The role of surface reactivity on the coating of 3D substrates and nanostructured materials in CVD and ALD

Angel Yanguas-Gil[1]

1 Argonne National Laboratory, Lemont, IL 60439 (USA)

The use of diffusivities to model the reactive transport of high surface area materials, including under Knudsen flow conditions, has a long history that goes back to the seminal works of Knudsen and Thiele.[1,2] In particular, the definition of effective diffusivities allows us to treat problems involving complex porous materials that are commonplace in areas such as energy storage and catalysis and that are much harder to tackle using ballistic deposition approaches. Under certain conditions, these models allow us to derive analytic expressions to the reactive transport inside high surface area materials that we can use to predict the conformality of a given process.

In this work, we explore how diffusivity models can be applied to model the coating of high surface area materials by CVD and ALD. In the case of CVD, we show how through the use of such models, we can establish a connection between the pressure dependence of the growth rate and a process's ability to coat high surface area materials.[3] This dependence can be codified in terms of an analytic expression that can be used to evaluate the conformality of a given CVD process. This equation also helps us rationalize the conditions required to achieve superconformal deposition in terms of the surface kinetics. In the case of ALD, a diffusive model leads to a general expression that provides dose times in terms of the sticking probability, generalizing the well-known expression introduced by Gordon *et al* for any 3D substrate or nanostructured material for which a single diffusivity can be defined.[4,5]

Interestingly, in both cases Thiele's modulus appears as the key parameter controlling the conformality of both CVD and ALD processes for the simplest case of first-order kinetics: while in the CVD case, this parameter determines the transition between conformal and non-conformal deposition, in the case of ALD this parameter controls the infiltration dynamics during the self-limited growth inside high surface area materials.[6]

While in CVD the ability to coat high surface area materials can be deduced from the dependence of the growth rate with pressure, the time-dependent nature of ALD makes the experimental characterization of the relevant parameters involved in the coating of high surface area materials more challenging. Here we present a simple method based on the evolution of growth profiles at a reactor scale. We show how, under highly symmetric conditions, it is possible to derive an expression that connects the time-dependent saturation profiles inside a reactor with the underlying surface kinetics.[7] We exemplify this method for three different precursors: trimethylaluminum, titanium tetraisopropoxide, and diethyl zinc. Finally, we demonstrate how we can use these experimental values to predict the growth dynamics under more challenging conditions. Two cases will be briefly shown here: fast pulsing ALD with a spurious CVD component, and the prediction of throughputs for the coating of high surface area materials using spatial ALD.

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