

## ALD Fundamentals

### Room Grand Ballroom H-K - Session AF1-MoA

#### ALD Growth Mechanisms I

**Moderators:** Simon Elliot, Schrödinger, Inc., Angel Yanguas-Gil, Argonne National Lab

1:30pm **AF1-MoA-1 Hybrid Computational Fluid Dynamics / Machine Learning Approaches to Reactor Scale Simulations and Optimization of ALD, ALEt, and LPCVD Processes**, *Angel Yanguas-Gil, S Letourneau, A Lancaster, J Elam*, Argonne National Laboratory

As the range of potential applications of atomic layer deposition increases, it is becoming increasingly important to understand how processes scale up to large area substrates and complex substrate geometries. Compared to the number of processes available, there is still a scarcity of tools to explore the interaction between surface kinetics, gas phase transport, and thin film growth at a reactor scale. These tools can help us answer not only key questions regarding the economics or scalability of a given process in terms of throughput or precursor utilization, but they can help us develop a better understanding and intuition of processes and simulate the output of commonly used in-situ techniques such as quartz crystal microbalance or mass spectrometry.

In this work we describe an open source code developed at Argonne to simulate processes based on self-limited and non-self limited surface kinetics at a reactor scale. This code, which is freely available, is built on top of OpenFOAM, a free, open source Computational Fluid Dynamics software. In combination with open source mesh generators such as GMSH, our code provides a simple workflow to explore the role of surface kinetics and the scale up of ALD, ALEt, and LPCVD processes.

To validate our model, we have established a comparison between simulations and experimental results obtained at two different cross-flow ALD reactors. We have then used synthetic growth profiles as a starting point to explore the ability of machine learning approaches to extract relevant information from growth profiles and other experimental datasets. In particular, we have explored the use of artificial neural networks to extract relevant kinetic data from reactor profiles and extrapolate saturation profiles based on a reduced set of experiments.

1:45pm **AF1-MoA-2 Scalable Kinetic Monte-Carlo Model for Parasitic Reactions in Silicon Nitride Growth using 3DMAS Precursor**, *Gem Shoute, T Muneshwar*, Synthergy Inc., Canada; *D Barlage, K Cadien*, University of Alberta, Canada

Atomic layer deposition (ALD) is a cyclical self-limiting reaction deposition technique that heavily depends on the characteristics of the chosen precursor. Currently, there are a limited number of ALD models that can give insight into key growth characteristics of a precursor such as ideal growth per cycle (GPC). Whether a self-limiting reaction can be achieved is determined by several factors related to the precursor itself, including its exposure and purge times and substrate temperature ( $T_{SUB}$ ), all which affect the GPC of the desired material. For instance, the silicon nitride ( $Si_3N_4$ ) precursor, tris(dimethylamino)silane (3DMAS), saturates at  $T_{SUB}$  up to  $\sim 150$  °C but beyond this temperature window, it exhibits dependence on its exposure time resulting in a non-saturated growth. While saturation indicates ideal ALD behavior, the latter observation implies the presence of parasitic reactions that are concurrent with ALD reactions, resulting in non-ideal ALD growth. These non-idealities are especially prominent in aggressive topologies such as high aspect-ratio structures which are a staple of numerous applications today. In this study, we will model the expected GPC of 3DMAS using a scalable kinetic Monte-Carlo approach (sKMC). The expected GPC vs.  $T_{SUB}$  relationship is compared to the experimental results of 3DMAS  $Si_3N_4$ . The discrepancies between the expected and experimental GPCs are attributed to additional parasitic reactions and interpreted through the lens of the sKMC model. Further developing these models is an important step towards rapid characterization of precursors and would serve as a useful tool for selecting the appropriate precursor for a given application.

2:00pm **AF1-MoA-3 Diffusion and Aggregation in Island-Growth and Area-Selective Deposition**, *Fabio Grillo*, ETH Zurich, Switzerland **INVITED**

Diffusion and aggregation phenomena play an essential role in many thin film processes [1]. Yet, their importance in atomic layer deposition (ALD) has been overlooked by most fundamental studies, which focus primarily on surface chemistry. This is not surprising because the latter governs the

growth process when this proceeds in a layer-by-layer fashion, which is often the case. However, chemistry alone cannot account for the formation and growth of islands or nanoparticles during the so-called “nucleation delay”. In this talk, I will present a theoretical framework that captures the kinetics of island-growth in ALD by accounting for diffusion and aggregation phenomena [2-4]. The framework is based on rate-equation and Kinetic-Monte-Carlo (KMC) models that build not only on the classic formulations of thin film nucleation kinetics but also on insights borrowed from research fields such as colloidal synthesis and catalyst sintering. These models describe the growth process as a balance between the cyclic generation of adatoms, arising from ALD surface reactions, and their aggregation due to non-equilibrium physical phenomena. The latter include: (1) adatom diffusion, (2) island formation by adatom aggregation, (3) island migration and coalescence (i.e., dynamic coalescence), (4) adatom attachment, and (5) inter-island exchange of atoms driven by the Gibbs–Thomson effect (i.e., Ostwald ripening). Throughout the talk I will demonstrate how these models can be used to relate the evolution of experimental observables such as the island-size distribution to well-defined growth mechanisms. For example, I will show how dynamic coalescence can govern nanoparticle growth during ALD of noble metals and how different surface diffusion rates can have a dramatic effect on the extent of the “nucleation delay”. Finally, I will present KMC simulations showing how surface diffusion can induce topography-dependent growth in area-selective ALD.

[1] Venables, J. A., *Philosophical Magazine* 1973, 27 (3), 697–738.

[2] Grillo, F.; Van Bui, H.; Moulign, J. A.; Kreutzer, M. T.; van Ommen, J. R., *The Journal of Physical Chemistry Letters* 2017, 8 (5), 975–983.

[3] Grillo, F.; Moulign, J. A.; Kreutzer, M. T.; van Ommen, J. R., *Catalysis Today* 2018, 316, 51–61.

[4] Soethoudt, J., Grillo, F., Marques, E. A., van Ommen, J. R., Tomczak, Y., Nyns, L., Delabie, A., *Advanced Materials Interfaces* 2018, 5(24), 1800870.

2:30pm **AF1-MoA-5 Surface Kinetics in ALD and ALE: Computing the Cooperative Effect by Automated Enumeration of Reaction Pathways with Spectator Adsorbates**, *Thomas Mustard*, Schrödinger, Inc.; *S Elliot*, Schrödinger, Inc.; *T Hughes, A Bochevarov, L Jacobson, S Kwak*, Schrödinger, Inc.; *T Morisato*, Schrödinger K.K., Japan; *J Gavartin*, Schrödinger, Inc., UK; *S Pandiyan*, Schrödinger, Inc., India; *M Halls*, Schrödinger, Inc.

The deposition or etching of solid films by ALD or ALE proceeds via reactions between gas-phase molecules and surfaces. The kinetics of such reactions have been previously computed to be strongly influenced by the local environment on the surface around the reaction site, which is called the ‘cooperative effect’ [1]. The activation energy at a reactive site has been shown to be affected by, or even dictated by, the presence of nearby co-adsorbed fragments or molecules, which otherwise take no part in the reaction and so may be termed ‘spectators’. In the case of ALD, this means that previously-inert ligand remnants on the surface can become reactive once sufficient numbers of other ligands adsorb in their neighborhood. This has been experimentally verified in the case of low-temperature ALD of  $Al_2O_3$  from TMA+ $H_2O$  [2].

Including a proper description of the cooperative effect is a serious challenge for first principles simulations of surface reactivity. One way forward is to sample the chemical space by automating the systematic investigation of the factors contributing to the cooperative effect. Specifically, we show how spectator Lewis acids and bases at various coverages and distances affect the activation energy for adsorption and proton transfer on the functionalized surfaces that are typically present during ALD of  $Al_2O_3$ .

To study the surface reactivity, we have generated an  $(Al_2O_3)_{16}$ -based cluster model of the (1 0 0) bilayer structure of  $q-Al_2O_3$ . We computed the activation energy for adsorption of  $H_2O$  onto an open Al site at the center of the cluster and for its dissociation into H+OH. The cluster is terminated with OH groups on its sides, but has space on top for up to 32 spectator molecules to surround the reactive site at distances ranging 2-6 Å. As spectator molecules we have considered various sizes of alkyl, alkoxy, hydroxyl and halide groups, so as to probe both electronic and steric effects. All possible arrangements of spectator adsorbates were generated automatically with enumeration tools in the Schrödinger *Materials Science Suite* [3]. The reaction pathway for dissociative adsorption of  $H_2O$  was then re-computed for each new spectator environment revealing how the activation energy changes with spectator identity and proximity.

We discuss the importance of the results for our understanding of thin film deposition and related fields such as heterogeneous catalysis. We also look

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forward to the prospects for efficient and systematic computation of complex surfaces.

[1] M. Shirazi, S. D. Elliott, *Nanoscale* 7 (2015) 6311-6318

[2] V. Vandalon, W. M. M. Kessels, *J. Vac. Sci. Techn. A* 35 (2017) 05C313

[3] <http://www.schrodinger.com/materials>

2:45pm **AF1-MoA-6 An Immiscible Fluids Approach for Correctly Predicting Agglomerate Dynamics during Particle Atomic Layer Deposition (Particle ALD)**, *Julia Hartig*, *A Weimer*, University of Colorado - Boulder

Particle agglomeration can significantly impact performance of fluidized bed reactors when running particle atomic layer deposition (Particle ALD). The fine powders frequently used in Particle ALD tend to agglomerate due to large interparticle forces, blocking surface sites and inhibiting surface coating uniformity. By modeling the agglomeration process during coating, steps can be taken to facilitate agglomerate breakup and mixing, thereby enhancing surface coating uniformity. However, current models of gas-solid flows which preserve the gas-solid interface, an important component for modeling ALD, have several limitations when incorporating agglomeration. Many of these approaches fail to address agglomerate size distributions or the dynamic formation and breakup process of fluidized agglomerates, shortcomings which remain a significant challenge to studying fluidized bed Particle ALD. In this work, we propose an alternative modeling approach which naturally accounts for the dynamic nature of fluidized agglomerates by treating the fluidizing gas and particles as two immiscible (non-interpenetrating) fluids. Agglomerates are modeled using dynamic "bubbles" whose interior consists of many primary particles from the solids phase. The position, shape and formation/breakup of these agglomerate "bubbles" are allowed to change with time as dictated by the corresponding transport equations. With this model, we can investigate the formation and breakup of agglomerates without prior knowledge of the agglomerate size characteristics. This study provides some preliminary agglomerate size distribution results from fluidized bed Particle ALD simulations and compares these results to experimental data from previous literature studies.

3:00pm **AF1-MoA-7 The Time-Resolved Interface between ALD and CVD**, *Henrik Pedersen*, Linköping University, Sweden **INVITED**

ALD (atomic layer deposition) is possibly the most important evolution of CVD (chemical vapor deposition). To a first approximation, ALD can be described as CVD where the precursor flows are separated in time. In other words, ALD is a time-resolved form of CVD. Despite this, CVD typically has a negative connotation in the ALD community. The phrase "CVD-component" is used to point to a process deviating from the idealized ALD behavior, where continual growth occurs.

The time-resolved precursor supply in ALD enables the self-limiting surface chemistry, rendering the very high degree of surface control which is the hallmark of ALD. However, CVD does not need to be time-resolved to have a very high degree of surface control. There are several examples in the literature of continuous CVD filling deep trench structures.<sup>1,2</sup> A time-resolved precursor supply without a self-limiting surface chemistry is another important evolution of CVD as it can be used for growing semiconducting nanowires on a patterned surface without the need for a catalyst<sup>3</sup> and can afford deposition of ternary or quaternary materials in some materials systems<sup>4</sup>.

CVD can also be made time-resolved by controlling the amount of energy available to the process over time. While this is difficult to do with a thermally activated CVD process, a process driven by the energy provided in a plasma discharge can easily be time-resolved in energy. This has allowed self-limiting processes with constant flow of precursors<sup>5</sup> and an enhanced ability to use ionic species for film deposition<sup>6</sup>.

This talk will discuss the time-resolved interface between CVD and ALD but also how continuous CVD can outcompete time-resolved CVD for some films: a recent example is nearly conformal B-C films in a 2000:1 structure by continuous CVD at 700 °C and 5 kPa.<sup>7</sup> The talk will also seek to nuance the view of a "CVD-component" in ALD processes and discuss how the time component can be used as a process knob in ALD.

## References:

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