

Tutorial: Modelling reactivity and growth in atomic layer deposition

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Atomic layer deposition is unusual in that it is defined through its chemical mechanism: self-limiting reactions of a gaseous precursor with the solid substrate. Understanding ALD growth thus requires a detailed understanding of reactivity and inertness, and thus of the mechanism of gas-surface reactions. Generally, ALD seems to result from the abortive dissociative chemisorption ('sticking') of the precursor in each pulse onto a surface that has been appropriately functionalised in the previous pulse. Many different reactions are in continual competition during the various phases of the cyclic growth experiment, responding to the changes in gas pressure and concentration of surface species. The outcome of this competition is of course determined by kinetics and for a successful ALD process the desired growth reactions should be much more rapid than the undesired – and possibly uncontrolled – non-ALD reactions.

To design, analyse or improve an ALD process in a rational way therefore requires knowledge of the underlying chemical mechanism. A remarkable level of detail about the mechanism can be obtained from characterisation under typical process conditions *in situ* to the ALD reactor using techniques such as quadrupole mass spectrometry, quartz crystal microbalance, infrared spectrometry and synchrotron X-ray methods. Atomic-scale modelling using density functional theory (DFT) provides a complementary view, which is the main subject of this tutorial [1]. DFT is a reliable, accurate, parameter-free approach to computing electronic structure and hence chemical structure and bonding, leading eventually to thermodynamics and kinetics.

In principle, the kinetics of every conceivable growth reaction and side reaction for a given system of substrate and reagents should be evaluated and compared. Clearly, this is rarely possible, but fortunately there are short-cuts. Comparing the activation energies of selected key reaction steps may be sufficient to answer specific questions about a process, and this is the most frequent approach that is taken (Figure 2). The common approach for ALD modelling is to use DFT to calculate the pathways for precursor adsorption, ligand migration and by-product formation on the surface, yielding reaction energies and activation energies for each step and indicating whether the reaction is thermodynamically or kinetically favourable at the temperature of interest (if the effect of entropy is included). Surfaces may be modelled using either periodic slabs or finite clusters.

Increases in computational power allow ever larger model systems to be simulated, or a wider variety of models (Figure 3). Large cells allow more complex arrangements of multiple adsorbates to be simulated, giving a superior model of the saturated surface during ALD. On the other hand, a large volume of small calculations, using the thermodynamics of one key reaction as a metric, allows high-throughput screening to be carried out, and this has been successfully applied to precursor optimisation (Figure 1).

The ALD process is manifest across many length scales. The pulsed flow of gases into meter-scale reactors, around millimeter-scaled geometries, leads to chemical reactions between atoms, which aggregate into nanometer-thick films and coat micron-scaled pores or particles. It is clearly impossible to describe explicitly all of these length scales in one model, and most simulations are 'multi-scale' insofar as they involve coupling between selected length scales according to the property of interest. The problem of timescale in ALD is perhaps even more acute than that of length scale, since a combination of fast and slow reactions contribute to film growth, and the pressure changes as gases are pulsed and purged over second-long timescales. Kinetic Monte Carlo is one approach to combining reaction events with disparate time scales so as to reveal the evolution of the overall process in time (Figure 4).

[1] "Modelling mechanism and growth reactions for new nanofabrication processes by atomic layer deposition", S. D. Elliott, G. Dey, Y. Maimaiti, H. Ablat, E. A. Filatova, G. N. Fomengia, *Adv. Mater.* 28 (2016) 5367–5380

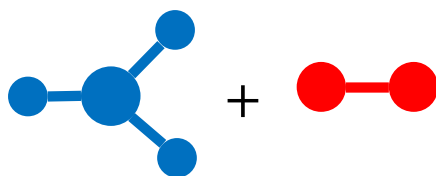


Figure 1. The deposition process is ultimately driven by the mutual reactivity of the precursors, which can be evaluated with gas-phase calculations of the precursor molecules. This yields information about bond strengths and thermodynamics that can give qualitative insights into the reaction mechanism, but no information on structure. This approach is useful for high-throughput screening.

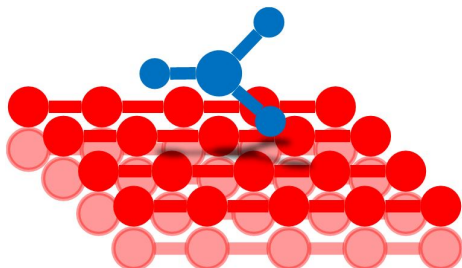


Figure 2. Bringing a single precursor molecule close to a model 2D surface (cluster or slab) allows computation of the structure and energetics of the chemisorption reaction steps, thus quantifying the ALD mechanism. The bonds thus formed are the basis of the primary structure of the target material.

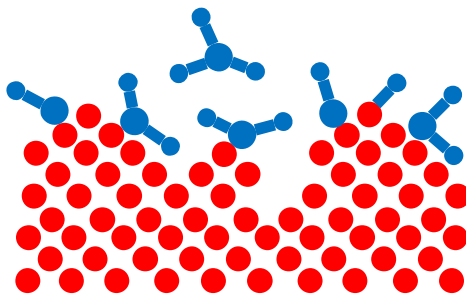


Figure 3. Recent work shows that higher accuracy data about reaction pathways can be obtained with larger and more realistic models of the local environment around a reaction site, featuring multiple precursor fragments interacting with a zone of multiple surface layers. More work at this scale may reveal structural motifs that lead to particular crystal structures through densification. This corresponds to the secondary structure of polymers, e.g. in MLD.

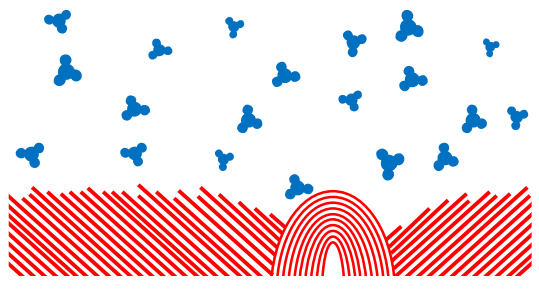


Figure 4. A future goal is to simulate the evolution of film morphology (or the tertiary structure of MLD polymers) through the fully-3D aggregation of nanoscale units, while still describing reactions with the same level of atomic level accuracy. Multi-scale modelling such as kinetic Monte Carlo may help achieve this goal.