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Pulsed-bed atomic layer deposition setup for powder coating

H. Tiznado *, D. Domínguez, F. Muñoz-Muñoz, J. Romo-Herrera, R. Machorro, O.E. Contreras, G. Soto

Universidad Nacional Autónoma de México, Centro de Nanociencias y Nanotecnología, Km. 107 Carretera Tijuana-Ensenada, Mexico

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ABSTRACT

Atomic layer deposition (ALD) provides a method for coating conformal, pinhole-free, chemically bonded, and ultra-thin films on particle surfaces. ALD is based on one or more cycles, each cycle comprising two half-reactions. As such, ALD is a process inherently discrete in time, where the coating thickness can be controlled as a function of number of cycles. A popular scheme for achieving uniform coats on powders is to combine ALD reactors with fluidization conditions. However, fluidization is not easy to attain because it is strongly dependent on particle size, density, morphology, and surface roughness. This article proposes that a pulsed-bed, instead of a continuous fluidization, is easier to achieve in most ALD reactors. Taking advantage of the discrete nature of the ALD process, with simple changes in the configurations of purge and carrier gases, the pulsed-bed mode can be completed. An adaptation made to a regular ALD reactor to work in this mode is presented. The inclusion of a capsule for powder, valve relocations, and control of times were all necessary modifications. It was found that the pulsed-bed is a very convenient alternative for research purposes, since it can coat powders of different morphological characteristics, such as carbon nanotubes, flower-like ZnO micro-arrays, and $YCrO_3$ particles.

1. Introduction

Coating technologies have been widely used for years to modify the physical and chemical properties of materials. Covering powder supports with metallic nanoparticles to create a catalytic active surface is one illustrative example [1]. The development of techniques that allow for the production of coated powders, particularly those addressing flexible configurations to tailor to the nature of the powder to be processed, is of high priority for coating technologies. Only recently, with the development of nanotechnology, coating technology expanded its applications to conformal coatings at the nanometer scale. At present, 3D shaped-surface morphologies can be homogeneously and uniformly coated with ultra-thin layers.

Lately, coated powders, which are regarded as core–shell structures, have become a subject of great interest, triggering the development of many approaches for producing them; nevertheless, at the moment, the atomic layer deposition (ALD) method appears to be the leading technique [2]. ALD is a versatile technique that can be used to coat and functionalize surfaces with either single or multiple components. The foremost advantage of ALD is its ability to control the coating thickness down to the atomic level as a function of the number of ALD cycles. ALD technology can be applied to almost any type of material or size and morphology of powders (the core), producing conformal coatings with pinhole-free and chemically bonded layers (the shell). The potential applications of the ALD technique are endless; for example, a magnetic core with a ceramic shell generates a non-conductive magnetic material with infinitesimal electric losses; a dielectric shell on a ferroelectric ceramic core might be the basis for resonators, supercapacitors, and multiferroic nanostructures [3–6]; or an oxide shell can be formed on semiconductor cores to produce nanowire photodiode arrays [7].

A common ALD configuration for growing quality coatings on powders involves setting up fluidized bed conditions in the reactor [8–13]. A bed of solid particles can be sustained in the fluidized state if the upward gas flowing through the bed is kept within the proper velocity range [14–17]. Thus, for this kind of configuration it is required to simultaneously establish gas dynamics for the ALD precursors compatible with the fluidized conditions. That is, the purge time to extract the previous reactant and the dose hold to saturate the surface with the next one should be harmonized with the appropriate gas velocity to sustain the fluidized state. However the initial conditions, like bed mass, agglomeration kinetics, and particle size itself, are always varying from one powder to another; thus, switching between different powders is not straightforward because new specific conditions should be determined. Additional issues like bubbles, slugs and gas channeling should be addressed as well. Early and recent experimental studies, as well as mathematical modeling, have established that the pulsed bed approach is able to solve these problems [18–30]. Furthermore, it has been demonstrated that the pulsed operation improves the reactor performance for diverse applications [31–34]. The pulsed-bed operation results from feeding an intermittent gas flow that expands the bed during the pulse and let it contract afterwards [19]. Taking advantage of the discrete nature of the ALD process, the pulsed-bed approach to fluidization appears to have certain advantages for powder coating applications, specifically processing powders of dissimilar characteristics might become an easier task. During each rapid off–on transition

* Corresponding author. Tel.: +52 646 175 0650x438.
E-mail address: tiznado@cnyn.unam.mx (H. Tiznado).

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the bed undergoes pneumatic transport; a short period might behave in fluidized state-like; and then slowly set down to a static bed condition. In each gas pulse the bed acquires a new arrangement where the previously buried grains might become exposed to the reactants. The aim of the present work is to demonstrate the feasibility of operating ALD reactors in the pulsed-bed mode for research purposes. With very simple modifications made to a typical ALD system, without directly addressing the continuous fluidized bed problem, the setup is able to handle powders of any density and diverse morphological characteristics as well as planar substrates such as silicon wafers and glass slides. To demonstrate the capabilities of the ALD setup, core–shell structures of scientific importance were synthesized. Three powders of completely different characteristics were coated with Al_2O_3 or TiO_2. The shell thickness control at the nano-level is demonstrated. Such illustrative cases that correspond to applications include carbon nanotubes (CNTs), ZnO flower-like microarrays, and $YCrO_3$ ferromagnetic particles.

2. The ALD setup

The ALD system used in this work is based on a home-made, fully automated hot-wall reactor. A description of the original experimental setup can be found elsewhere [35]. Using trimethyl-aluminum (TMA) and tetrakis (dimethylamino) titanium (TDMAT) as the metal precursors and water as the oxidizing agent, the ALD system is capable of growing Al_2O_3 and TiO_2 films. Fig. 1 shows the main components of the modified ALD system. All metal precursors are held together in a main manifold independent of that controlling the water. To coat powder-like materials in a free-standing state, a special powder holder (see Fig. 2), which will be referred to as the capsule, is placed in the tubular reactor (22.3 mm inner diameter). The capsule closely fits the reactor walls and nearly occupies the entire inner volume to force the precursors to flow through the capsule, while at the same time optimizing the ALD cycle time. The capsule was fabricated by assembling two opposite filters with a short coupling (21.8 mm outside diameter). The filters are composed of sintered porous metal (bronze or stainless steel) obtained from Swagelok™ and Parker™ and are available in pore sizes ranging from 0.5 to 140 μm, allowing the system to process fine to coarse powders without material losses. The capsule (10 cm^3 in volume and 10 cm long) has a capacity to handle 2 cm^3 of material loads. Two control valves were installed before and after the reaction chamber to trap/release the precursors. The first valve ($\mathbf{V_m}$) is located at the output of the metal precursor manifold, whereas the second one ($\mathbf{V_p}$) is located at the exhaust of the reaction chamber.

Fig. 2. Photograph of the powder-holder piece composed of two opposite filters of sintered porous metal (filter elements available in pore sizes ranging from 0.5 to 140 μm).

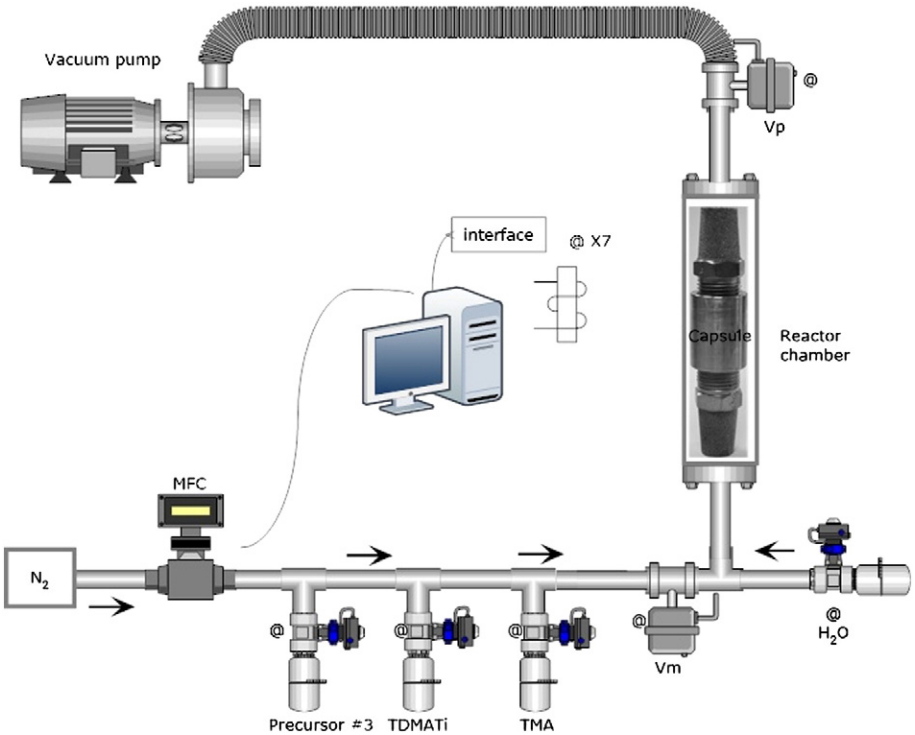

Fig. 1. Scheme (not to scale) of the ALD system configuration. @: solenoid actuator; MFC: mass flow controller.