What theory can tell us about ALD mechanism

Tutorial

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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. To design, analyse or improve an ALD process in a rational way therefore requires knowledge of the reactivity and inertness during gas-surface reactions. A remarkable level of detail about the mechanism can be obtained from characterisation under typical process conditions *in situ* to the ALD reactor. A complementary view is provided by atomic-scale modelling using density functional theory (DFT), 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 ALD 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 (precursor adsorption, ligand migration and by-product formation) may be sufficient to answer specific questions about a process. Increases in computational power allow ever larger model systems to be simulated, allowing more complex arrangements of multiple adsorbates to be simulated. Automated high-throughput computational screening may also be carried out, using the thermodynamics of one key reaction as a metric, and this has been successfully applied to precursor optimisation.

The ALD process is manifest across many length scales and time scales, since a combination of fast and slow reactions contribute to film growth in nanoscale features, and the pressure changes as gases are pulsed and purged over second-long timescales within a metre-scale reactor. Kinetic Monte Carlo is one approach to combining reaction events across disparate scales so as to reveal the evolution of the growing film in time.

[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