| **Simulation Parameter / Observable / Task (*) directly observable in experiments.** | **Methodology Used** | **Example Material / Type (if applicable)** | **Notes / Example references** |
|---|---|---|---|
| Decomposition and binding / chemisorption mechanisms/mode (kinetics and thermodynamics) | DFT/HF/post-HF/ML + kMC+ MD Hybrid ONIOM method, CCSD(T), MP2, B3LYP & HF/6-31G(d,p) Climbing image-(CI)-NEB, RMD simulations using LAMMPS | Various ALD (mainly Al2O3) + TiO2 + $Cu(acac)_2$ , $Ti(CpMe_5)$ + $ZrO_2$ | 76, 169, 75, 131, 77, 80, 171 |
| Growth rate*, and temperature dependence (kinetics) of growth rate*; based on chemisorption process | DFT + kMC+ MD<br>CFD<br>Mass balance; LBM Monte Carlo | TiO2 ALD<br>Various ALD<br>Zinc Oxide | 73,78,83,93,96,157,158,159,160,161,162,163,164,165, 97, 95 |
| Surface desorption, diffusion and reaction rates | Mainly DFT + kMC + MD | Various ALD/ALE | Also involves reading from tables |
| Binding affinity and sticking coefficients of adsorbate (precursor/etchant/inhibitor) | mainly DFT + kMC and MD<br>Potential extension to ML<br>Empirical and numerical (ANSYS) | HfO2 ALD, Pt precursors on graphene | 70,74,79,100,162,166,167,168, 148, 147 |
| Film (materials) properties: uniformity, roughness, density, temperature profile (thermal conduction), chemical composition (element analysis)* | CFD and numerical, Mass balance | | |
| Designing (/screening) new ALD precursors, ALE etchants or AS inhibitors (SMIs, SAMs) | DFT and ML (combined with structure prediction) only | Silicon and Carbon precursors | 178 |
| Predict cation ratios in ternary oxides (elemental analysis) | Mass balance; LBM Monte Carlo | | |
| Carrier gas flow and temperature profile | GCM/CAMD; CFD; MC Mass balance | HfO2 ALD, Alumina | 70,74,79,100,162,166,167,168, 149 |
| Modelling the morphology evolution | Mass balance; LBM Monte Carlo | | 56,66,86,94,179,180 |
| Modelling the precursor exposure on 3D substrates | Continuum Fluid Dynamics (CFD) and ANSYS | | 56,66,86,94,179,180 |
| Surface coverage by the adsorbate<br>Surface coverage as a function of time or rotation speed (spatial ALE of Al2O3) | DFT+kMC<br>Continuum Fluid Dynamics (CFD) | Various ALD/ALE | Coatings 2023, 13, 558v<br>Reactor-scale |

| | | | |
|---|---|---|---|
| Design and operation variables, e.g. the gap distance, purge and precursor gas flow rates, substrate velocity, and vacuum pressure have on the substrate film etching per cycle and uniformity. | Continuum Fluid Dynamics (CFD) | spatial ALE of Al2O3 | Coatings 2023, 13, 558v |
| Precursor pressure inside the reactor<br>Simulated quartz crystal microbalance (QCM) and quadrupole mass spectrometry (QMS) plots | Continuum Fluid Dynamics (CFD) | TiO2 ALD from titanium tetraisopropoxide and titanium tetrachloride precursors. | Reactor-scale |
| Growing of nanoclusters | DFT, QM/MM calculations using ONIOM implementation (DFT and classical MM) | Copper oxide nanoclusters on porphyrin | 175 |

* directly observable in experiments.

**Key parameters / observables and reference methodology***

Atomistic (nano-mesoscale)

- Energy barrier (kinetics), and reaction energies (thermodynamics)  (DFT and kMC)
- Sticking coefficient, surface coverage and binding affinity
- etc.

Continuum (meso-macroscale)

- Surface coverage (CFD)
- Film uniformity, roughness, density, temperature profile (thermal conduction), chemical composition

* directly observable in experiments.

**Glossary:** Continuum Fluid Dynamics CFD; Group Contribution Method GCM; Computer-Aided Molecular Design CAMD; The Lattice Boltzmann Method LBM; (Kinetic) Monte Carlo kMC/MC; Hartree-Fock HF

**References**

A comprehensive overview and relevant studies can be found in Nanomaterials 2022, 12, 831 (See Table 2)

Also see Coatings 2023, 13, 558
Review of atomic layer deposition process, application and modeling tools - ScienceDirect

Reactor scale simulations of ALD and ALE: Ideal and non-ideal self-limited processes in a cylindrical and a 300 mm wafer cross-flow reactor | Journal of Vacuum Science & Technology A | AIP Publishing