Atomic Layer Etching Process Specification Document
Simulation Use Case

Atomic Layer Etching?

Atomic Layer Etching (ALE) is a cyclic, self-limiting process that enables precise removal of material at the atomic scale. It operates through sequential surface reactions, typically involving a modification step followed by a removal step. The self-limiting nature of ALE ensures controlled etching with minimal surface damage, making it an essential technique in advanced semiconductor manufacturing. The ability to precisely remove material at the atomic level allows ALE to be utilized in various applications where precision and selectivity are crucial.

In the context of simulation, ALE is modelled to better understand its fundamental mechanisms, optimize process parameters, and predict etch rates and uniformity. Computational techniques such as molecular dynamics, kinetic Monte Carlo simulations, and density functional theory are frequently employed to replicate and analyse ALE behaviour. These simulations aid in refining ALE recipes and predicting process outcomes before experimental validation, reducing the need for extensive physical testing and accelerating process development.

One of the defining characteristics of ALE is its self-limiting reaction mechanism, which ensures that each reaction step saturates at the monolayer level, leading to controlled and uniform material removal. The process offers flexibility in controlling anisotropic and isotropic etching, depending on whether plasma-based or thermal ALE is employed. Another critical advantage of ALE is its ability to minimize surface damage, preserving the integrity of the underlying material, unlike conventional etching techniques. Additionally, ALE exhibits high material selectivity, allowing for the precise removal of targeted materials while leaving adjacent structures unaffected. These properties make ALE highly suitable for nanoscale device fabrication, where precision is paramount.

Inputs and Outputs of the ALE Process

The ALE process requires several key inputs to function effectively. The primary inputs include chemical precursors, often halogen-based gases such as chlorine (Cl_2) or hydrogen fluoride (HF), or plasma species in the case of plasma-enhanced ALE. An external energy source, whether thermal energy for thermal ALE or plasma excitation for plasma ALE, is necessary to drive the process. The substrate material, which can be a semiconductor, dielectric, or metal film, is the target for etching. Additionally, process parameters such as temperature, pressure, gas flow rates, plasma power (if applicable), and exposure time must be carefully controlled to maintain process stability and efficiency.

The outputs of the ALE process include the precisely etched material, where atomic-scale layers are selectively removed from the surface. By-products in the form of volatile compounds are also produced and must be efficiently evacuated from the chamber to prevent contamination. Additionally, the surface of the material undergoes chemical modifications that

can influence subsequent processing steps, necessitating careful planning of post-etch treatments.

To ensure optimal performance of the ALE process, several factors must be carefully managed. The process window must be optimized by selecting appropriate precursors, temperatures, and exposure times to maintain the self-limiting behaviour of the reactions. Proper surface activation is often required to enhance surface reactivity and ensure uniform etching across the entire substrate. Selectivity is another critical factor, as controlling precursor chemistry and energy input is essential to selectively etch target materials while avoiding unintended damage to adjacent layers.

Understanding the trade-offs between plasma-based ALE and thermal ALE is crucial for selecting the appropriate method for a given application. Plasma-enhanced ALE provides higher etch rates and anisotropic control, while thermal ALE offers damage-free etching with more uniform material removal. Maintaining stable chamber conditions, including pressure control, precursor flow, and exhaust management, is essential for reproducibility and process stability. Finally, validating simulation models with experimental data ensures that computational predictions accurately represent real-world process behaviour, leading to improved process development and refinement.

Parameter List with definitions

Simulation Parameter / Observable / Task (*) directly observable in experiments.	Definition
Decomposition and binding/chemisorption mechanisms/mode (kinetics and thermodynamics)	Investigation into the underlying mechanisms that drive ALE processes. Includes calculation of energy barriers for reaction steps, Gibbs free energy. Determination of kinetic and thermodynamic favourability. Can also include study of product formation, investigating what is actually formed in the reaction cycle (the amount/density of these).
Excitation Dynamics	Study of the effects of photon excitation of electrons and how this affects mechanisms of reaction and energies.
Etch rate*, and temperature dependence (kinetics) of etch rate*; based on chemisorption process	Investigation into the rate at which etching occurs, this can be per time or per cycle. It can also be investigated in relation to dependence on temperature or surface coverages.
Surface desorption, diffusion and reaction rates	Study of various rates of reactants on the adsorption surface. How they move in relation to the surface and process
Binding affinity and sticking coefficients of adsorbate (precursor/etchant/inhibitor)	Energy barriers to the adsorption of reactants, how likely these molecules are to bind to the surface as a result.
Film (materials) properties: uniformity, roughness, density, temperature profile (thermal conduction), chemical composition (element analysis)*	Investigation of the properties of the film at various points in the ALE process. This is often a good metric for the selectivity of a process.
Designing (/screening) new ALE etchants or AS inhibitors (SMIs, SAMs)	Using simulations to evaluate etchants' likelihood for success in an ALE application.

Carrier gas flow and temperature profile	Continuum level simulation of the engineering properties of a reactor, and how this will affect the process.
Modelling the morphology evolution	Investigating how the film changes as the process occurs
Cycle Timings	Study of timings of cycle steps, time taken for half cycles to occur etc.
Surface coverage by the adsorbate Surface coverage as a function of time or rotation speed	Modelling how the well the adsorbate may cover the surface, whether it is easy to find all available spaces or if blocking occurs. How this is affected by temperature or other factors.
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.	Reactor scale modelling aimed at optimising the engineering properties of the process.
Precursor pressure inside the reactor	Modelling of the engineering properties within the reactor, specifically the pressure the precursor is at and how this affects the ALE process.

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

Simulation Definitions

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

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

* Directly observable in experiments.

Density Functional Theory *- From review paper https://doi.org/10.1515/ntrev-2022-0084*

DFT is applied in material science to compute the electronic configurations of solids and atoms. It is defined as a quantum mechanical (QM) modelling methodology applied in chemistry, material science, and physics to describe the electronic structures of a many-body system (predominantly the ground state), precisely atoms, the condensed states, and molecules. Nowadays, it is used in binding energy calculations of molecules and the band structure of solids in chemistry and physics, respectively. In atomic layer deposition, the DFT can be used to explore the reaction mechanism between the first precursor and the substrate. It can be used to calculate the electron density and electronic configurations at this stage. Where the first precursor fails to bond with the surface of the substrate, DFT can be used to explain why this happens. DFT calculations can also be used to improve the conditions of the

substrate so that it is favourable for bonding with the precursor. After purging the by-products and excess first precursor, the second precursor is pumped into the reaction chamber. DFT can be used to map the reaction pathway between the first and second precursors. It can be used to predict the nature of the reaction and the by-products from this reaction. DFT can be applied to predict the thin film's mechanical and electrical properties. DFT can be used to validate the experimental conclusions, differentiate between possible opportunities to be explored, or create a foundation for experiments.

Molecular Dynamics *- From review paper https://doi.org/10.1515/ntrev-2022-0084*

Molecular dynamics (MD) simulation is a computational procedure for computing the transport properties and equilibrium of a classical many-body system. MD focuses on the dynamics of atoms, molecules, and clusters in the condensed and liquid states. It is used in many engineering and science disciplines like chemistry, physics, and materials engineering to determine the motion and equilibrium conditions of each atom or molecule. During the first stage of the atomic layer deposition process where the first precursor is forced into the reaction chamber, molecular dynamics calculations can be used to predict the kinetic properties of molecules such as material structure and complex and the stability of the substrate–precursor 1 bond. It can predict the binding energy between the substrate and the first precursor molecules. In the second stage where the by-products and excess first precursor are purged, MD can be applied to predict the mechanism of removal. In the third stage where the second precursor is pumped into the reaction chamber, MD simulations can be used to predict the nature of the reaction, the binding energy between the first and second precursor atoms, and the stability of the bond. It can also be applied in the fourth stage the same way as the third stage since these purging stages have the same principles. Molecular dynamics can be used to predict the thermodynamic properties of the deposited thin-film material, based on intermolecular interactions. The deposited thin film can be analysed by MD simulations to predict free binding energy, the heat of vaporisation, and boiling point. According to Sator, the molecular dynamics method is valid in both equilibrium and non-equilibrium physical phenomena. Molecular dynamics is a useful computational approach that may be used in simulating various physical phenomena if there is satisfactory computation power.

Monte Carlo

(Kinetic) Monte Carlo Simulations allow for the simulation of larger scale processes than DFT or MD as they do not explicitly include the same level of accuracy in the calculation, they do however take DFT calculation as input to their algorithm. These calculations are often used to calculate rates of etching or the surface coverage of etchants as the simulation of many molecules on a lager surface is very possible, where it is not with DFT or MD.