspond, from left to right, to the 0, 1, 3, 5, 7 and 9-cycle samples. The pills have a diameter of about 10mm, and 5mm height.

3.3.2 Characterization of the sprayed panels

To investigate the appearance of the cured powder coating, we initially sprayed the Al₂O₃coated particles on the panels using a corona discharge gun. However, the powder did not stick properly to the aluminium panel, presumably due to a reduction of the charge transference between the spraying gun and the powder caused by the alumina coating. In addition, the poor adhesion of the powder coating to the panel and the reduced flowability of the coated particles resulted in a curing of the paint that lacked proper adhesion to the panel. These observations suggested a detrimental effect of the alumina films on the curing of the particles, as observed in the characterization of the coated particles. To overcome the adhesion problems, we prepared mixtures, with a 1:1 mass ratio, of regular uncoated brown powder coating particles and the Al₂O₃-coated white powder coating. We used brown powder coating to facilitate the observation and characterization of the painted panels. In total, we sprayed seven panels with the mixtures of brown and white particles, i.e. 0, 1, 2, 3, 5, 7 and 9 cycles, and cured them in the oven at 160 °C for 10 minutes. Visual inspection of the panels (Fig. 3.7a) indicated a change in the appearance regarding both colour and roughness for the sample coated with more than 2 cycles. The panels prepared with the uncoated white powder and the 1-cycle powder (Fig. 3.7a, (0) and (1)) showed a predominant white colour, while brown colour dominated the panels prepared with the 2-, 3-, 5-, 7- and 9-cycle samples (Fig. 3.5a, (3), (5), (7) and (9)). We illuminated the panels with LED light sources (Fig. 3.7b) in a dark environment to visualize the reduction of the gloss of the paints due to increased roughness. The panels (0) and (1) are smooth, as can be seen by the reflection of the light on the surface. Increasing number of cycles induced roughness of the surface, shown as a diffused reflection of the LED lights for the (2), (3), (5), (7) and (9) panels.

Fig. 3.7. (a) Piece of the sprayed panels after curing at 160 °C for 10min, prepared with the mixture of white powder coated with 0, 1, 2, 3, 5, 7 and 9 cycles, and uncoated brown powder coating paint (from left to right). The dimensions of the panels shown are 22×25 mm. The same panels were illuminated with LED lights in a light environment (b) and dark environment (c) to show the gradual decrease in the glossiness of the panels with the thickness of the alumina films that coated the primary particles used in the preparation of the panels.

The measurements of the surface roughness with a profilometer (Fig. 3.8a) and the gloss of the paints with a gloss meter (Fig. 3.8b) showed a similar transition to the one in the glossiness measurements observed in the panel coated with the 2-cycle powder (Fig. 3.7c). Both measurements agreed: the rougher the surface is, the more light it will scatter, resulting in a less glossy paint. The value of the surface roughness increased with the number of cycles, reaching a constant value of about 9 µm after 7 cycles, which corresponds to 1/3 of the particle size. With the hot stage microscope (Fig. 3.3 and Supplementary Information 3.E) we found that more particles were successfully contained when increasing the number of cycles. We observed a similar trend in the surface roughness measurements, which reached a levelled-off value. The alumina film deposited after 2, 3 and 5 cycles did not succeed to encapsulate the full particles above the glass transition temperature, so that part of the core flowed out the alumina shell. On the other hand, the particles coated with 7 and 9 cycles were completely confined by the alumina film, increasing the surface roughness, where we presume that the brown softened powder formed a continuous layer in which the coated white powder is suspended. We observed a similar trend in the values of the gloss, which significantly dropped for 2 or more cycles, in agreement with the observation of the surface roughness. Values of the gloss above 60 correspond to a gloss surface, while below 35 the surface is considered to have a matt finish, according to the internal standards of DSM Powder Coating Resins. Both surface roughness and gloss measurements agree with other results in which we found that the alumina film after 2 cycles altered the flowing of the single particles, and the mixing with the brown particles.

Fig. 3.8. (a) Measurement of the roughness of the panels sprayed with a 1:1 mixture of alumina-coated and uncoated Uralac powder. Error bars represent the standard deviation of the measurements. (b) Gloss measurements of the panels sprayed with a 1:1 mixture of alumina-coated and uncoated Uralac powder.

To study the transition in colour and roughness observed for the panels, and take a closer look at the surface, we used an optical microscope (Fig. 3.9) and SEM-EDX (Fig. 3.10 and 3.11). With the optical microscope, we observed a difference in the distribution of the cured white and brown powder coated paint. The panels sprayed with uncoated (Fig. 3.9a) and 1-cycle powder (Fig. 3.9b) coating particles showed an homogeneous distribution of the brown and white colour, explained by the good flow of the white powders. The panel prepared with the 3-cycle sample (Fig. 3.9c) did not show a homogenous pattern of the colours, caused by the partial confinement of the white powder and the consequent decrease of the flow and mixing between both white and brown powder after softening. To evaluate this panel (Fig. 3.9c) we modified the incident angle and intensity of the light source to overcome the reflection on the panel cause by the roughness, creating a yellowish colour. It seems that in Fig. 3.9a and 3.9b both white and brown particles softened, flowed and mixed homogeneously, creating a uniform pattern. While Fig. 3.8c suggests that while the brown powder softened, the white powder partially did, creating a kind of suspension of white grains in a brown uniform matrix.

Fig. 3.9. Images from the optical microscope. Panels sprayed with (a) uncoated powder, (b) 1-cycle coated powder, and (c) 3-cycle coated powder.

Fig. 3.10. SEM pictures using topology mode (BET) (**a**, **c**, **e**) and composition mode (BEC) (**b**, **d**, **f**) of the panels prepared with uncoated particles (**a**) and (**b**), 3-cycle particles (**c**) and (**d**), and 9-cycle particles (**e**) and (**f**). The duplet of pictures for each sample represent the same area of the panel.

To investigate the formation of the roughness, we evaluated the sprayed panels with the combination of SEM (Fig. 3.10) and EDX (Fig. 3.11). We used two different SEM modes to look at the surface: Back-scattering Topology BET, (Fig. 3.10a, 3.10c and 3.10e), and Back-scattering Composition BEC, (Fig. 3.10b, 3.10d and 3.10f).

We observed that the panels sprayed with the uncoated particles (Fig. 3.10a) did not show roughness in the BET mode, in agreement with the visual observation of the panels (Fig. 3.7). Nevertheless, the BEC-mode picture revealed darker and brighter areas (Fig. 3.10b). As we expected, BET-mode images of the 3-cycle (Fig. 3.10c) and the 9-cycle (Fig. 3.10e) panels confirmed the presence of surface roughness, which are related with the location of the darker areas observed in the corresponding BEC-mode pictures (Fig. 3.10d and 3.10f). We used EDX analysis (Fig. 3.11) to examine the composition of the darker and brighter areas in the BEC-mode images, and to determine how they relate with the roughness in the BET-mode images.

We performed EDX analysis in the full area shown in the images of Fig. 3.11, and performed spot analysis in the bright (1) and darker (2) areas. We found that the brighter areas (white bars in Fig. 3.11) showed a higher concentration of Ba and S, while the darker areas (black bars in Fig. 3.11) had a dominant concentration of Ti. That relates to the presence of BaSO₄, which is the filler in the brown powder coatings, and white pigment TiO₂ used in the preparation of the white powder coatings. In agreement, the concentration of aluminium is higher in the darker areas, which correspond to the Al₂O₃-coated white powder. Other compounds identified by EDX analysis, such as C, O and N, are not included in Fig. 3.10, which related the presence of darker and brighter areas with the roughness, and the EDX analysis (Fig. 3.11), which determined the presence of white pigment and the filler used in the brown powder in the darker and brighter areas respectively, evidences that the roughness is caused by the Al₂O₃-coated particles, and thus, the reduction in the gloss of the paints.

Fig. 3.11. SEM images using BET mode for the samples sprayed with 0 cycles (**a**), 1 cycles (**d**) and 3 cycles (**g**), and BEC mode for the samples with 0 cycles (**b**), 1 cycles (**e**) and 3 cycles (**h**). (**c**), (**f**) and (**i**) shows the EDX analysis of the full image (green bars), spot 1 (red bars) and spot 2 (blue bars).

Finally, we evaluated the mechanical resistance of the paints prepared with the Al_2O_3 -coated powder coating particles using the *reverse impact test* (*Supplementary information 3.G*). After the impact of the steel ball, we used a stereomicroscope to observe the cracks on the surface of the panel (Fig. 3.12). The contrast and brightness of the pictures in Fig. 3.12 were modified to have a better visualization of the formation of the cracks. In the centre of the images (Fig. 3.12) we can see the deformation of the panel after the impact, on which the cracks would appear. We found that all the panels showed a good impact resistance.

From the results obtained, we conclude that powder coating particles coated with only 2 cycles of alumina induced a granular textured paint, characterized by a rough and matte surface finish with enough surface resistance. Nevertheless, this product could be further developed in the preparation of the alumina-coated powder and in the production of the painted panels. For instance, the dosing and purging time, in combination with the number of cycles, during the alumina coating could be further optimized towards a more time-efficient process. Likewise, variables such as the particle size and the ratio of mixture of the coated-to-uncoated powder would influence the appearance, i.e. roughness, gloss and colour, and the mechanical resistance of the paint. Nevertheless, this work did not aim at obtaining an industrial solution for the production of a matte powder coating paint, but at proving the applicability of gas-phase techniques on particles, such as ALD or CVD, to modify or

improve the properties of industrial products, as in this case, where we induced roughness while maintaining the good mechanical properties of a DSM standard powder coating paint.

Fig. 3.12. Reverse Impact test, performed over the painted panels with 0, 1, 3, 5, 7 and 9 cycles. The thickness of the paint was around 50 μ m in all the samples. The contrast and brightness of the pictures were modified for a better visualization of the cracks.

3.4 Conclusions

We showed that a thin coating of aluminium oxide deposited on particles of a standard dry powder coating paint delayed or even completely suppressed fluid-like flow above the glass transition temperature. As a result, the appearance of the final paint layer could be tuned between a gloss finish and a matte one, depending on the pre-treatment of the paint particles. We deposited these alumina films, with different thicknesses, on the powder coating particles in a fluidized bed reactor at 27 °C and 1 bar, using trimethylaluminium and water as precursors, in a process similar to ALD with a growth of about 3.5 nm of Al₂O₃ per cycle. We found that 2 coating cycles, which deposited an amount of alumina equivalent to a 6 nm average film thickness, was sufficient to alter the flow of the particles and the appearance of the paint. More cycles resulted in thicker alumina coatings and further modified the paint behaviour, whereas more than 5 cycles had little additional effect. The suppression of flow was not caused by delayed melting due to thermal insulation by the alumina films, as determined by differential scanning calorimetry. Rather, the film acts as a hard physical shell that prevents material release from the core, that softens irrespective of the coating around it. The thickness of the film is not important as long as it covers the entire particle. We calculated that the thinnest shell is strong enough to contain the core, even when the core softens and expands due to heating, using an order-of-magnitude analysis in a thin-wall spherical-vessel model. We found, after interpretation of the results from SEM and EDX, that Al_2O_3 can readily alter the flowing behaviour and induce roughness in paints, while keeping the mechanical resistance comparable to the reference paints.

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3.A Powder coating paint characterization

3.A.1 Particle Size Distribution

To determine the particle size, which is used later in the calculation of the alumina-film thickness, we used a *Beckman Coulter LS 230 Diffraction Particle Size Analyser*. We obtained a value for the Sauter mean diameter $(d_{3,2})$ of 33 µm (Fig. 3.A.1).



Fig. 3.A.1. PSD of DSM Uralac ® powder coating paint used in the ALD experiments

3.A.2 Composition

This is the composition of the powder coating used in the Al_2O_3 -coating experiment [6].

Component	Mass percentage [%]
DSM Uralac® P 3210 resin	62.4
HAA (β -Hydroxyalkylamide) cross-linker	3.3
TiO2 white pigment	33
Flow control agent	1
Degassing agent	0.3

 Table 3.A.1. Composition of the powder coating paint used in the coating experiments.

3.A.3 Density calculation

We measured the density of the powder using a 25 mL volumetric flask, and ethanol with known density. We placed a weighted mass of powder, and filled the flask with ethanol. By subtracting the added ethanol volume to the flask volume, we determined the volume occupied by the amount of powder placed inside the flask. We performed error propagation to determine the uncertainty of this measurement, obtaining a density for the powder of 1500 \pm 100 kg/m³. The details of the calculation are shown in Table 3.A.2.

	V flask [mL]	mass powder [g]	V EtOH [mL]	$\rho_{powder} [\text{kg/m}^3]$
value	25	19.2	12.2	1497
error	0.5	0.5	0.5	92

Table 3.A.2. Calculation of the density of the powder.

3.B Characterization techniques

To calculate the Al₂O₃ film thickness, we measured the mass fraction of aluminium on the coated samples (x_{Al}) with a PerkinElmer Optima 5300 Induce Coupled Plasma – Optical Emission Spectroscope. We performed DSC measurements on the coated samples using a TA Instruments DSC Q-20 device. To evaluate the confinement of the Al₂O₃-coated particles, we placed several particles on a Metler ToledoFP82 HT Hot Stage to heat up the sample above the glass transition temperature of the powder. The heating procedure, which is controlled with a Metler Toledo FP90 Central Processor, consisted of a ramp-up of 10 °C/min from room temperature to 70 °C, followed by an isothermal state at 70 °C for 3 minutes before the samples were brought back to room temperature. The hot stage was placed under a Bresser MPO-401 light microscope using a 4x magnification objective to observe the particles. We performed a Pill Flow test as a measurement of the curability of the powder. For that, we applied a pressure of 5000 psi to prepare pills with the uncoated and Al₂O₃-coated coated samples, and placed them on an aluminium Q-panel. This panel was introduced in the oven with an inclination of 45°, and heated up to 170 °C, which is the curing temperature. As the temperature increased above the glass transition, the particles started to flow down the panel, until curing. The comparison was based on the measurement of the trail of the pills when flowing down the panel, which indicated whether the alumina coating influenced the curing of the powder.

The sprayed panels with the mixture of uncoated-coated Uralac were evaluated under a *Leica EZ4* optical microscope, and a *JEOL JSM 6010LA* SEM microscope equipped with EDX detector to determine the surface topology and its composition. Furthermore, we measured the roughness of the panels using a *VECCO DEKTAK8 Stylus Profilometer* with a scanning force of 1.0mg, and a scan speed of 4mm/s. We used a Byk-Gardner haze-gloss meter to measure the gloss at 20 and 60° according to both standards ASTM-D-523/70 and ISO 2813. Finally we studied the resistance of the panels under the impact of a 0.45 kg ball in the reverse of the panel falling from 1.5m height. The resistance and flexibility of the powder coating paint, and how well it is cured, were assessed by the number of cracks that appeared on the panels for two different paint thickness: 50 µm and 75 µm. We evaluated the area of the impact on the panels with a *Zeiss Discovery V8* stereomicroscope. The appearance of crack qualified whether the powder coating paint produced with the alumina-coated primary particles showed the same resistance as the standard Uralac powder coating paint.

3.C Calculation of the alumina film thickness

This calculation is based on the measurements of the mass fraction of aluminium (x_{Al}) on the coated samples, obtained from the ICP-OES. From this value, we calculated the volume of aluminium oxide per particle (V_{Al2O3}^{1P}) related to the mass fraction of aluminium. Subsequently, we calculated the thickness of the alumina film δ considering spherical particles. To account for uncertainty in the film thickness $\Delta\delta$, we determined the error considering the error in the particle size $\Delta d_{3,2}$, the aluminium oxide $\Delta \rho_{Al2O3}$. We used the equations below to calculate the film thickness δ , and its error $\Delta\delta$. The error for the mass fraction Δx_{Al} is 3% of the value measured from ICP-OES, for the particle size $\Delta d_{3,2}$ is 15 µm, for the density of the alumina $\rho_{Al_2O_3}$ used to calculate the film thickness is 2500 kg/m³ [47]. More details of the calculation are given in [15].

$$\delta = \frac{\left(\frac{A \cdot x_{Al}}{1 - A \cdot x_{Al}} \cdot \frac{\rho_{powder}}{\rho_{Al2O3}} \cdot d_{3,2}^3 + d_{3,2}^3\right)^{\frac{1}{3}} - d_{3,2}}{2} \qquad (\text{eq. 3.C.1})$$

$$A = \frac{M_{Al2O3}}{M_{Al}} \cdot 0.5$$
 (eq. 3.C.2)

$$\Delta\delta = \sqrt{\left(\frac{\partial\delta}{\partial\Delta d_{3,2}} \cdot \Delta d_{3,2}\right)^2 + \left(\frac{\partial\delta}{\partial x_{Al}} \cdot \Delta x_{Al}\right)^2 + \left(\frac{\partial\delta}{\partial\rho_{powder}} \cdot \Delta\rho_{powder}\right)^2 + \left(\frac{\partial\delta}{\partial\rho_{Al2O3}} \cdot \Delta\rho_{Al2O3}\right)^2} \quad (eq. 3.C.3)$$

Table 3.C.1. Results from ICP-OEScharacterization

# ALD	%Al ICP	δ_{Al2O3}
cycles	[%w]	[nm]
0	0.64 ± 0.02	0
1	$\textbf{0.67} \pm 0.03$	1.9 ± 0.9
2	0.73 ± 0.09	5.7 ± 2.6
3	0.85 ± 0.21	13.3 ± 6.1
5	0.84 ± 0.20	12.7 ± 5.8
7	1.13 ± 0.49	31.1 ± 14.4
9	1.10 ± 0.46	29.2 ± 13.5



Fig. 3.C.1. Calculation of the thickness of Al_2O_3 for different number of cycles. The error bars indicate the uncertainty of the measurement.

3.D DSC measurements

We performed the DSC measurements using a multiple-step heating/cooling process to prevent that the *entalphic relaxation* of the powder could influence the interpretation of the results for the glass transition temperature. Fig. 3.D.1 (left) shows the full heating/cooling process, while Fig. 3.D.1 (right) only shows the last heating and cooling cycle. The figures shown in the manuscript represent the last heating cooling cycle, similar to the one plotted in Fig. 3.D.1 (right).



Fig. 3.D.1. DSC profiles for the uncoated samples, showing the full heating/cooling process (**left**), and the reduced heating/cooling (**right**).

3.E Hot Stage Microscopy images.





Fig. 3.E.1. Hot stage pictures before (25 °C) and after heating, for the samples with 0, 1, 2, 3, 5 and cycles. We observe a difference for the samples with 2 and less cycles, which melted and coalesced, and the samples with 3 and more cycles, where most of the particles showed resistance to temperature.

# cycles	0	1	2	3	5	7	9
N particles analysed [-]	136	130	120	140	137	156	136
T max [°C]	70	70	70	70	70	70	70
Contained particles [%]	0	0	5	41	62	97	100

3.F Calculation of the tensile stress of the alumina film

3.F.1 Equations

We base this calculation in the book Mechanics of Solids and Structures, by Roger T. Fenner and J.N. Reddy [41], by modelling a core-shell particle as a thin-walled spherical vessel.



Fig. 3.F.1. Model proposed with the force balance to calculate the tensile stress of the film.

$$\int_{0}^{R} p \cdot dA = \int_{R}^{R+\delta} \sigma_{c}^{Al2O3} \cdot dA \qquad (eq. 3.F.1)$$

$$dA = 2 \cdot \pi \cdot r \cdot dr \qquad (\text{eq. 3.F.2})$$

Developing the equation above, and assuming that $2 \cdot R \gg \delta$, we obtain:

$$p \cdot \pi \cdot \frac{d_{3,2}^{2}}{4} = \sigma_c^{Al2O3} \cdot \pi \cdot \delta \cdot (2 \cdot R + \delta) = \sigma_c^{Al2O3} \cdot \pi \cdot \delta \cdot d_{3,2}$$
(eq. 3.F.3)

$$\sigma_c^{Al2O3} = \frac{p \cdot d_{3,2}}{4 \cdot \delta} \tag{eq. 3.F.4}$$

For the strain of the shell of a thin-walled spherical vessel, we have two different contributions: radial direction (ε_r) and circumferential direction (ε_c). Similarly, the stress has the same two contributions (σ_r and σ_c).

$$\varepsilon_r = \frac{1}{E} \cdot [\sigma_r - v \cdot (\sigma_c + \sigma_c)] + \alpha \cdot \Delta T \qquad (eq. 3.F.5)$$

$$\varepsilon_c = \frac{1}{E} \cdot [\sigma_c - \upsilon \cdot (\sigma_r + \sigma_c)] + \alpha \cdot \Delta T \qquad (eq. 3.F.6)$$

The strain in radial direction ε_r only provides information about how much the thickness diminishes under the radial stress σ_r . However, the σ_r value is in the order of the inner

pressure, and therefore, very small compared to σ_c , which is proportional to the ratio $\frac{a_{3,2}}{\delta}$. According to this, we rewrite the circumferential strain ε_c as:

$$\varepsilon_c = \frac{1}{E} \cdot \sigma_c^{Al2O3} \cdot (1 - \upsilon) + \alpha \cdot \Delta T = \frac{1}{E} \cdot \frac{p \cdot d_{3,2}}{4 \cdot \delta} \cdot (1 - \upsilon) + \alpha \cdot \Delta T \qquad (\text{eq. 3.F.7})$$

We assume that the strain of the polymeric core ε_c^{core} will equal the strain of the alumina shell ε_c^{shell} . The strain of the core have two components: the thermal expansion and the compressibility of the liquid. On the other hand, the alumina shell will have a component related to the deformation induced by the stress based on the pressure σ_c^{Al2O3} which depends on the film material, and a component that shows the thermal expansion of the film, knowing that due to geometrical approximation $\varepsilon_c^{shell} = 3 \cdot \varepsilon_c$.

$$\varepsilon_c^{core} = \varepsilon_c^{shell}$$
 (eq. 3.F.8)

$$\varepsilon_c^{core} = \alpha_V \cdot \Delta T - \beta \cdot p \tag{eq. 3.F.9}$$

$$\varepsilon_c^{shell} = 3 \cdot \varepsilon_c = \frac{3}{4} \cdot \frac{p \cdot d_{3,2}}{E \cdot \delta} \cdot (1 - v) + 3 \cdot \alpha_L \cdot \Delta T \qquad (eq. 3.F.10)$$

$$p = \frac{(\alpha_V - 3 \cdot \alpha_L) \cdot \Delta T}{\frac{3}{4} \cdot \frac{d_{3,2}}{E \cdot \delta} \cdot (1 - v) + \beta}$$
(eq. 3.F.11)

$$\sigma_{c}^{Al2O3} = \frac{p \cdot d_{3,2}}{4 \cdot \delta} = \frac{d_{3,2}}{4 \cdot \delta} \cdot \frac{(\alpha_{V} - 3 \cdot \alpha_{L}) \cdot \Delta T}{\frac{3}{4} \cdot \frac{d_{3,2}}{E \cdot \delta} \cdot (1 - \upsilon) + \beta} = \frac{d_{3,2} \cdot (\alpha_{V} - 3 \cdot \alpha_{L}) \cdot \Delta T}{3 \cdot \frac{d_{3,2}}{E} \cdot (1 - \upsilon) + 4 \cdot \beta \cdot \delta}$$
(eq. 3.F.12)

Where ΔT is the difference in temperature between the final T_f and initial T_i state, d is the particle diameter, p is the increase in pressure between the inside and outside of the coreshell, δ is the alumina wall thickness, α_v is the volumetric coefficient of thermal expansion of the core material, α_L is the linear coefficient of thermal expansion of the alumina shell, E and v are the Young's modulus and Poisson's ratio of the aluminium oxide film, and β is the compressibility factor of the core material.

Once we have calculated the stress that results from the expansion of the softened resin, we can compare the values with the ones from the critical tensile stress before breaking. We can calculate these values using the values of the critical strain of alumina films $\varepsilon_{critical}$ with different thickness and the Young modulus of the ALD alumina films.

$$\sigma_{critical}^{Al203} = E \cdot \varepsilon_{critical} \tag{eq. 3.F.13}$$

F.2 Error propagation

We estimate the uncertainty of the previous calculations.

$$\sigma_c^{Al2O3} = \frac{d_{3,2} \cdot (\alpha_v - 3 \cdot \alpha_L) \cdot \Delta T}{3 \cdot \frac{d_{3,2}}{E} \cdot (1 - v) + 4 \cdot \beta \cdot \delta}$$
(eq. 3.F.14)

$$\Delta \sigma_c^{Al2O3} = \sqrt[2]{\left(\frac{\partial \sigma_c^{Al2O3}}{\partial \delta} \cdot \Delta \delta\right)^2 + \left(\frac{\partial \sigma_c^{Al2O3}}{\partial d_{3,2}} \cdot \Delta d_{3,2}\right)^2 + \left(\frac{\partial \sigma_c^{Al2O3}}{\partial \Delta T} \cdot \Delta (\Delta T)\right)^2}$$
(eq. 3.F.15)

$$\partial \sigma_c^{Al2O3}$$

$$=\frac{\left(\alpha_{V}-3\cdot\alpha_{L}\right)\cdot\Delta T\cdot\left[\frac{3\cdot d_{3,2}\cdot(1-\upsilon)}{E}+4\cdot\beta\cdot\delta\right]-\left[d_{3,2}\cdot(\alpha_{V}-3\cdot\alpha_{L})\cdot\Delta T\cdot\frac{3\cdot(1-\vartheta)}{E}\right]}{\left[3\cdot\frac{d_{3,2}}{E}\cdot(1-\upsilon)+4\cdot\beta\cdot\delta\right]^{2}}$$
(eq. 3.F.16)

$$\frac{\partial \sigma_c^{Al2O3}}{\partial \delta} = \frac{-4 \cdot \beta \cdot d_{3,2} \cdot (\alpha_V - 3 \cdot \alpha_L) \cdot \Delta T}{\left[3 \cdot \frac{d_{3,2}}{E} \cdot (1 - \nu) + 4 \cdot \beta \cdot \delta\right]^2}$$
(eq. 3.F.17)

$$\frac{\partial \sigma_c^{Al2O3}}{\partial \Delta T} = \frac{d_{3,2} \cdot (\alpha_V - 3 \cdot \alpha_L)}{3 \cdot \frac{d_{3,2}}{E} \cdot (1 - \upsilon) + 4 \cdot \beta \cdot \delta}$$
(eq. 3.F.18)

Critical tensile stress that the alumina films can withstand before breaking. The values of the critical strain (figure below) were reported by Jen et al. 2011 [46].

$$\varepsilon_{critical} = -0.664 \cdot \ln \delta + 3.4147 \qquad (eq. 3.F.19)$$

$$\Delta \varepsilon = \sqrt[2]{\left(\frac{\partial \varepsilon}{\partial \delta} \cdot \Delta \delta\right)^2} = \sqrt[2]{\left(\frac{-0.668}{\delta} \cdot \Delta \delta\right)^2}$$
(eq. 3.F.20)

$$\sigma_{critical}^{Al2O3} = E \cdot \varepsilon \tag{eq. 3.F.21}$$

$$\Delta \sigma_{critical}^{Al2O3} = \sqrt[2]{\left(\frac{\partial \sigma_{critical}^{Al2O3}}{\partial \varepsilon} \cdot \Delta \varepsilon\right)^2} = \sqrt[2]{(E \cdot \Delta \varepsilon)^2}$$
(eq. 3.F.22)

To calculate whether the alumina shell would break or not, we use the following equation for the breakage probability $\varphi_{breakage}$:

$$\varphi_{breakage} = \frac{\sigma_c^{Al2O3}}{\sigma_{critical}^{Al2O3}}$$
(eq. 3.F.23)

$$\Delta \varphi_{breakage} = \sqrt[2]{\left(\frac{\partial \varphi_{breakage}}{\partial \sigma_c^{Al203}} \cdot \Delta \sigma_c^{Al203}\right)^2 + \left(\frac{\varphi_{breakage}}{\partial \sigma_{critical}^{Al203}} \cdot \Delta \sigma_{critical}^{Al203}\right)^2}$$
(eq. 3.F.24)

$$\frac{\partial \varphi_{breakage}}{\partial \sigma_c^{Al2O3}} = \frac{1}{\sigma_{critical}^{Al2O3}}$$
(eq. 3.F.25)

$$\frac{\varphi_{breakage}}{\partial \sigma_{critical}^{Al2O3}} = \frac{-\sigma_c^{Al2O3} \cdot \sigma_{critical}^{Al2O3}}{(\sigma_{critical}^{Al2O3})^2}$$
(eq. 3.F.26)

 Table 3.F.1. Calculated values of the tensile stresses

# cycles	1	2	3	5	7	9
δ [nm]	1.9	5.7	13.3	12.7	31.1	29.2
<i>p</i> [bar]	0.7	2.2	5.0	4.7	11.2	10.5
σ_c^{Al2O3} [bar]	3150 ± 60	3130 ± 70	3080 ± 90	3080 ± 80	2960 ± 140	2970 ± 130
$\varepsilon_{critical}[\%]$ [46]	3.0	2.3	1.7	1.7	1.1	1.2
$\sigma_{critical}^{Al2O3}$ [bar]	50800 ± 5250	38300 ± 5250	28700 ± 5250	29250 ± 5250	19000 ± 5250	19700 ± 5250
$\varphi_{breakage}$ [-]	0.06 ± 0.01	0.08 ± 0.01	0.11 ± 0.02	0.11 ± 0.02	0.16 ± 0.04	0.15 ± 0.04
Does it break?	no	no	no	no	no	no

3.G Results of several techniques

3.G.1 Pill Flow Test

Table 3.G.1. Length of the "tongue" of the pill flow test for the different number of cycles.

Sample	Flow	length
	[mm]	
0 cycles	99	
1 cycle	83	
3 cycles	71	
5 cycles	72	
7 cycles	51	
9 cycles	53	



the

Fig. 3.G.1. Pill flow test results.

3.G.2 Surface profilometry



Fig. 3.G.2. Representation of the areas of the samples that were measured with the profilometre.

ALD	N areas	Roughness	
cycles	[-]	[µm]	
0	4	0.3 ± 0.1	
1	7	0.7 ± 0.2	
3	30	4.1 ± 1.2	
5	10	5.4 ± 0.8	
7	17	10.1 ± 2.7	# cycles
9	17	8.8 ± 2.8	Fig. 3.G.3. Surface roughnes
			samples

3.G.3 Reverse impact test

# cycles	thickness [µm]	number cracks
0 avalaa	52	0
0 cycles	64	0
1 avalas	50	2
1 cycles	68	>25
3 cycles	60	2
	82	>25
5 cycles	56	0
	82	0
7 cycles	60	0
	76	>25
9 cycles	48	0
	80	<25

 Table 3.G.3. Number of cracks appeared after the impact test.

Chapter 4

The deposition mechanism of Al₂O₃ on QD films at atmospheric pressure and room temperature

Stability of quantum dot (QD) films is an issue of concern for applications in devices such as solar cells, LEDs and transistors. This paper analyzes and optimizes the passivation of such QD films using atomic layer deposition (ALD), resulting in enhanced optical stability. Crucially, we deposited alumina at economically attractive conditions, room temperature and atmospheric pressure, on PbSe EDA (1,2-ethanediamine) capped QD films using trimethylaluminum (TMA) and water as precursors. We performed coating experiments from 1 to 25 cycles on the QD films, finding that alumina formed from the first exposure of TMA, as determined by X-ray photoelectron spectroscopy (XPS) depth profiling measurements. XPS points to the presence of oxygen-rich compounds on the bare QD films, most likely from entrapped solvent molecules during the dip-coating assembly of the QD films. These oxygenated compounds and the amine groups of the organic ligands act as active sites to react with TMA in the first cycle, and this results in a fast growth of alumina. Using 10 cycles of ALD resulted in infilling (between the QDs) and overcoating (a layer on top of the QDs), to produce a product that was optically stable for at least 27 days. We also investigated the deposition of alumina with synthetic air as an alternative for the use of water as precursors. We found that the absence of physisorption of precursor molecules yielded a thinner coating, and the QD film oxidized during the first exposure to synthetic air. Depositing alumina on the QD films at ambient conditions is preferred, since the deposition of alumina occurs faster, and the production of the OD films is also carried out at room temperature and atmospheric pressure, allowing an interesting combination of both processes in a single go.

Submitted as: D. Valdesueiro, M. Krishna Prabhu, C. Guerra-Nuñez, C.S. Suchand Sandeep, Sachin Kinge, L.D.A. Siebbeles, L.C.P.M. de Smet, G.M.H. Meesters, M.T. Kreutzer, A.J. Houtepen, J.R. van Ommen. *The deposition mechanism of aluminium oxide on quantum do films at atmospheric pressure and room temperature*.

4.1 Introduction

This paper describes, analyzes and optimizes a passivation process for assembled films of colloidal quantum dots (QD). Such assembled QD films have come to the fore in potential applications for photovoltaic devices [1-7] due to their size-tunable band gap and ease of processing [4, 8]. In particular, colloidal QDs exhibit carrier multiplication [8-18], a process in which a high energy photon creates more than one charge carrier pair. That boosts the efficiency in applications such as photovoltaic devices, LEDs and transistors.

In optoelectronic devices, QDs are immobilized as films and separated by organic ligands that are bound to the QD surface. These ligands prevent sintering of the crystals and ensure electronic contact between the QDs [19, 20], but they also make the assembled structure more open, allowing oxygen to diffuse inside the film easily and degrade the crystals by oxidation. To begin with the positive aspects, the tunable physical separation between crystals impacts the absorption spectrum to allow the so-called *band-tuning*, while the electronic contact improves the charge-carrier mobilities. Good results have recently been obtained by using films of QDs capped with EDA (1,2-ethanediamine) and EDT (1,2-ethanedithiol) for applications in optoelectronic materials [21-24]. Returning to the adverse effect of reduced stability: the organic ligands act as separators, inducing voids inside the QD films that create a pathway for air to diffuse through and degrade the crystals irreversibly. In fact, the susceptibility to air oxidation [21], Ostwald ripening from solid-state diffusion [25], non-passivated surface states and the significant tunneling barriers [19, 20] found in these films have been the major challenges that have frustrated the use in working devices.

The open space created by the separating ligands also allows other molecules to diffuse into the film, and this feature is used in this paper: precursor molecules for coating the QDs can penetrate easily, such one can coat deep layers of QDs in the assembled film without diffusion limitations just as well as the outer layers of QDs close to the surface [26, 27]. Recently, atomic layer deposition (ALD) of aluminium oxide (a.k.a. alumina; i.e., Al₂O₃), carried out at 25–75 °C and ~0.15 Torr, was used to infill and overcoat PbSe QD films and stabilize them against air degradation [15, 28]. ALD of alumina involves cyclic, self-terminating, gas-phase reactions between trimethylaluminium (TMA) and an oxidizer, such as oxygen or water, to deposit thin and conformal films [29-31].

Crucially, we modified this ALD process to work at economically much more attractive conditions, room temperature and atmospheric pressure [32, 33]. Typically, Al₂O₃ ALD is carried out at near vacuum to ensure the removal of unreacted species from the substrate [34-36]. Obviously, avoiding vacuum would be attractive, and a room-temperature process would be completely compatible with the fabrication of the QD films, also done at ambient conditions [4]. The potential problem that requires analysis and optimization is the physisorption of unreacted species on the substrate, inducing a less precise chemical vapor deposition (CVD) type of growth characterized by the deposition of several layers of alumina in each cycle [33, 34, 37]. We show in this paper that indeed occurs, but that this not reduce the capacity of the alumina in enhancing stability. Replacing the liquid precursors, i.e., water, by gaseous ones, i.e., air, would reduce the accumulation of unreacted species on the QD films, providing a more precise control over the deposition of ultrathin films of alumina.

In previous work by Law and co-workers [15, 22, 28, 38], the deposition of alumina on QD films successfully prevented oxidation and photo-thermal degradation, allowing direct use in open air. According to reference [28], the alumina also acted as a matrix to prevent solid-state

diffusion of atoms, that reduced the tunneling barrier for charge transfer between the quantum dots and passivated the surface charge traps, thereby enhancing the charge mobility by one order of magnitude. However, despite the excellent performance of Al₂O₃-ALD on QD films as passivating material, there is a lack of studies on the deposition mechanism of alumina inside the films. Recent work done in the field has triggered interest into understanding the process of alumina deposition in the pores of quantum dot films [28]. Parameters such as the combined effect of temperature and pressure on the deposition of alumina, and the minimum amount of alumina that is required to fully protect the QD films from degradation, have not been investigated yet. Also, little is known about the growth of alumina in the pores of the QD film during the ALD process.

Here we demonstrate the deposition of alumina inside EDA capped PbSe QD films at room temperature and atmospheric pressure. The first cycles lead dominantly to infilling, i.e., the alumina grows between the QDs, and when the interstitial space between the QDs is filled, additional cycles lead to overcoating of the films, i.e., the formation of a layer of alumina on top of the QD film. For this aim, we investigated (i) the amount of alumina deposited at ambient conditions after different number of cycles, (ii) the deposition mechanism of alumina inside the films, (iii) the air-stability of QD films coated with different number of cycles, and (iv) the deposition of alumina using a diluted flow of dry air after 25 cycles and its stability under air. We observed the infilling of alumina from the first dosage of TMA and explain this by the reactivity of TMA molecules with hydroxyl and amine groups present as remaining of the solvent used during the sip-coating of the QD film and the organic ligands, respectively. Furthermore, we also demonstrate that efficient infilling with Al₂O₃ ALD at ambient pressure and room temperature is possible, significantly enhancing the speed and ease of the process. This could be combined with the fabrication process of the QD films, also done at ambient conditions, to develop a continuous process in which the OD films would be produced and passivated in a one-go process, using a similar technology as the spatial ALD reactors [39-41].

4.2 Experimental

4.2.1 PbSe QD solution

To prepare the OD solution, we used the following reactants: PbO (99,999%), oleic acid (technical grade, 90%), 1-octadecene (technical grade, 90%), diphenylphosphine (98%), anhydrous 1-butanol (98%), methanol (99.8%), n-hexane (95%), acetonitrile (99.8%) and tetrachloroethylene (TCE, >99%), which were purchased from Sigma-Aldrich, trioctylphosphine (TOP, >90%) and 1,2-ethanediamine (EDA, >99.5%), purchased from Fluka, and selenium powder (200 mesh, 99.999%), purchased from Alfa Aesar. In the preparation, 0.66 g of PbO were dissolved in a mixture of 30 mL of 1-octadecene and 2.2 mL of oleic acid, which were degassed at 100 °C for one hour under vacuum. 10.8 mL of that solution were injected into a solution 1 M of Se in TOP. Then, 84 uL of DPP (diphenylphosphine) were injected into 28.4 mL of the prepared Pb(oleate) at 180 °C. This mixture was allowed to react at 160 °C for 2 min to form ~6.4 nm QDs, determined from the first absorption peak, after which it was quickly cooled by a water bath. The QDs were precipitated with butanol/methanol mixture and centrifuged at 5000 rpm for 5 minutes. The precipitate was redissolved in hexane and washed with butanol/methanol mixture once again. The QDs were then dispersed in TCE for optical absorption measurements and in hexane for film preparation. All the synthesis was done in a Schlenk line under nitrogen atmosphere.

4.2.2 EDA in methanol solution

A 1 M solution of EDA in methanol was used to replace the long ligands, i.e. C18 chains, by short ligands, i.e. EDA, to couple the QDs electronically.

4.2.3 Quartz substrate

The dimensions of the quartz substrates used as support are 25 mm x 10 mm x 1 mm. The substrates were cleaned by sonication for 5 minutes in 5% Triton solution followed by 5 minutes sonication in water and finally 5 minutes sonication in ethanol, to ensure good adhesion of the QDs to the substrate. The quartz substrates were dried in a flow of nitrogen and clamped to the mechanical arm of the dip coater.

4.2.4 Fabrication of QD films

We deposited the PbSe QDs on quartz substrates via layer-by-layer dip-coating in three solutions inside a N_2 -purged glovebox: (i) PbSe QDs in hexane for 30 s, (ii) 1 M solution of EDA in methanol for 30 s, and (iii) rinsing solution of methanol for 30 s. The dip-coating of the substrates was repeated 20 times. The mechanical dip-coater used in the fabrication of the films was a DC Multi-8 from Nima Technology. The synthesized QD films were stored in a glovebox to avoid contact with air. The fabricated films had a thickness of approximately 35 nm, determined by a depth profile measurement by a stylus profilometer.

4.2.5 Alumina coating reactor

The alumina coating experiments were performed in an air-tight purpose-made reactor operated at atmospheric pressure and 27 °C. The operating temperature was controlled by an external IR lamp and measured with a thermocouple inserted in the reactor. The reactor consisted of a glass column, 42 mm of diameter and 140 mm in length, with a Teflon holder inside in which the QD films were placed facing downwards, so that they were exposed to the precursors during the coating. The holder has 10 slits, separated vertically by 1 cm, allowing the coating of multiple samples simultaneously. The glass column and the Teflon holder are fixed to the inlet and outlet connections with a ring, that sealed the reactor. The reactor was provided with two valves to maintain an oxygen-free environment. The QD films are loaded into the reactor inside a glovebox, to avoid that the QD are exposed to air, and then transported to the coating setup, in which we connected the reactor to the inlet of the precursors. A sintered stainless steel SIKA-R 20 AX distributor plate with a pore size of 37 µm was used to homogeneously distribute the flow of precursors inside the reactor. The offgas from the reactor is taken to a series of bubblers filled with Kaydol oil, to trap unreacted molecules of the precursors and the by-products of the coating reaction. The precursor bubblers, the glass column and the washing bubblers are placed inside a nitrogen-blanketing cabinet as a TMA safety measure. The cabinet is operated at an O_2 concentration below 6%.

4.2.6 Alumina coating precursors

Semiconductor grade trimethylaluminium (TMA), purchased from Akzo Nobel, distilled water and synthetic air were used as precursors, while pressurized N_2 grade 5.0 was used to transport the precursors to the reactor, and to purge it after each reaction. TMA and water were placed in a 600 mL WW-600 stainless steel bubbler and kept at 30 °C during the coating experiments. To have a comparable concentration of oxygen to the equivalent experiments with water, we mixed a flow of 0.5 L/min of N_2 with 0.1 L/min of dry air. Some of the experiments were done using H₂O as second precursor, and few others using synthetic air. A fixed gas flow of 0.6 L/min was chosen for all the experiments performed.

4.2.7 Alumina coating experiments

We used dosing times per cycle of 15 s - 5 min - 15 s - 5 min for the dosing sequence TMA – $N_2 - H_2O$ /synthetic air – N_2 to coat two QD films, which were placed at the same height of the holder in all the experiments. The same dosing times were used in all the coating experiments. We performed coating experiments at 27 °C and 1 bar with different number of cycles, i.e., 1, 3, 5, 8, and 25 cycles, using three different substrates: PbSe QD films prepared with EDA-methanol solution, PbSe QD films prepared using EDA-acetonitrile solution, and a dodecanethiol self-assembled monolayer on a gold-coated substrate. To study the air-stability, we prepared other Al₂O₃-coated films with 1, 10 and 25 cycles, using the same dosing and purging times, i.e. 15 s - 5 min - 15 s - 5 min - 0.5 s - 5 min. The total amount of both precursors dosed during the 90 shorter cycles would be equivalent to the amount one dosed during 3 cycles using the same dosing times as in the rest of the samples, i.e., 15 s - 5 min - 15 s - 5 min. For this reason, we refer to this 90-shorter-cycle sample as the sample coated with "3 equivalent cycles" (Figure 4.8b), in order to compare the air-stability with the rest of the coated QD films.

4.2.8 Characterization of the deposition of Al₂O₃

To study the deposition of alumina, we measured the concentration depth profile of the different elements with a Thermo Scientific X-ray photoelectron spectrometer (XPS) K-Alpha, equipped with a monochromatic Al K α radiation source and a pass energy of 100 eV for the survey scan, and ion-beam etching unit. The XPS device, which operates at ultrahigh vacuum, is equipped with an etching unit, that uses Ar⁺ ions with energy of 1000 eV and a raster size of 2 mm, to remove layers of the QD films with an etching rate of 0.5 nm/s (Supplementary Information SI I). We used the combination of the XPS and etching unit to measure the concentration depth profile of the coated substrates. During the XPS analysis, the spectra of the elements was charge-corrected with the adventitious carbon peak at 284.8 eV. We used the software Thermo Avantage 5.913 and Gaussian curves to deconvolute the peaks. During the XPS measurements, we used the flood gun to compensate for the positive charge. We used a microtome to prepare a slice of one alumina-coated QD film and examine it under a Tecnai F20 TEM microscope. We measured the film thickness of the alumina overcoat in 130 points from nine TEM images to determine the mean value of the alumina film and the standard deviation.

4.2.9 Characterization of the air stability of the coated QD films

The alumina-coated and uncoated QD films were exposed to air at 80 °C and UV light, and their optical absorption spectra were measured using a Perkin-Elmer Lambda 900 spectrophotometer, equipped with an integrating sphere. The position of the maximum peak of the band gap indicates the stability of the QD crystals, since the band gap absorption peak blue shifts and broadens in the case of oxidation of the PbSe QD films. We measured the absorption spectrum of all the uncoated QD films before the coating experiments. The coated QD films were exposed to air, and the optical absorption was measured periodically, from 1 to 63 days.

4.2.10 Preparation of the dodecanethiol self-assembled monolayer

We used the following solutions to prepare the self-assembled monolayer (SAM): dodecanethiol (>99.5%), ethanol (>99%) and nitric acid (63%), purchased from Sigma Aldrich. As substrate, we used 10 mm x 10 mm x 1 mm glass plates, sputter-coated with 200 nm thick gold layer (purchased from SSens BV, The Netherlands). The gold-coated substrates were washed in a 2% nitric acid solution for 5 min and then rinsed with ethanol and dried under nitrogen. The plates were then immersed in a 1 M solution of dodecanethiol in ethanol for 18 h. After that, the plates were taken out, washed with pure ethanol and dried under a nitrogen atmosphere.

4.3 Results and discussion

In this work, we infilled and overcoated QD films with alumina at atmospheric pressure and room temperature. We used PbSe QD films with a thickness of 35 nm, measured with a stepprofilometer, consisting of 6 nm QDs separated by EDA organic ligands. In each experiment, two films were placed in the ALD reactor holder at the same height. Alumina ALD is typically deposited using TMA and water as precursors according to the general reaction mechanism consisting of two subsequent reactions, in which || denotes the surface species [29].

Reaction A: $\parallel - Al - OH + Al(CH_3)_3 \rightarrow \parallel - Al - O - Al(CH_3)_2 + CH_4$

Reaction B: $\|-Al - O - Al(CH_3)_2 + 2H_2O \rightarrow \|-Al - O - Al - (OH)_2 + 2CH_4$

In reaction A of the first cycle, functional groups are needed to react with the precursor molecules and initiate the deposition. These active sites can be any group that readily reacts with TMA molecules, such as hydroxyl and amine groups [29, 42]. During the first cycles, both precursors can diffuse through the voids of the QD films, depositing alumina inside the film, i.e., the infilling stage. By increasing the number of cycles, the voids would get fully infilled and the precursors react on the surface of the QD film, creating an overcoating (Fig. 4.1).



Fig. 4.1. Cartoon showing (from left to right) an uncoated, an infilled and overcoated QD film (red spheres) with alumina (blue matrix).

4.3.1 Deposition of Al₂O₃ using water as precursor

We performed 1, 3, 5, 8 (Fig. 4.2) and 25 cycles (Fig. 4.3), at 27 °C and 1 bar, to study the growth of alumina inside the PbSe QD films. In the concentration depth profile, we observed the evolution of the intensity of the different peaks of Pb4f and Se3d belonging to the QDs, Al2p coming from the deposited alumina, C1s from the EDA ligands, Si2p from the quartz substrate and O1s from both deposited alumina and quartz substrate.



Fig. 4.2. XPS concentration-depth profile of the PbSe QD films coated with alumina after (**a**) 1 cycle, (**b**) 3 cycles, (**c**) 5 cycles and (**d**) 8 cycles of ALD. The depth profiles were obtained by etching the QD films with Ar^+ ions.

During the initial ALD cycles, i.e., 1 and 3 cycles (Fig. 4.2a and 4.2b), both TMA and water penetrated all the way to the wafer through the pore network between the QDs and deposited as alumina in the entire film. This is clearly seen from the atomic percentages of Pb, Se and

Al in Fig. 4.2a, that remain more or less constant with the increased etching of the assembled film, all the way down to the quartz substrate. Similarly, the depth profiles of the films coated with 5 and 8 cycles (Fig. 4.2c and 4.2d) show that alumina is deposited down to the quartz substrate. In Fig. 4.2c, the amount of Al slightly decreases with increasing etch depth. This indicates that diffusion limitations start to occur as the overcoated layer becomes thicker. Also Figs. 4.2b-c show that he layer grows, because the atomic percentage of aluminium increases with increasing number of cycles.

Fig. 4.3a shows that overcoating of alumina has occurred in the sample coated with 25 cycles, since only the signals of Al and O are present during the first tenths of nanometers in the concentration depth profile (Fig. 4.3a). The Al:O ratio is around 1.5 in the overcoating as expected for Al_2O_3 molecule. The overcoating can also be clearly seen in the cross sectional TEM image of a 25-cycle sample (Fig. 4.3b). The XPS profile and TEM image in Fig. 4.3 do not correspond to the same sample, but to two different batches. We can see that by the thickness of the PbSe QD film, which is larger than in the XPS depth profile.



Fig. 4.3. (a) XPS depth profile of the QD sample coated with 25 cycles of alumina. (b) Cross-section TEM image of the 25-cycle QD film, in which the alumina overcoating is visible.

Carbon was also detected on the surface of the alumina overcoating in the 25-cycle QD film (Fig. 4.3a). This carbon signal probably originated from unreacted methyl groups from the TMA molecules, although it quickly decreased to an atomic percentage close to zero after etching the upper layers of the coated sample. This shows that the amount of unreacted methyl groups is negligible within the alumina overcoat. Once the alumina overcoat is etched away and the QD film measured, the atomic percentage of C increased again, most likely from the EDA ligands. In the XPS spectra of the films coated with 1, 3, 5 and 8 cycles (Fig. 4.2), C1s was also detected in a similar atomic percentage. This indicates that the alumina does not replace the organic ligands, but would deposit around them and on the surface of the QD film, and after a several cycles, the alumina formed an overcoating, although we do not have a clear evidence about the transition between the infilling and overcoating regimes (Fig. 4.2 and 4.3).

To gain more insight into the deposition process, we first calculated a growth per cycle (GPC) of alumina during the infilling, considering that the alumina only deposits on the surface of the QD crystals. And secondly, we studied the deposition of alumina on different substrates to study the reaction of the precursors in the QD films and define a reaction mechanism. For that, we dosed TMA to different substrates, i.e., a QD film prepared with methanol as solvent,

a QD film prepared using acetonitrile as solvent, and a substrate covered with a dodecanethiol self-assembled monolayer.

4.3.2 Estimation of the growth per cycle of Al₂O₃

To calculate the amount of alumina deposited in each cycle, we modelled the PbSe QD film as an array of monodispersed spheres, with a particle diameter (d_P) of 6.4 nm, separated by 1,2-ethanediamine organic ligands. We assumed that alumina was only deposited on the surface of the QD crystals. The atomic ratio between Pb and Se atoms in a QD is, in average, 1.9:1 according to the XPS results (Fig. 4.2). An excess of Pb is common for PbSe QDs [43, 44], although we note that the ratio observed here is higher than usually reported. We used the atomic ratio of Pb and Al in the film coated with 1 cycle (Fig. 4.2a), to calculate the number of atoms of aluminium in one QD. Using the molecular mass of Al₂O₃ and its density [35], we calculated that 0.6 nm of alumina were deposited in the first cycle. Considering an average value of the GPC for alumina ALD on nanoparticles of 0.15 nm [45-49], and that the theoretical size of an Al₂O₃ monolayer is about 0.38 nm [34], we estimate that 1.5 monolayers of alumina were deposited per cycle during the infilling of the QDs films. However, this value of the GPC could be lower if we consider that alumina could deposit also around the organic ligands. More detail of the calculation can be found in the Supplementary Information 4.B.

4.3.3 Study of the deposition mechanism of Al₂O₃

The GPC of alumina during infilling and the relatively large overcoating-film thickness measured from TEM (Fig. 4.3b) indicates that the deposition of alumina is faster than the one expected for ALD experiments, i.e., 0.1-0.2 nm per cycle. Working at ambient conditions can involve a CVD-type of growth due to accumulation of unreacted precursor molecules on the substrate [33]. However, we found a high deposition of alumina during the first cycle, where no unreacted precursors were present. To explain this, we investigated three possible mechanisms. First, we studied whether TMA molecules could physisorb on the ligands by exposing a dodecanethiol self-assembled monolayer (SAM) film to TMA. Secondly, we investigated if there are any remaining solvent molecules entrapped in the QD film that may act as active sites. This was realized by measuring the concentration depth profile of an uncoated QD film prepared using different solvents while dip-coating. And third, we considered whether the amine groups from the EDA organic ligands could act as active sites and react with TMA molecules.

4.3.4 Study of the reaction of TMA on a dodecanethiol SAM

We used a self-assembled monolayer of dodecanethiol on a gold substrate to study whether TMA molecules would physisorb on the organic ligands. If true, it would eventually result in a faster deposition of alumina. We prepared the dodecanethiol SAM, and loaded it into the coating reactor inside a glovebox to prevent contact with air and humidity, and carried out a half-coating cycle, i.e., we just exposed the film to TMA. We measured the atomic percentages on the surface of the exposed SAM (Fig. 4.4), finding a small amount of aluminium. In case TMA molecules would physisorb on carbon groups, we would have found a larger amount of aluminium with XPS. This result suggests that TMA does not physisorb on carbon groups, thus it is unlikely that it would on the EDA organic ligands with similar

methyl groups. We calculated that a full monolayer of physisorbed TMA would produce an atomic percentage of about 3.5%, while in Fig. 4.4 it is only ~ 0.3% (Supplementary information 4.C). This is an order of magnitude difference; of course, a SAM is different from the 3D complex structure of ligands in the assembled QD film, but the results obtained here are convincing enough to, as a first approximation, rule out physisorption of carbon groups.



Fig. 4.4. Atomic concentrations from XPS on the surface of the SAM after being exposed to TMA.

4.3.5 XPS depth profile of an uncoated QD film

We measured the concentration depth profile of the uncoated QD film to study the presence of solvent molecules (Fig. 4.5). As expected, no Al traces were detected; however, O1s signals were observed. This may point to the presence of oxygenated compounds that could possibly react with TMA molecules during the first cycle causing a fast deposition of alumina.



Fig. 4.5. XPS concentration depth profile of an uncoated QD film.

To determine the nature of the source of oxygen, we studied the spectra of the elements detected by XPS after etching 7 nm of the PbSe QD film (Fig. 4.6). At this depth, N1s signals were observed, which can be attributed to the NH bonds present in the EDA organic ligands, and a Se Auger peak, both in the same range of binding energies (Fig. 4.6a). The intense peak at 284.8 eV (Fig. 4.6b) indicates the presence of C-C bonds [50-53]. The peaks at 286.1 and 288.7 eV are attributed to C atoms bound to electronegative atoms [53-55], such as –COOH or –COH (Fig. 4.6b). These results are consistent with the presence of a peak at 533 eV, which is typical of –OH groups (Fig. 4.6c). The acid groups may originate from the oleic acid used to prepare the colloidal solution of PbSe QD crystals, while the observed alcohol features could come from the methanol used during the fabrication of the QD films via dip-

coating. To conclude this part, the XPS spectra gives strong evidence of the presence of oxygen-rich compounds and –NH bonds, which would readily react with TMA molecules during the first cycle, causing a fast deposition of alumina.



Fig. 4.6. XPS spectra of the different elements found in an uncoated PbSe QD film, at an etch-depth of approximately 7 nm. (a) Elements corresponding to the QD film, such as nitrogen and selenium. (b) C1s region spectrum, showing different contributions of carbon, including alcohol and acid bonds, and (c) hydroxyl groups.

To investigate a possible role of the solvent used during dip-coating, we exposed three QD films, prepared in different manners, to a single pulse of TMA without completing the cycle with water. These three samples were: (i) QD film prepared using a solution of EDA in methanol (Fig. 4.7a), exactly the same as the QD films that were coated with alumina; (ii) QD film prepared exactly the same way as the previous one, but drying it after the fabrication for 24h in a vacuum chamber at room temperature (Fig. 4.7b); (iii) QD film prepared using a solution of the EDA ligands in acetonitrile instead of methanol (Fig. 4.7c), aiming to reduce the presence of oxygenated compounds inside the QD films and study the reaction between TMA molecules and nitrogen-based functional groups, such as $-NH_2$ from the EDA ligands and -CN from the acetonitrile. In the sample that was not dried (Fig. 4.7a), hardly any nitrogen was detected. We found, however, that by decreasing the exposure time to the beam N_2 could be detected (Fig. 4.7b and 4.7c). The rest of elements showed similar profiles between the samples with no treatment and drying post-treatment (Fig. 4.7a and 4.7b). Oxygen was detected in the sample prepared with acetonitrile (Fig. 4.7c). One would expect this sample to contain much less oxygen than the samples prepared with methanol. This suggests that the oxygen might come from the remaining oleate on the QDs surface, as it is known that protic solvents such as methanol are more efficient in removing oleate [56], which also explains why the QD film prepared with acetonitrile is thinner than the ones prepared with methanol.



Fig. 4.7. XPS depth-profiles after dosing one pulse of TMA to (**a**) a QD film prepared with a solution of EDA ligands in methanol, (**b**) a QD film prepared with a solution of EDA ligands in methanol and dried for 24h under vacuum, and (**c**) a QD film prepared with a solution of EDA ligands in acetonitrile.

4.3.6 Reaction between TMA and amine groups

As the third possibility, we could explain the high deposition of alumina by the reaction between TMA molecules and the amine groups of the EDA organic ligands. According to the general scheme of Al₂O₃-ALD, TMA would react with hydroxyl groups to form alumina. However, it does not necessarily have to begin with OH groups. Al₂O₃ has been deposited on boron nitride (BN) hexagonal platelet-like particles via ALD [46]. BN surfaces contain both hydroxyl and amine functional groups [57-59], which would react with TMA molecules. In addition, ammonia has been used as second precursor in ALD, to deposit aluminium nitride (AlN) [30, 42], proving the reactivity between TMA and amine groups. Therefore, the amine groups from the EDA ligands could act as active sites where TMA can chemisorb during the first cycle. In the second cycle, after the first exposure of water, only hydroxyl groups would be available for reaction, since amine groups cannot be regenerated by using water as second precursor.

We conclude that the fast deposition of alumina during the first cycle cannot be explained by one single cause, but rather as the contribution of the hydroxyl and amine active sites present in the uncoated film and the large excess of precursor molecules, which resulted in a CVD-type of deposition. We note that, while unexpected, this allows very easy and rapid infilling of these QD films by a single exposure to TMA at room temperature and atmospheric pressure.

4.3.7 Study of the air stability of Al₂O₃-coated QD films

We investigated the passivation efficiency of the alumina coatings with different film thickness. We evaluated four samples: uncoated QD film, film coated at 27 °C with an amount of alumina equivalent to 3 cycles (see section 4.2.7), film coated with 10 cycles at 70 °C, and film coated with 25 cycles at 27 °C. In this study, we used a solution of EDA in methanol to prepare the QD films. The three coated films and one uncoated QD film were placed in an oven and exposed to air at 80 °C, and separately to UV light, similarly to the accelerated test for photovoltaic devices [60]. We measured the optical absorption spectra periodically, and compared them with the spectra of each film before the coating experiment, shown as the 0 days curves. We assessed the stability of the QD films by measuring the position of the maximum of the peak in the optical absorption spectra, which corresponds to the band gap of the QD film. The peak exhibits a blue shift and broadens due to the oxidation of the QDs, which results from an effective reduction of the QD size, as seen for the uncoated QD film (Fig. 4.8a). The quick oxidation of the QDs agrees with previous studies [21]. We found that 3 cycles does not deposit enough amount of alumina to fully passivate the QD film (Fig. 4.8b). However, the film coated with 10 cycles was stable upon air exposure at least for 27 days (Fig. 4.8c). This film was coated at 70 °C rather than 27 °C as was done the other films. We think that at 70 °C, less amount of alumina would be deposited since unreacted molecules could not physisorb as easily as at room temperature. That means that we could safely assume that 10 cycles at 27 °C would stabilize the QD film also, and probably with lower number of cycles. As expected, 25 cycles at 27 °C provided full protection of the QD film (Fig. 4.8d), at least for 63 days. We found that the optimum for the stabilization of these PbSe QD films was between 3 and 10 cycles. Therefore, going to higher temperatures would not be required to protect the QD films from oxidation after a relatively small number of cycles.



Fig. 4.8. Optical absorption spectra of (**a**) uncoated QD film, (**b**) QD coated at 27 °C with an amount of alumina equivalent to 3 cycles, (**c**) QD coated with 10 cycles at 70 °C, and (**d**) QD coated with 25 cycles at 27 °C, measured periodically after exposure to air at 80 °C and UV light. The coating experiments were carried out at 27 °C.

4.3.8 Study of the deposition of Al₂O₃ using synthetic air as oxidizer

To complete this study, we used an alternative second precursor, a diluted flow of air instead of water, to investigate whether we could reduce the deposition rate of alumina and get closer to the ALD growth, since it is easier to remove the excess of oxygen molecules. We performed 25 cycles, and measured the concentration profile with XPS (Fig. 4.9a). It seemed that both infilling and overcoating occurred, although in this case the overcoating thickness is thinner than the one with water (Fig. 4.3a). Water has a strong tendency to adsorb on the surface, specially at room temperature and atmospheric pressure [61]. Contrary to that, when using a diluted flow of air as in our case, no accumulation would be produced as the unreacted molecules of oxygen would be expected to leave the reactor. That results in lower deposition rates, and therefore, a thinner overcoating layer of alumina. However, we found that the QD film showed signs of oxidation during the coating with oxygen (Fig. 4.9b); this was not observed when using water as co-reactant. We performed an additional coating experiment with 1 cycle, using synthetic air as second precursor, to study the oxidation of the QDs. We measured the optical absorption of the films before and after coating them with 1 and 25 cycles, and found a blue shift of the band gap. The shift of the band gap is similar for both 1and 25-cycle QD films, indicating that the crystals mainly oxidized during the first cycle. The band gap shifted to a wavelength of 1800 nm, very similar to the shift of the uncoated OD film after air exposure (Fig. 4.9b), which shifted to 1750 nm approximately. That indicates that using a synthetic stream of air as second precursor, even with a low concentration of oxygen, fully degraded the QD crystals, thus not being an adequate oxidizer for the deposition of Al_2O_3 on QD films.



Fig. 4.9. (a) XPS depth profile of PbSe QD film coated with 25 cycles of alumina, using synthetic air as oxidizer. (b) Optical absorption spectra of QD films coated with 1 and 25 cycles of alumina when using synthetic air as oxidizer.

4.4 Conclusions

We deposited alumina on PbSe QD films at room temperature and atmospheric pressure, using an ALD-like approach. During the first cycles, the alumina infilled the voids of the QD films, and after several cycles, there was a transition at which an alumina overcoating was formed. The combination of infilling and overcoating for a number of cycles between 3 and 10 effectively passivated the QD film, which did not show any oxidation after an exposure to air at 80 °C and UV light for a maximum time tested of 27 days. We calculated that during the first cycle, we deposited about 1.5 monolayers of alumina on the QD crystals. We think that this fast growth is the combination of the dosage of excess of precursors, and the presence of hydroxyl and amine groups inside the film, which acted as active sites. Having a higher deposition rate of alumina at atmospheric pressure and 27 °C, was beneficial to infill and overcoat the QD films faster to stabilize the samples against oxidation. Finally, we deposited alumina using synthetic air as second precursor, instead of water, to reduce the physisorption of water molecules that produced the rapid growth of alumina, obtaining a thinner overcoating than the one deposited with water. However, the PbSe crystals degraded even during the first exposure to synthetic air. This work shows that depositing alumina on QD films at atmospheric pressure and room temperature gives results that are similar to those obtained at lower pressures. Working at ambient conditions facilitates the processing of QD films, since less equipment is required, and can be coupled directly to the fabrication of QD films, which is also done at atmospheric pressure and room temperature.

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4.A Validity of XPS measurements to determine film thickness

Determining the thickness of the alumina overcoating with XPS is not accurate, since the beam of X-rays has a penetration depth in which the concentration of the elements is measured. We fixed an etching rate of 0.5 nm/s, although it depends on the material etched; a harder material would etch slower than a softer one. Despite the etching depth measured from XPS cannot be considered as the conclusive film thickness, we can still use these values to compare the depth profiles between the different coated QD samples.

4.B Estimation of the growth per cycle of Al₂O₃

To calculate the amount of alumina deposited in each cycle, we modelled the PbSe QD film as an array of monodispersed spheres, with a particle diameter (d_P) of 6.4 nm, separated by 1,2-ethanediamine organic ligands. We assumed that alumina was only deposited on the surface of the QD crystals. We used a density of the QD of 8.3 g/cm³, and a calculated molecular mass for the QD of 162.3 g/mol, based on the atomic masses of Pb and Se, and the Pb:Se atomic ratio. Using the size, molecular mass and density, we calculated the volume, $1.4 \cdot 10^{-19}$ cm³, and the number of moles, $7 \cdot 10^{-21}$ mol, of one QD. Therefore, one QD consists of $4.6 \cdot 10^{-21}$ mol of Pb and $2.4 \cdot 10^{-21}$ mol of Se. In the XPS profile of the 1-cycle coated film (Fig. 4.2a), we measured the same atomic percentages of Pb and Al. Hence, there were also $4.6 \cdot 10^{-21}$ mol of aluminium in each QD, that corresponds with $2.3 \cdot 10^{-21}$ mol of aluminium oxide, since there are two moles of aluminium in one mole of aluminium oxide. Using the density of the aluminium oxide of 2.5 g/cm³ [35] and molecular weight, 102 g/mol, we calculated a volume of alumina (V_{Al2O3}) in each crystal of 9.3 $\cdot 10^{-23}$ cm³. We used (Eq. 1) to calculate a film thickness of alumina (δ_{Al2O3}) of 0.6 nm in each QD crystal. This calculation considers that the volume of the Al₂O₃-QD core-shell is the sum of the volume of the QD crystal and the volume of the alumina.

$$\delta_{Al2O3} = \frac{1}{2} \cdot \left[\left(\frac{6}{\pi} \cdot V_{Al2O3} + d_P^3 \right)^{1/3} - d_P \right]$$
(Eq. 4.B.1)

By using an average value of the GPC for alumina ALD on nanoparticles of 0.15 nm [45-49], we estimated that 4 monolayers of alumina were deposited per cycle during the infilling of the QD dots.

4.C Concentration of a monolayer of TMA physisorbed on the dodecanethiol SAM

The atomic percentages measured with XPS after one exposure of TMA are shown in the table below.



Fig. 4.C.1. Atomic content of the dodecanethiol after exposure to TMA.

As expected for dodecanethiol, the ratio C/S is about 12. The physisorption of a full monolayer of TMA on the SAM would mean that one TMA molecule would physisorb in each of the dodecanethiol chains, therefore, we would have the same atomic percentage of S than of Al. In addition, the number of carbon atoms would increase as well due to the three methyl groups in a TMA molecule. Therefore, recalculating the atomic percentages, we could expect 3.5% of sulfur and aluminium, 51% of carbon, 41.5% of gold and 0.5% of oxygen.
Chapter 5

Producing SiC tracer particles using gas-phase deposition of Al₂O₃ at ambient conditions

We have enhanced the radio-activation efficiency of SiC (silicon carbide) particles, which by nature have a poor affinity towards ¹⁸F ions, to be employed as tracers in studies using PEPT (Positron Emission Particle Tracking). The resulting SiC-Al₂O₃ core-shell structure shows a good labelling efficiency, comparable to γ -Al₂O₃ tracer particles, which are commonly used in PEPT. The coating of the SiC particles was carried at 27 ± 3 °C and 1 bar in a fluidized bed reactor, using trimethylaluminium and water as precursors, by a gas phase technique similar to atomic layer deposition. The thickness of the alumina films, which ranged from 5 to 500 nm, was measured by elemental analysis and confirmed with FIB-TEM (focus ion beam – transmission electron microscope), obtaining consistent results from both techniques. By depositing such a thin film of alumina, properties that influence the hydrodynamic behaviour of the SiC particles, such as size, shape and density, are hardly altered, ensuring that the tracer particle shows the same flow behaviour as the other particles. The paper describes a general method to improve the activation efficiency of materials, which can be applied for the production of tracer particles for many other applications too.

Submitted as: D. Valdesueiro, P. Garcia-Trinanes, G.M.H. Meesters, M.T. Kreutzer, J. Gargiuli, T. Leadbeater, D.J. Parker, J. Seville and J.R. van Ommen. *Enhancing the activation of silicon carbide tracer particles for PEPT applications using gas-phase deposition of alumina at room temperature and atmospheric pressure.*

5.1 Introduction

Positron Emission Particle Tracking (PEPT) is a powerful non-invasive technique to follow the motion of individual particles in industrial processes [1, 2], which are opaque to other tracking methods [3-5]. The positron emitter most commonly used in such studies is ¹⁸F, which has a half-life of 110 minutes. The level of radioactivity of the tracer will define the performance of the PEPT measurement, which depends on the intensity of the signal in the "positron camera" detectors to reconstruct the trajectory of the tracer in the three dimensions [6]. Using a tracer with low emission intensity results in poor resolution of the spatial location of the tracer [7-9].

In previous PEPT studies [10-12], tracers have been produced either by direct irradiation of the sample in a suitable cyclotron, converting oxygen in the sample directly to ¹⁸F, or by irradiation of water, which is then exchanged with, or attached to, molecules on the surface of the tracer. The trajectory of the tracer is understood to be representative of the motion of all the particles in the system, which is only the case if the emitting particle is identical, from a granular-matter point of view, to the particles of interest. This can be readily achieved if the particles can adsorb the emitter. However, in some cases this does not occur. This work deals with the problem that appears when the particles do not adsorb the emitter. Then, one can take a different particle to be used as tracer, accepting the mismatch in some properties, or one can develop a particle that emits sufficiently and remains practically identical to the other particles. This paper explores this last option for silicon carbide (SiC) particles.

SiC particles are used as a heat transfer medium in fluidized beds to harvest solar energy in concentrated solar thermal plants [13, 14]. The advantages of SiC in this application include high heat capacity, high sintering temperature, good availability and low cost. The favourable properties of fluidized beds regarding mixing and processability at large scale make them attractive in energy applications such as gasification and combustion of biomass, and chemical looping combustion [15-17]. In all these applications, ensuring and quantifying the good circulation of the particles is essential, and for this PEPT is a uniquely powerful technique. Unfortunately, SiC hardly adsorbs ¹⁸F.

We demonstrate the production of a core-shell structure to be used as a PEPT tracer particle that better adsorbs the radioactive ions than the core itself. We used SiC as core material and deposited films of Al_2O_3 using a gas-phase coating technique, similar to atomic layer deposition (ALD), using trimethylaluminium (TMA) and water as precursors, at atmospheric pressure and room temperature [18]. Providing the native SiC particles with a thin coating that can be made radioactive is an attractive alternative to enhance the labelling efficiency of these particles , defined as the ratio of radioactivity absorbed by the SiC particles to the radioactivity of the water solution [19]. Historically aluminium oxide has proved to be a very successful material used for PEPT tracers due to its high affinity for ¹⁸F ions [20].

The SiC particles used here, with an average particle size $(d_{3,2})$ of 68 µm and density of 3210 kg/m³ (*Supplementary information 5.A*), have the required thermal properties and fluidization behaviour (Geldart A type [21]). However, the inert surface of SiC particles causes poor adsorption of ¹⁸F. Other particles with higher labelling performance, such as ion exchange resins or γ -Al₂O₃ particles [22], are effective as emitters, but their different density, size and shape make them poor tracers in this application because their trajectory is different from the SiC particles in the fluidized bed.

ALD is used to deposit inorganic compounds with accurate control based on a set of two reactions repeated a certain number of times [23, 24]. ALD has been applied either to functionalize [25, 26] or protect [27, 28] the surface of flat substrates or powders. We used ALD to reproduce the affinity between ¹⁸F ions and the surface of γ -Al₂O₃ particles [20, 22]. Normally, ALD of alumina is performed at about 170 °C and absolute pressures of about 1 mbar to ensure the removal of the excess of precursors from the reactor, and obtain atomic growth of the films, i.e. between 0.1 and 0.2 nm per cycle [29-31]. We carried out the coating of SiC particles in a fluidized bed reactor^{30, 31} at 1 bar and 27 °C. At these conditions, the removal of the excess of precursors is diminished, and this excess can physisorb on the surface of the SiC particles [32], resulting in a CVD (chemical vapour deposition) type of reaction and thus, higher growth per cycle (GPC) of alumina [18, 33].

To further accelerate the growth of the alumina films, we treated two samples with oxygen plasma prior to coating to increase the initial surface density of hydroxyl groups, crucial to initiate the deposition of alumina (reaction A). The surface of SiC is formed by carbon- and silicon-terminated groups. While carbon-terminated groups are stable and rather inert, silicon-terminated groups are prone to oxidation [34, 35], providing the SiC surface with hydroxyl groups. By using stronger oxidising media, such as oxygen plasma, we can increase the initial density of hydroxyl groups on the surface [36, 37], enhancing the deposition of alumina during the first cycles, achieving higher GPC. Nevertheless, having relatively high GPC is a good compromise between depositing thick films of Al_2O_3 in a fast way, improving the activation with ¹⁸F, and preserving the particle properties relevant for the hydrodynamic behaviour of the particles, i.e. size, shape and density.

This experimental paper describes a generic method –using gas phase deposition of alumina– for making tracer particles that closely resemble the original particles. The resulting alumina films are very thin compared to the size of the original particles, and therefore have a negligible influence on properties such as size, shape and density. We demonstrate this with the specific example of the improved labelling efficiency of SiC particles towards ¹⁸F ions. For that, we coated five samples of SiC with different thicknesses of Al₂O₃ films, using two deposition temperatures, and surface prefunctionalizing treatment in two of the experiments. After the coating, we radio-activated the five samples with ¹⁸F ions, and compared the activity with the uncoated SiC and γ -Al₂O₃ particles. We demonstrate the use of an activated SiC-Al₂O₃ coreshell particle as a tracer in a PEPT experiment on fluidizing SiC particles. Using this novel tracer, more accurate studies on the hydrodynamic behaviour of SiC particles can be performed, increasing knowledge of their behaviour in industrial applications such as direct solar harvesting.

5.2 Experimental

 Al_2O_3 films were deposited in a purpose-built fluidized bed reactor consisting of a glass column of 26 mm in diameter and 500 mm in length. Two stainless-steel

distributor plates with pore size of 37 μ m, placed at the bottom and top of the column, are used to obtain a homogeneous distribution of the gas inside the column and to prevent particles from leaving the reactor. The reactor and the rest of the setup have been described in detail previously [18, 38]. We use TMA and water as precursors to deposit Al₂O₃ films according to the reaction mechanism (A) and (B). In an ALD process, the surface species in reactions (A) and (B), respectively OH* and CH₃*, determine the completion of the reactions, and once they are depleted, the reactions end. That confers the self-terminating feature to the ALD process, which ensures atomic growth of the aluminium oxide film. N₂ is pulsed into the reactor in between the reactions for purging purposes. This cycle of reactions can be repeated to grow thicker coatings of aluminium oxide.

(A) SiC-OH* + Al(CH₃)₃ \rightarrow SiC-O-Al(CH₃)₂* + CH₄

(**B**) SiC-O-Al(CH₃)₂* + 2 H₂O
$$\rightarrow$$
 SiC-O-Al-(OH)₂* + 2 CH₄

We calculated the dosing time for TMA based on the maximum amount of TMA molecules that can be accommodated on the surface of the particles [23], considering the steric hindrance between the methyl groups of the TMA, and 0.12 nm as the ligand radius for a TMA molecule [39]. We measured with BET (Brunauer-Emmett-Teller) a specific surface area of 0.12 m^2/g for the SiC particles, and calculated the total particle surface area inside the column for the 8.00 g of powder loaded in the column in each experiment. A N₂ flow of 0.8 L/min, which corresponds to a superficial gas velocity of 2.5 cm/s, was applied to fluidize the powder. To calculate the amount of TMA we dose to the column, we assumed that at the bubbler temperature of 30 °C, TMA is found as dimers [40, 41] and that the components follow the ideal gas law. We estimated, using the model proposed by Mayer et al. [42], a saturation of the N₂ bubbles with TMA of about 50%. With these assumptions, we calculated a dosing time of 2.6 seconds for TMA and 2.0 seconds for water to obtain saturation of the particles with the precursors (Supplementary information 5.B). In order to ensure a faster growth of the alumina films, and therefore, have a higher improvement in the radio-activation of the SiC particles, we overdosed both precursors to the reactor by a factor of about 120 more than the calculated times. With this, we established the dosing times for the sequence of TMA-N₂-H₂O-N₂, in 5-10-4-10 minutes in all the coating experiments.

We considered that at ambient conditions, the large amount of excess molecules of precursor introduced in each cycle will accumulate on the surface of the particles, resulting in a parasitic-CVD type of growth and thicker films [18]. In addition, we pre-functionalised two samples with oxygen plasma before the coating to obtain a higher GPC. For that, SiC was uniformly spread over a glass Petri dish and introduced into a Harrick Plasma PDC-002 plasma cleaner device for 1 minute; the pressure of the chamber was kept at 6 mbar. Immediately after exposing the SiC to the oxygen plasma, the powder was introduced inside the column to start with the coating experiments.

In total, we performed experiments at five different settings, modifying the number of cycles, operating temperature and pre-functionalization of the SiC particles (Table 5.1). At 100 $^{\circ}$ C, we performed two experiments with 5 and 7 cycles. To increase the layer thickness, we lowered the temperature to 27 $^{\circ}$ C and performed 20 cycles. We carried out the oxygen plasma functionalization, and performed 20 and 40 cycles. In all the experiments we kept constant the initial mass of SiC powder loaded inside the reactor

(8.00 g), the flow of nitrogen (0.8 L/min), and dosing times of the precursors and purging N_2 (5–10–4–10 minutes).

To characterize the coating process, we calculated the thickness of the alumina films (δ_{ICP}) from the elemental analysis of the samples carried out with a Perkin Elmer Optima 500 ICP-OES (Induced Coupled Plasma – Optical Emission Spectroscopy). We obtain the mass fraction of aluminium (x_{Al}) from ICP, from which we calculate the thickness of the alumina coating [18]. For this calculation, we used a density for the SiC particles of 3210 kg/m³, and for alumina of 2500 kg/m³ [43]. We measured a fraction of aluminium of 0.0007 in the uncoated SiC particles, and used this value to correct the fraction of aluminium in the coated samples, to consider only the aluminium deposited as Al₂O₃ in the calculation of the film thickness directly from a TEM (Transmission Electron Microscope) image for the sample with 40 cycles. For that, we produced a lamella in the nanometre range of the coated SiC using FIB (Focused Ion Beam) [44] combined with TEM.

Extending the earlier discussion, radio-activation of the tracer can be achieved according to three different techniques: direct activation, ion exchange and surface modification [7, 45]. In this work, we used a procedure similar to the ion exchange method, using 18 F as radioactive source [6]. To activate the particles we prepared an extremely dilute solution of ¹⁸F ions in pure water produced by bombardment with an energetic³He beam from the Birmingham MC40 cyclotron. Oxygen atoms within the solution are converted into ¹⁸F ions in the two competing reactions described by Fan *et* al [7]. A sample of our coated particles was immersed into the solution for around one hour allowing contact between ¹⁸F ions and the Al₂O₃ surface layer of the coated SiC particles. The liquid was evaporated and the particles dried, thus allowing their recovery and subsequent measurement. The activity of the samples was measured with a CRC-15R Capintenc Inc. radioisotope calibrator [45]. To compare the activation of the different SiC samples and the γ -Al₂O₃, we calculated the relative activity as the ratio of the activity of the particles, with a value in the µCi range, and the activity of the radioactive solution, in the mCi range. Finally, to confirm the applicability of the tracer particle produced, we used one radio-activated particle of the SiC sample coated for 40 cycles with aluminium oxide to perform a PEPT experiment in a fluidized bed. We fluidized SiC for 30minutes in a column of 90mm in diameter and 500mm in length, and reconstructed the trajectory of the tracer particle based on the triplets $(\bar{x}, \bar{y}, \bar{z})$ measured by the ADAC "positron camera" [2].

5.3 Results and discussion

Table 5.1 shows the experiments carried out with different numbers of coating cycles (5, 7, 20 and 40 cycles), different reaction temperatures (100 and 27 °C) and prefunctionalization of the powder with O₂ plasma. As we expected, the mass fraction of aluminium (x_{Al}) and, therefore, the thickness of the alumina films (δ_{ICP}) increased with: (i) an increasing number of cycles, (ii) a decrease in the reaction temperature, and (iii) the pre-functionalization of the SiC particles (Table 5.1). We obtained a GPC of 1-2 nm for the experiments at 100 °C, which is calculated after dividing the thickness of the alumina film over the number of cycles. When reducing the temperature to 27 °C we achieved a GPC of 9 nm after 20 cycles. This shows the influence of the temperature on the accumulation of unreacted precursor molecules. In addition, we observed an increase in the GPC after the functionalization of the SiC particles with O_2 plasma for the experiment with 20 cycles. That can be explained by an increase of the surface density of hydroxyl groups during the plasma treatment, which will promote a larger deposition during the initial cycles of the experiment. We obtained a GPC from 1 to 12 nm in the different experiments, which is much larger than the characteristic GPC for ALD, typically 0.1-0.2 nm [18, 46-49]. This is due to the long dosing times of both precursors, far beyond the dosage to fully saturate the surface of the particles. At 27 °C, the molecules of the precursors in excess accumulate on the surface, losing the self-terminating feature of the ALD reactions, and inducing higher GPC [18]. Based on the GPC, these experiments cannot be considered as ALD. However, neither do the GPC values in this work indicate a typical CVD mechanism, where the precursors are dosed simultaneously to the reactor, and films grow with rates around 0.1 µm/min for similar metal oxides [50], nor as Rapid ALD process [51], where the precursors acts as catalyst to deposit layers of about 2 nm per cycle.

Table 5.1. Mass fraction of aluminium, determined by ICP, and the thickness of the alumina film, calculated from the results from ICP, for the different experiments.

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# cycles	O ₂ Plasma	T [°C]	<i>x_{Al}</i> [-]	δ_{ICP} [nm]	GPC [-]	
5		100	0.02	5.5 ± 0.6	1.1 ± 0.1	
7		100	0.06	16.5 ± 1.7	2.4 ± 0.2	
20		27	0.67	183.2 ± 19.4	9.2 ± 1.0	
20	•	27	0.84	229.4 ± 24.3	11.5 ± 1.2	
40	•	27	1.79	484.2 ± 52.3	12.1 ± 1.3	

To validate the thickness calculated from the elemental analysis, we measured the thickness of the Al_2O_3 film of the sample coated for 40 cycles using FIB combined with TEM and EDX (Fig. 5.1 and *Supplementary information 5.C and 5.D*). To prepare a lamella with FIB, we first deposited a protective layer of platinum of about 100 nm to avoid damaging the alumina film during the bombardment of ions (*Supplementary information 5.C*). We placed the lamella under the TEM, and measured a film thickness of about 400 nm (Fig. 5.1) after measuring the thickness at 50 points taken from two TEM images. This result is comparable to the one calculated from elemental analysis, 484 ± 52 nm (Table 5.1).



Fig. 5.1. FIB-TEM image of the SiC sample coated for 40 cycles of Al_2O_3 . The film thickness is about 400nm.

In Fig. 5.1, lighter areas in the alumina film are visible. These might be air pockets or pores in the film. We verified the porosity of the alumina film of the sample coated for 40 cycles of Al_2O_3 with BET measurements (*Supplementary information 5.E*). The specific surface area measured for the uncoated SiC particles, 0.12 m²/g, is near the detection limit. The larger diameter of the coated sample produces a decrease in the BET surface area, falling below the detection limit of the measuring device (*Supplementary information 5.E*). That can be seen by the shape of the BET isotherms for the coated sample, which is similar to that for an empty measuring probe. Nevertheless, the pores seen in Fig. 5.1 would have produced a strong increase of the surface area, especially since we are working near the detection limit. It might be that these non-homogeneities found in the alumina film (Fig. 5.1) are either inaccessible to the nitrogen during the BET measurement, or produced during the sample preparation with FIB. In any case, these cannot be measured with nitrogen adsorption.

Fig. 5.2a shows the activity of the samples relative to the activity of the radioactive water used in the activation, expressed as a percentage. Between the uncoated sample (0.009%) and the γ -Al₂O₃ (0.143%), we observed an increase in the relative activity with the thickness of the alumina film. The samples with the thin coating (5 and 7 cycles) showed a slight improvement with regard to the uncoated SiC. The experiment with 20 cycles of Al₂O₃ at 27 °C showed a strong improvement of the activity, which was further increased when the SiC particles were pre-functionalized with the oxygen plasma. The sample with 40 cycles at 27 °C, and O₂ plasma pre-treatment showed the best relative activity, 0.108%. As we expected, the efficiency of the radio-activation increased with the thickness of the alumina films (Fig. 5.2b). The sample with 40 cycles shows a relative activity comparable to the one of γ -Al₂O₃, often used as tracer.



Figure 5.2. (a) Relative activity, in percentage, of the uncoated SiC, coated samples and the γ -Al₂O₃ sample. (b) Relative activity of the coated samples with respect to the film thickness. In both pictures, the vertical error bars represent the standard deviation of the activity measurements over the square root of the number of measurements. The horizontal error bars in Fig. 5.2b represent the error introduced in the calculation of the film thickness, based on the error of the ICP-OES equipment and the density of the alumina film.

To evaluate the properties of the SiC sample coated with 40 cycles, we calculated an equivalent density of the core-shell particle using (Eq. 5.1) and compared the value to the uncoated SiC (Table 5.2). For that, we defined the core-shell density ($\rho_{core-shell}$)

as a weighted average considering the volume fractions of SiC (φ_{SiC}) and the alumina coating (φ_{Al2O3}).

$$\rho_{core-shell} = \frac{d_P^3}{(d_P + 2 \cdot \delta_{Al2O3})^3} \cdot \rho_{SiC} + \frac{(d_P + 2 \cdot \delta_{Al2O3})^3 - d_P^3}{(d_P + 2 \cdot \delta_{Al2O3})^3} \cdot \rho_{Al2O3}$$
(Eq. 5.1)

We calculated the density of the core-shell for the 40-cycle sample, since it showed the thickest alumina film and the highest relative activity with ¹⁸F. For this sample, an alumina film of 484nm corresponds to a volume fraction of alumina (φ_{Al2O3}) of 0.03. Considering the density of SiC of 3210 kg/m³, and the density of Al₂O₃ deposited with ALD at room temperature of 2500 kg/m³ [43], we obtained a density of the core-shell of 3180 kg/m³. This represents a density difference of 0.8% with respect to the uncoated SiC (Table 5.2), which is a negligible difference as far as the particle dynamic behaviour is concerned. Moreover, we consider that neither the size nor the shape of the SiC particles substantially changed with the alumina film, since the thickness of the alumina film is much smaller than the particle diameter. Therefore, we can conclude that the deposited alumina film does not alter the density, shape and size of the SiC particles, which are the most relevant properties for the hydrodynamic behaviour of fluidizing particles.

Table 5.2. Density comparison of the uncoated SiC and the sample coated with 40 cycles.

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	SiC	Al ₂ O ₃ -SiC
d [µm]	68	68.8
δ _{Al2O3} [µm]	-	0.4
φ_{SiC} [-]	1	0.97
φ_{Al2O3} [-]	0	0.03
$\rho [\text{kg/m}^3]$	3210	3185

We used a radio-activated particle of the SiC sample coated with Al_2O_3 during 40 cycles to perform a PEPT experiment. During the 30 minutes that the experiment lasted, we obtained over 17000 x,y,z locations in time (Fig. 5.3), which translates to an average sampling frequency of about 10 Hz. The size of the tracer will affect the activity, which influences the sampling data, and eventually may affect the precision of the PEPT reconstruction; i.e. smaller particles result in lower activities which result in lower spatial resolution [19].

In this work, we used as tracer the same 68 μ m particles as in the rest of the bed, coated with 40 cycles of aluminium oxide. The corresponding average activity was 22 μ Ci which allowed accurate measurement of the position of the tracer at a frequency of 10 Hz. The bare SiC particles, with an activity of 2 μ Ci, would have allowed only measurements at a lower frequency (~1 Hz). The most relevant dynamics in fluidized beds take place in the frequency range 0-6 Hz based on pressure fluctuations [52], or even the lower part of that range based on solids motion. In the case of the experiment with the 40-cycle SiC, we found that the power spectrum has little powder above 2 Hz, such as sampling at 10 Hz is sufficient to capture all the dynamics, while sampling at 1 Hz would certainly miss relevant dynamics.



Figure 5.3. (a) 3D representation of the trajectory of the SiC-Al₂O₃ tracer during the 10 first seconds of fluidization in the PEPT experiment. (b) Representation of all the data points during the 30 minutes of the PEPT experiment. The projections of the data in each of the planes are shown with red, green and blue symbols. (c) Mobility of the tracer in each of the axes during the first 200 seconds of the PEPT experiments. Within this 200 second period, in the first 20 seconds there is no fluidization, so that the tracer remained stationary near the bottom of the bed of particles.

In Fig. 5.3a we see the trajectory of the tracer during the first 10 seconds of fluidization. We observed that the intensity of the SiC sample coated with 40 cycles provides sufficient data points for the PEPT algorithm to be applied and for description of the location and movement of the tracer. In Fig. 5.3b, we show all the data points recorded during the 30 minutes of the experiment. The projections of the data points on the different planes give an idea of the uniform spread of the measured locations inside the fluidized bed, illustrating that tracking was possible throughout the measurement volume. Fig. 5.3c shows the mobility of the tracer in each of the three axes over a duration of 200 seconds. During the first 20 seconds of the measurement (Fig. 5.3c), there was no fluidization and the tracer rested almost at the bottom of the bed of particles, and once the fluidized began, the tracer started moving inside the bed.

Despite the lower activity and sampling frequency for the alumina-coated SiC tracer when compared to other tracers, the coating method used here allowed us to track and reconstruct the 3D trajectory of a SiC particle, which would have been impossible without the alumina coating. This generic approach could be extended to other types of applications where a tracer particle is needed, such as PEPT or RPT (Radioactive Particle Tracking).

5.4 Conclusions

We demonstrated that initially inert particles, such as SiC, can be activated with ¹⁸F ions by modifying the surface of the primary SiC particles. For that, we deposited aluminium oxide films on the SiC particles in a fluidized reactor using a gas-phase coating technique similar to atomic layer deposition. Contrary to conventional ALD, we carried out coating at atmospheric pressure and room temperature. At these conditions, we fed the precursors in large excess to ensure a fast growth of the alumina films. On the sample coated for 40 cycles, which was pre-functionalized with O₂ plasma, we deposited a film of about 500 nm, resulting in a GPC of about 12 nm. This 40-cycles coated sample presented a labelling efficiency with ¹⁸F similar to that for the γ -Al₂O₃, which is often used as a tracer. We conclude that the layer is thick enough to enable sufficient activity, yet thin enough to make the changes in density, size and shape of the particles negligible.

We showed that the activated core-shell structure formed by the SiC particle coated with an Al_2O_3 film of about 500 nm can be used as a tracer particle in a typical PEPT experiment. The emission intensity of this tracer was sufficient to reconstruct its trajectory inside the bed of particles albeit at suboptimal performance (i.e. low location rate and corresponding lower precision than generally quoted for PEPT). That proves that the deposition of alumina films can be used to produce tracers, mainly consisting of the same material as the bulk. This will enable researchers to obtain more accurate information about the flow patterns in systems with moving particles.

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5.A Properties of SiC powder and γ -Al₂O₃ used as tracer



Fig. 5.A.1. TEM picture and PSD of the F220 SiC used in this work.

provided by the site i 220 provider		
	SiC F220	γ - Al ₂ O ₃
$\rho [\text{kg/m}^3]$	3210	3950
$ ho_{bulk} [\text{kg/m}^3]$	1550	1220
d _{3,2} [μm]	68	48
$C_P [kJ/m^3 \cdot K]$	2150	-
T _{sintering} [°C]	1620	-
$k [W/m \cdot K]$	18	-
u_{mf} [mm/s]	5.5	-
u_{mb} [mm/s]	8	-

Table 5.A.1. Physical properties of SiC F220 and γ - Al₂O₃ used in this work. Information provided by the SiC F220 provider

5.B Calculation of the dosing time the precursors

Table 5.B.1. Properties of SiC F220 particles and fluidization experiment.

BET SiC [m ² /g]	0.12
mass SiC [g]	8.00
d _{sic} [μm]	68
Total Surf Area [m ²]	0.96
Flow N ₂ [L/min]	0.8

Table 5.B.2. Parameters for TMA [53] used in the steric hindrance model[23]

$r_{L,TMA}$ [nm]	0.125
$a_{L,TMA}$ [m ²]	5.4 E-20
N _{TMA,needed} [molec]	1.8 E+19
N _{TMA,needed} [mol]	2.9 E-05
N _{H20,needed} [mol]	4.4 E-05

Table 5.B.3. Calculation of the dosage times based on the ideal gas law.

P_{TMA}^{vap} [atm]	0.021
P_{H2O}^{vap} [atm]	0.042
<i>T</i> [°C]	30
C _{TMA} [mol/L]	8.6 E-4
<i>F_{TMA}</i> [mol/min]	6.9 E-4
<i>t_{TMA}</i> [s]	2.6
<i>C_{H20}</i> [mol/L]	1.7 E-3
<i>F_{H20}</i> [mol/min]	1.4 E-3



5.C Preparation of the sample lamella with FIB-TEM

Fig. 5.C.1. Steps in the preparation of the lamella with FIB-TEM.

5.D FIB-TEM and EDX spectra



Fig. 5.D.1. TEM image of the lamella of the coated sample, and the EDX spectra for the different components.



5.E Study of the porosity of the alumina films

Fig. 5.E.1. Absorption and desorption isotherms for the uncoated SiC F220 powder (a), and the sample coated with 40 cycles (b).

Chapter 6

Outlook

The purpose of this chapter is to identify the questions that remained open and to provide a broader perspective on the applicability of our work. We describe how our approach can be further refined by optimizing certain process variables, such as the dosing time of the precursors and the purging time. We also propose a detailed study on how to improve the fluidization of fine cohesive particles. In addition, we discuss the deposition of other compounds at ambient conditions, and the necessity to study the toxicology of the ultrathin coatings before being applied to biological materials. Finally, we present an evaluation of ALD for product development.

6.1 OPEN QUESTIONS AND COMPLEMENTARY STUDIES

These are the following six key questions that are addressed in this section, including suggestions for further investigation.

- (i) Optimization of the results obtained in the previous chapters
- (ii) Characterization of the strength of the alumina films
- (iii) Necessity for accurate characterization techniques
- (iv) Industrial implementation of ALD on powders
- (v) Investigation of the interparticle forces
- (vi) Study of different fluidization assistance methods

6.1.1 Optimization of the results obtained in the previous chapters

In chapters II, III, IV and V, we showed how thin alumina films, deposited at ambient conditions, improved the performance of three materials: a powder coating paint, PbSe quantum dot (QD) films, and a silicon carbide (SiC) tracer. Despite that, further research could be conducted to refine the production of these materials towards industrial implementation. In this section we discuss the variables that have an influence in the coating process, and how we can modify them to optimize the end product.

In chapter II, alumina films were deposited at ambient conditions with the same growth per cycle (GPC) as in pure atomic layer deposition (ALD) processes, i.e., 0.1-0.2 nm, by controlling the dosing time of the precursors. Also, an increase in the dosing time of the precursors resulted in thicker alumina films, and therefore, higher GPC. At ambient conditions, the purging flow of nitrogen was not sufficient to remove the unreacted precursor molecules from the surface of the substrates. It would be worthwhile to investigate whether we could achieve an efficient removal of the accumulated molecules with longer purging times. And complementarily, we could study whether using shorter purging time would have an influence on the film thickness. Unravelling the influence of the purging time on the alumina film thickness would be useful to either eliminate the parasitic CVD growth of alumina, or to reduce the process time by shortening the purging step. For example, a purging reduction of 50%, from 10 to 5 minutes, would be reflected in a cycle time decrease of about 15%, on average, for the experiments shown in chapters II, III, IV and V.

Reduction of the cycle time can be also achieved by playing with the temperature of the precursor bubblers. An increase in this temperature results in an increase in the concentration of precursor in the nitrogen flow to the reactor. Therefore, less time would be required to transport a certain amount of precursor molecules to the reactor. As an example, the vapour pressure of trimethylaluminium (TMA) at 30 °C is 21 mbar, while at 80 °C is 200 mbar. This increase in the temperature translates in a ten times reduction of the dosing time of TMA. Nevertheless, we did not consider this possibility in our experiments since we wanted to keep the reactor at room temperature during the whole coating process because of the thermal sensitivity of the materials we worked with, i.e., polymeric particles and quantum dot crystals.

In chapter III, we showed the production of a matte powder coating paint by encapsulating the particles of a glossy powder coating with alumina. We found that 2 cycles influenced the final surface properties of the powder coating paint without altering its mechanical properties. However, there are a number of variables in this process that can be further optimized to increase the tunability and production rate of the matte powder coating product.

1. We should investigate different ways to feed faster the same amount of precursors to the reactor by increasing the dosing time and reducing the number of cycles simultaneously. We could benefit from the accumulation of precursor molecules on the substrate to deposit the alumina films faster. A hot stage microscope could be used to quickly determine if the alumina coating with longer dosing times shows similar barrier performance as the one shown in chapter III.

2. The particle size of the powder coating could have also an influence, since the gloss or matte surface appearance depends on the surface roughness. Smooth surface would reflect the incident light, while irregular surface would scatter it, producing a glossy and matte surface, respectively. In our opinion, smaller particle sizes would reduce the surface roughness while keeping the matte finish, since it is likely that the encapsulated particles could still scatter the incident light. This would provide more options to finely tune the appearance of the powder coating paint.

3. It would be interesting to investigate a reduction of the coated-to-uncoated mass ratio of powders used in the preparation of the mixed paints. In chapter III, a ratio 1:1 was used. However, by reducing this ratio we could produce larger amounts of matte powder coating paint with the same amount of alumina-coated powder. It has to be investigated the properties of the final product, such as roughness, gloss and mechanical resistance, with different mass ratios.

In chapter IV, PbSe QD films, which are prone to oxidation, were stabilized by depositing aluminium oxide at ambient conditions. According to theoretical estimation, we deposited around four monolayers of alumina in each cycle, finding that after 25 coating cycles the QD films were successfully passivated for at least 60 days in an air environment. Despite these good results, we still do not know the minimum amount of alumina required to passivate the PbSe crystals. For that, we would need to perform experiments with a number of cycles between 10 and 25, to determine the minimum number needed. Additionally, we should increase the dosing times of the precursors to deposit the same amount alumina with lower number of cycles. The concentration depth profile of the different elements, obtained with XPS (X-ray photoelectron spectroscopy), and the passivation efficiency of the alumina coating, assessed with the measurement of the optical absorption spectra, would be used to compare different samples. Furthermore, other coating materials, such as zinc oxide (ZnO), could be used to passivate the QD films. In principle, the deposition of ZnO, using diethyl zinc (DEZ) and water as precursors, could be carried out at room conditions since DEZ, also a metal alkyl, is as reactive as TMA. Additionally, ZnO would increase the electron mobility inside the QD film [1]. This study would provide a promising alternative to the production of QD films with enhanced properties, and could improve the efficiency of the solar cell technology.

In chapter V, we deposited alumina films on SiC particles to improve the labelling efficiency of the core materials towards ¹⁸F radioactive ions. The best result suggested that even if the

SiC particles coated with 400 nm of aluminium oxide had a slightly lower relative activity than the γ -Al₂O₃ particles, they had sufficient activity to be detected by the positron emission particle tracking (PEPT) sensors. However, a thicker film of alumina could be deposited to investigate the influence of the film thickness on the activity of the core-shell particle. This could be tested by increasing the dosing times of the precursors, increasing the number of cycles, or both. A higher activity of the tracer would result in a higher sampling frequency, and therefore in a more accurate reconstruction of the trajectory of the tracer. Nevertheless, the sampling frequency not only depends on the activity of the tracer, but also on other parameters such as the diameter of the column, the nature of the material of study and the velocity of the tracer.

In these three applications, we have benefited from the accumulation of unreacted precursor molecules at atmospheric pressure and room temperature to deposit several layers of alumina per cycle. Typical values of the GPC of alumina are 0.1-0.2 nm, while in our experiments we had film growths ranging from 0.14 to 13 nm of alumina per cycle. Otherwise, we would have had to carry out a much larger number of cycles in each experiment to obtain similar results. Therefore, it would be interesting, as stated above, to investigate a further increase in the dosing times to further reduce the process time, and thus, increase the production rate. This study could be combined with the investigation of the alumina film properties, such as density, porosity or presence of unreacted species. These measurements can be done using TGA (thermo gravimetric analysis), BET N₂ adsorption (Brunauer-Emmett-Teller) and ICP-OES (induced coupled plasma – optical emission spectroscopy) combined with TEM (transmission electron microscopy). Reducing the dosing and purging times could result in a shortened deposition of alumina, while maintaining good control over the film thickness.

From all these parameters, we consider that the most interesting to investigate are the ones that lead to a reduction in the cycle time, i.e., the dosing and purging times, since they could be directly applied in the work shown in this thesis. Additionally, obtaining a similar alumina coating in a shorter time would be interesting for an industrial implementation.

6.1.2 Characterization of the strength of the alumina coating

During the coating process in a fluidized bed, particles are constantly colliding with other particles and the walls of the reactor. Therefore, investigating the physical properties of the coated particles, and in particular the mechanical resistance of the deposited alumina films, would be important for the production and final application of the core-shell structures. Techniques such as nano-indentation and attrition tests could be used to determine the strength, Young modulus, Poisson's ration, coefficient of restitution and attrition resistance of the alumina films. The nano-indenter provides force-displacement curves of a tip penetrating the coating. Nevertheless, this measurement is challenging for particles, since the particles can have different facets, and should remain immobile once the indenter is applied on their surface. The force-displacement forces are used to determine the energy dissipated during the indentation, giving a measurement of the elasticity of the alumina coatings. On the other hand, the attrition test could be done with a vortex shaker [2]. In this technique, a mass of particles is introduced in a glass cylinder which is placed in the vortex shaker with a rotational speed from 1500 to 2500 rpm. The glass cylinder has a input for a gas, and an output that is connected to a particle sizer device to measure the distribution of the fines formed. A sample of the fines generated could be analysed with EDX, to determine whether the fines are coming from the core or the shell materials. This measurement provides an indication of the strength of the particles and the coating upon collision.

6.1.3 Necessity for accurate characterization techniques

Good analytical characterization of the core-shell particles is crucial to interpret the experimental results correctly. Different techniques rely on different properties to characterize the material. For example, transmission electron microscope (TEM) can be used to clearly measure a film thickness of few nanometres of alumina deposited on TiO_2 nanoparticles, as in chapter II, since both have a similar length scale. However, measuring the thickness of a few nanometre film deposited on a 30 μ m polymer particle, as in chapter III, is not straightforward. In this section we discuss the capabilities and limitations of different analytical techniques to characterise ultrathin films in both nanoparticles and micron-size particles.

The core-shell particles produced in this thesis could be classified in two groups: $d_P/\delta_{film} \sim$ 0.1 and $d_P/\delta_{film} > 500$, where d_P is the particle diameter and δ_{film} is the film thickness. The first group corresponds to the core-shells in which film thickness is approximately one order of magnitude smaller than the particle size, as in the coating of TiO_2 nanoparticles (chapter II). This material offered a straightforward characterization, since the size and volume of the core and coating are in the same order of magnitude. This allows direct measurement of the composition with ICP-OES, and easy visualization with TEM. In addition, the large values of the specific surface area of nanoparticles, usually > 10 m^2/g , enable the use of surface techniques such as BET N₂ adsorption, XRD (X-ray diffraction spectroscopy), FTIR (Fourier transform infrared spectroscopy) and TGA, amongst others. These techniques are used to measure the surface area and porosity of a sample (BET), crystal structure and composition of the coating (XRD and FTIR), or the humidity content and the presence of any other volatile components (TGA). Therefore, we can accurately determine the chemical composition and infer other properties of the coating such as density. On the other hand, some techniques are not suitable for nanoparticles or nanoparticle agglomerates, such as nano-indentation. This technique can provide information on the mechanical properties of the alumina coatings. However, there are some challenges in its application. Namely, the size of the indenter tip is similar to the size of the nanoparticle, and the non-uniform geometry of the agglomerates complicates the interpretation of the force-displacement measurements.

Larger core-shell particles, in which the size of the core is in the micron range and the film in the nanometre range, disallow the use of some of these techniques, as the measured values would approach the detection limit of the equipment. For instance, ICP-OES would measure mainly the composition of the core material, since the volume of the coating is very small compared to the volume of the particle. In the case of the SiC tracer (chapter V), the volume of the core material (68 μ m SiC) represents 97% of the total volume of the core-shell (Al₂O₃ film thickness of 400 nm). Therefore, the compounds of the coating would be found in very low concentrations. Additionally, using TEM is not straightforward for two reasons. First, the microscope has to use large magnification on the edge of the particle, which may induce artefacts on the images. And secondly, the micron sized particles would absorb a large part of the beam of electrons causing low contrast between the particles and the coating. Surface techniques, such as FTIR, BET or XRD, are not practical due to the low values of the specific surface area of the non-porous micron sized particles, which is about 0.1 m²/g. For example, BET requires a total surface area of about 5 m² to measure accurately the specific surface

area. However, the testing tube can only allocate a few grams of powder. Some techniques such as FIB-TEM (focused ion beam transmission electron microscope) can be used to observe the film thickness of the larger core-shell particles. A thin lamellae of the core-shell, that is prepared with FIB by ion bombardment, can be introduced into the TEM to measure the film thickness and perform elemental analysis with EDX (energy dispersive X-ray spectroscopy). However, the sample preparation is time consuming and requires specific equipment. Hence, FIB-TEM is not an optimal technique to measure the film thickness in a systematic manner. Finally, other techniques to study the macroscopic behaviour of the coreshell, such as DSC (differential scanning calorimetry) and HSM (hot state microscopy), are favoured with larger particle sizes.

In general, there is a large interest in the coating of micron and nano-size particles to be used in catalysis, food, pharmaceutical and other fields. Depositing ultrathin films of a wide range of materials by ALD for tailored functionalization is of especial interest [2]. For micron-size particles, characterization is considerably more challenging, while particle processing is more straightforward, especially in fluidized beds. On other hand, handling and coating of nanoparticles is not an easy task, one reason being the strict operation protocols to avoid dispersion of nanoparticles onto the environment. Nonetheless, the nano scale offers more techniques for simple and accurate characterization of the coated nanoparticles.

6.1.4 Industrial implementation of ALD on powders

ALD has been used to produce tailored materials with improved performance in a variety of fields, such as catalysis, solar cells, Li-ion batteries and many others [3]. However, these experiments were done, in most of the cases, at lab scale [4, 5]. Based on the enhanced performance of the materials after depositing a few nanometre films, the next step would be the implementation at an industrial scale. In this section, we briefly delineate some general ideas on how to attempt an scaled up production of engineered materials using ALD.

Reactors for coating of powder can have different designs [5]. Ongoing work at the Product and Process Engineering (PPE) group (Chemical Engineering Department, Faculty of Applied Sciences, Delft University of Technology) focuses on studying two reactor configurations: a fluidized bed reactor operating in batch mode, and a pneumatic transport reactor operating in a continuous mode [6, 7]. Some advantages and disadvantages of both reactors are discussed below.

The fluidization technology is well-known and widely expanded in industrial activities such as food and pharmaceutical. Fluidized bed reactors (FBR) allow the processing of a large amount of solids of a variety of particle sizes. Additionally, FBRs can operate optimally with different capacities of solids, since it only requires the adaptation of the dosing times to the amount of solids inside the reactor. A down side of large fluidized beds would be the mixing between the precursors and solids, since the hydrodynamic behaviour of the solid can deteriorate when scaling up the diameter of the fluidized beds [8]. The second reactor configuration is a pneumatic transport reactor [6], that consists of a tube through which the particles are transported in a diluted gas stream of nitrogen, with the precursors being injected at different locations. This type of reactor provides a continuous production of nano-structure materials [7]. The current prototype can perform one cycle of ALD; nevertheless, the scaling up of this reactor can be done by connecting several one-cycle reactors in series, in a modular manner, to perform more than one cycle. This reactor has a length of about 37 m, giving

enough time for the precursors to mix and react at the particle surface. Scaling up of these two reactor configurations is a worthwhile research challenge, providing a promising future for industrial ALD production.

6.1.5 Investigation of the interparticle forces

The fluidization of cohesive particles, as described in the introduction of this thesis, is hindered by the tendency of the particles to form agglomerates. This results in the formation of preferential paths and channels, dead zones, poor gas-solid mixing, and non-suspended particles [9, 10]. Three interparticle forces are considered to play a major role in the particle agglomeration in fluidized beds: van der Waals, electrostatics and hydrogen bonding [11-13], while capillary force would be only relevant at high humidity level, usually above 70% [14]. However, the role of each force is not well defined yet.

Determining the contribution of each force is crucial to reduce or prevent the influence of the agglomeration on the fluidization. The van der Waals force is an inherent force based on the properties of the particles, thus, it would be difficult to influence without changing the material of study. Electrostatics can be prevented by grounding the equipment, or dispersing a solvent in the fluidization gas to increase its conductivity and dissipate the charges inside the reactor [15]. Similarly, dispersing isopropyl alcohol in the gas stream was reported to reduce the hydrogen bonding between hydrophilic particles [12]. This research would investigate the influence of dispersing a liquid in the fluidizing gas on the electrostatic forces and the hydrogen bond formation. For this study, 15 µm SiO₂ particles were fluidized in a pseudo-2D column, in which several induction probes we placed in contact with the external wall of the column. The induction probes consisted of an isolated co-axial cable connected to a copper plate on one side, which was in contact with the column, and to an amplifier on the other side. The probe could detect the change in the charge related to the agglomerates fluidizing in front of the probe [16-18]. Additionally, we could measure the bed height for a certain fluidization gas velocity, and the pressure drop and pressure fluctuations at different points of the bed, to characterize the quality of fluidization. This study would be done using two types of particles, i.e., hydrophilic and hydrophobic SiO₂, and three different fluidizing gases, i.e., dry nitrogen, nitrogen with a relative humidity of 20% and nitrogen with dispersed isopropyl alcohol. These six experiments would provide an evidence on the influence of the solvent used in any of the interparticle forces considered, namely, electrostatics and hydrogen bonding.

This study would contribute in the scaling up of a fluidized bed system. Nevertheless, care must be taken when using this approach in the coating process. Altering the composition of the fluidizing gas by dispersing a solvent will, most likely, induce undesired reactions with the coating precursors.

6.1.6 Study of different fluidization assistance methods

Despite the agglomeration of fine cohesive particles during processing in FBR, a good fluidization can be achieved by supplying external energy to the system in the form fluidization assistance methods. This supply could be as mechanical and acoustic vibration, mechanical stirring, secondary gas injection using a microjet, pulsed gas flow, centrifugal and electric field, amongst others [10, 19-22]. Although many of them have been investigated, there is not a detailed comparison. It would be useful to define an optimal fluidization aid,

based on the amount of energy added to the system and its influence on the fluidization quality. In order to find the optimum, one could use a model to approximate the microscopic properties of the agglomerates, such as size and porosity, by measuring the macroscopic properties of the system, i.e., bed height [23, 24]. This model is a modified version for nanoparticle agglomerates of Richardson-Zaki equation [25], which describes the settling mechanism of a particle surrounded by other particles. By a simple measurement of the settling velocity of the bed once the fluidization gas is switched off, we can obtain information about the structure of the fluidized agglomerates. The validation of this model can be done using a high speed camera connected to a borescope which is inserted in the fluidized bed [26], allowing the measurement of the size and settling velocity of the fluidized agglomerates. Additionally, the energy balances of the fluidizing system would be a complementary tool to study the different assistance methods.

6.2 BROADENING THE APPLICABILITY OF THIS WORK

6.2.1 Deposition of other compounds at ambient conditions

In chapter II, we demonstrated the deposition of ultrathin films of alumina, using TMA and water as precursors, at 27 °C and 1 bar. But, is it possible to deposit other coating materials at room temperature and atmospheric pressure? Alumina can be deposited at ambient conditions due to the high reactivity of the TMA molecules, which readily react in the presence of a small concentration of oxygenated compounds, such as air or water, even at room temperature. This high reactivity is characteristic for metal alkyls, which are pyrophoric, so they can catch fire when in contact with an oxidizer, such as TMA. Other metal alkyls that could be used for ALD reactions at moderate temperature are zinc, boron and magnesium alkyls [27-29], since supposedly they are also highly reactive.

6.2.2 Biocompatibility study of ultrathin films

The deposition of alumina at atmospheric pressure and room temperature opens the door to the application of nanometre coatings to heat sensitive materials such as polymers, food and pharmaceutical products. However, the toxicology of the alumina films should be investigated, especially if we use biological compounds as core material. Some studies have been done on the toxicity of metal nanoparticles on E-coli bacteria and zebrafish embryos [30-35]. Thus, can we use a similar approach to study the toxicology of nanometre-thick alumina coatings? For that, we can describe some experiments to study their toxicity. We would select a non-toxic powder as material of study, such as a food ingredient, and we would deposit alumina films with different thicknesses at ambient conditions. To investigate the toxicology, we prepare cultures of our cell of study, e.g., *E-coli*, and assess their reproduction capability. Under the same conditions, we prepare identical cultures and add different amounts of the coated powders and same amounts of powder with different film thickness, to investigate the effect of the coated powder amount and alumina film thickness on the E-coli. In parallel, we would prepare a control experiment consisting of a culture with the uncoated powder. In this way, we can compare whether the alumina films have a toxic effect on the bacteria, and whether this toxicity level would depend on the amount of powder and/or thickness of the alumina film. A follow up study could use a living system that resembles more the human cells. Applying nanocoatings to biological materials, i.e., food and pharmaceutical compounds, could be of great interest. However, toxicology studies such as the one described in this section are necessary to determine the effects of these ultrathin coatings on living systems.

6.3 ANALYSIS OF ALD FOR PRODUCT DEVELOPMENT

ALD is a powerful coating technique since it provides atomic control over the amount of compound deposited on a substrate, i.e., flat supports, irregular geometries, and porous and non-porous powders [36]. In this section, we describe why ALD is an interesting technique to produce nanostructure materials, from the process and product point of view.

Looking from a process perspective, there is a need to move towards sustainable production methods to reduce the impact on the environment in general. In this respect, ALD scores highly as a sustainable technology. As being a gas-phase technique, the mass of waste per mass of product, the so-called E-factor [37], is lower than in liquid-based coating techniques. Such techniques usually require an energy-intensive drying step to evaporate the solvent used, which is absent in ALD. Although several ALD processes, such as the ones to deposit noble metals, require relatively high temperatures (200-300 °C), we have shown that with a highly reactive precursor, such as trimethylaluminium, coating at room temperature is possible. ALD – when expressed in film growth per unit of time – is a relatively slow process; its use is doubtful when films of >> 10 nm are needed. The precursors are typically expensive, which can be an addition economic driver to keep the film thickness as low as possible.

From a product point of view, ALD is also highly interesting, since depositing small amounts of compounds can readily enhance the properties of materials, such as in photocatalysis and Li-ion batteries [7, 38]. ALD allows controlling the amount of precursor deposited based on the two self-terminating reactions, which only take place as long there are surface sites available, ensuring a highly utilization of the precursors. That becomes of vital importance to deposit scarce and costly materials, such as Pt [39], used in the production of catalysts. ALD is a versatile technique to produce catalysts for several reasons [40]. It can be used to deposit one [7, 41] or two active phases [42], and to deposit a protective overcoating to prevent the active phase from sintering at high temperatures [43]. Additionally, the size and dispersion of the catalytically-active clusters is also important in the production of nanostructured catalysts, since the surface area determines their activity. Therefore, having small and dispersed clusters of a ALD process can nicely control the size and distribution of the catalytic nanoparticles deposited with the number of coating cycles, as can be seen in the production of TiO₂ photocatalyst decorated with Pt clusters [4].

Finally, just as an overview, ALD has been used in a wide variety of applications, such as in the production of semiconductor devices [44], in the fabrication of supercapacitors [45], in the production of Li-ion batteries [46], in synthesis of catalysts [40], in the fabrication of photovoltaic devices [47], and in the enhancement of phosphor materials with photoluminescence properties [48]. It is to be expected that ALD, as an important part of the nanotechnology toolbox, will be used for even more products in the near future.

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List of Publications

Papers

- 1. D. Valdesueiro, G.M.H. Meesters, M.T. Kreutzer, and J.R. van Ommen. Gas-phase deposition of ultrathin aluminium oxide films on nanoparticles at ambient conditions. Materials, 2015. 8(3): p. 1249-1263.
- 2. D. Valdesueiro, P. Garcia-Triñanes, G.M.H. Meesters, M.T. Kreutzer, J. Gargiuli, T. Leadbeater, D.J. Parker, J. Seville, and J.R. van Ommen. Enhancing the activation of silicon carbide tracer particles for PEPT applications using gas-phase deposition of alumina at room temperature and atmospheric pressure (*submitted for publication*).
- 3. D. Valdesueiro, H. Hettinga, J.P. Drijfhout, P. Lips, G.M.H. Meesters, M.T. Kreutzer, and J.R. van Ommen. Tuning roughness and gloss of powder coating paint by encapsulating glassy particles with thin Al₂O₃ films (*submitted for publication*).
- 4. D. Valdesueiro, M. Krishna Prabhu, C. Guerra-Nuñez, C.S. Suchand Sandeep, S. Kinge, L.D.A. Siebbeles, L.C.P.M. de Smet, G.M.H. Meesters, M.T. Kreutzer, A.J. Houtepen, and J.R. van Ommen. The deposition mechanism of aluminium oxide on quantum dot films at atmospheric pressure and room temperature (*submitted for publication*).

Proceedings

- 1. D. Valdesueiro, G.M.H. Meesters, and J.R. van Ommen. Coating Fine Particles with an Ultrathin Film in a Fluidized Bed. In Proceedings of *International Conference of Particle Technology ParTec2013*, Nuremberg, 23-25 April 2013.
- 2. D. Valdesueiro, G.M.H. Meesters, and J.R. van Ommen. Microscopic characterization of mechanically assisted fluidized beds. In Proceedings of *Fluidization XIV: From Fundamentals to Products*, Noordwijkerhout, 26-31 May 2013.
- 3. G.M.H. Meesters, D. Valdesueiro, and J.R. van Ommen. Coating Fine Particles with Ultrathin Films using Atomic Layer Deposition. In Proceedings of 2013 AIChE Annual Meeting: Global Challenges for engineering a Sustainable Future, San Francisco, 3-8 November 2013.
Acknowledgements

This thesis is the result of four years of research at the Product and Process Engineering (PPE) group. The Marie Curie Actions, under the program PowTech Initial Training Network, and DSM Coating Resins in Zwolle, funded this project. In this chapter, I take the opportunity to thank to many people that contributed to this thesis, and without whom, the previous chapters would not have been written.

First of all, I would like to thank to my promotor, Michiel Kreutzer, and co-promotors, Ruud van Ommen and Gabrie Meesters. It has been great to work under your guidance and supervision. Michiel, your analytical thinking and critical feedback have made this work better. Always identifying the loose ends and challenging to find explanations to all the details. Thanks, it was fun working with you! Ruud, I am really lucky to have had you as supervisor. Your support has been essential to make it all the way until here. Thank you for your meticulous revisions and dedicated supervision, for all the quick talks in the early mornings, and for having always a constructive feed-back. Your contribution has been priceless for me from the beginning of the project. Thank you very very much! Gabrie, you added to the project your industrial expertise and large network, and above all, a young spirit and a lot of stories and anecdotes during the progress meetings. I enjoyed every non-scientific discussion along these years. Thank you for bringing to the table your industrial point of view.

It is logical to think that without supervisors, it is not possible to complete a PhD. I would like to add to it that, without the technical support at the lab, would not be possible either. Mojgan Talebi, Mark de Niet and Peter Gouweleeuw, you have done a tremendous contribution to this work. Thank you very much! Doing experiments without your help would just have been inconceivable. Mojgan and Mark, we spent so many hours in front of the ALD setup, and not only coating particles, but placing and replacing valves, lines and bubblers, troubleshooting and a couple of times even observing the pyrophoricity of TMA... Your constant positive attitude converted these tedious work into enjoyable tasks. It was great having your support at the lab! And Peter, until you left for your retirement, you have been the watchman of the Proeffabriek. You fixed everything that we messed in the lab, quickly and precisely, making possible that this project never was never stopped due to technical difficulties. In addition, I would like to thank the administrative work of Elly Hilkhuijsen, Caroline Monna, Els Arkesteijn, Astrid Barrow and Marian de Bruijn. You make working at PPE much easier for us. I would also like to thank a lot of people at the ChemE and other departments for the technical support in the analysis of samples: Marcel Bus, Bart Boshuizen, Duco Bosma, Piet Droppert, Ben Norder, Ruben Abellon, Baukje Terpstra, Meng Yue Wu, Bart van der Linden and Willy Rook. Thanks for your help!

Special thanks to all the people I had the pleasure to collaborate with. The people at DSM in Zwolle: Jan Pieter Drijfhout, Cindy van Tent, Hans Hettinga, Priscilla Lips and Paul Vercoulen. Working with you was an important part of the project, and each time I went to

Zwolle to do experiments I felt like coming back home. Thank you! Likewise, I would like to thank to all the collaborators in different projects. Arjan Houtepen, Suchand Sandeep, Ruud Westerwaal, Zhi Zhou, Bert Hintzen and Pablo García-Triñanes. Depositing alumina films on your special materials was an important addition to this thesis. Thank you for your effort and compromise. I enjoyed working with you! In addition, I would like to thank also to the LO, BSc and MSc students that I supervised during the PhD. Tim, Jacob, Jochem, Sam, Minouk, Joost, Hayati, Niek, Louis, Sophie, Gaurav, Mahesh, Shiva, Marybeth, Ricardo and Carlos, thanks a lot for your dedication and contribution to this work!

I would like to thank also to all the people from the Marie Curie network, and in particular, to the fellow ESR's. There were many stories and highlights in each Powtech meeting... The drinks in Paris and Cork, the trains and the Oktoberfest party with Mr. Tambourine in Zurich, the bowling in Budapest, the visits to the hospital and the Poco Loco factory in Gotteborg, or the road trip in China. The Powtech program was really fun, and a great complement to this PhD!

I have special words for all the colleagues and office mates at PPE and the Proeffabriek. Michiel, Ruud, Pouyan, Volkert, Peter, Henk, Mojgan, Wim, David, Nasim, Mahsa, Duong, Barbara, Michiel, Rajat, Bhaskar, Amer, Venky, Hrushi, Piotr, Josette, Daoyin, Jilian, Zhi Zhou, Piotr, and especially, Hao, Jesús, Javi, Wenjie, Alberto, Samir, Durgesh, Floris, Dayinta, Yogesh, Lilian, Aris, Andrea, Fabio. All the VriMiBo's, after work drinks and brewing attempts, betting events and shooting competitions, social activities and road trips, Fun Fridays... It has been a wonderful experience to share these four years with you, and I can certainly say that doing a PhD at PPE is, amongst many good things, a fun experience. I also want to remember the friends with whom I spent a great time in Delft, eating fish on Saturdays, playing board games, poker nights, basketball... You all contributed greatly to have a relaxing and fun time in Delft.

Finally, I would like to thank to the most important part for me: my parents and family. Gracias por todo lo que me habéis dado, vuestro apoyo incondicional y ser un ejemplo. Siempre os tengo presentes y os siento cerca. Esto es en gran parte vuestro también.

Curriculum Vitae

David was born on 31 January 1984 in León, Spain. In 2009 he graduated in Chemical Engineering from the University of Valladolid, Spain. David conducted his engineering thesis between September 2008 and June 2009 at the University of Maribor, Slovenia. In 2010 David worked in the production factory of INERGY Automotive Systems in Arévalo, Spain. In August 2010, he moved to Zwolle, The Netherlands, to work for the technology department at DSM. In July 2011, David started his PhD in the Department of Chemical Engineering within the Faculty of Applied Sciences. His promotor was Prof. dr. Michiel T. Kreutzer, and his co-promotors were Dr. ir. J. Ruud van Ommen and Dr. ir. Gabrie M.H. Meesters. Since September 2015, he works in Delft IMP as process engineer.