

10 Steps to ALE Process Development

Develop, optimise and characterise atomic layer etching (ALE) processes

Atomic Layer Etching (ALE) is a method to remove an amount of material with a high level of control over both the film thickness and the film properties. As written by Kanarik “ALE is useful not because it is perfect but because it offers more control than conventional etching techniques”. While significant parallels exist between the development of Atomic Layer Deposition (ALD) and ALE processes, the requirements and considerations for an ALE process are different since ALE must, by its very nature, target already deposited layers. This blogpost considers general ALE processes and thus makes distinctions between directional and omnidirectional processes and between plasma and thermal processes.

The development path in this document is outlined in a theoretical chronology. The material and process of interest may benefit from reordering and/or repeating of some steps. It is advised to look at the process as a whole and define critical steps/outcomes to the steps before starting full development to identify the optimum development path.



1. Directionality & Reactant Selection

Is directionality desired and which reactants will be used to volatise elements?

Depending on the context in which the ALE process is to be placed, it must be determined whether the desired structures should be etched directionally, followed by what chemistry can be employed. An anisotropic (or directional) process as illustrated in Figure 1a) requires directional species thus favouring an ion-driven plasma-based process, which can be used to dig down into a surface to create trenches/holes. An isotropic (omnidirectional) process (Figure 1b) may be more likely to be driven by non-directional species (either from a plasma or a gas) to remove material around exposed 3D structures.

Depending on the type of to-be-etched material, an etch chemistry must be chosen such that volatile species can be created with all elements in the material. Inspiration can be taken from existing processes, such as those reported in the ALE database on AtomicLimits, for similar materials. Is the material sensitive to high temperatures? Thermal processes may require (too) high temperatures whereas plasma processes offer highly reactive species at relatively low temperatures. What mechanisms have been used in processes for similar materials and can learnings be taken from the reactant groups (fluorinating / oxygenation / chlorinating / TMA-like / diketone) in these processes?

A Gibbs free energy change analysis, such as a Natarajan-Elliott analysis, may be performed on a candidate chemistry to give an indication as to whether a certain chemistry may work as a candidate. A negative Gibbs free energy change indicates energetically favourable reactions, allowing a comparison to be made between the energetic favourability of self-limiting reactions and continuous reactions for a proposed chemistry. The selection process should also include practical considerations such as which tools are available and suitable for an ALE process to determine which chemicals may be used and at which temperatures a process can safely be run.

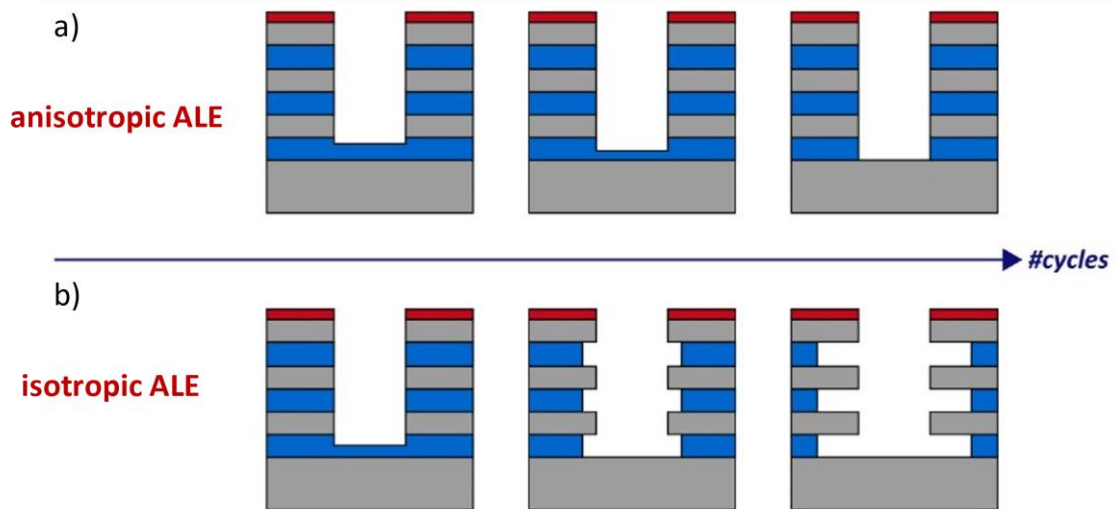


Figure 1: Representation of the differences between (a) a directional (anisotropic) etch process and (b) one which works equally in all directions (isotropic). An anisotropic process may be used to etch through a stack (blue and grey) perpendicular to the surface to create a trench whereas an isotropic process may also be used to etch parallel to the surface in deeper layers (blue).



2. Thickness Decrease

Is material removed from the surface when exposed to the etch chemistry?

Before a full process can be developed, the basic etch chemistry should be tested to ensure that the material is removed. This may be done experimentally by exposing a sample to a prototype (proto-) ALE process using the basic building blocks of the proposed chemistry. Published literature may give an estimate of expected saturation points, exposures beyond this point may improve the chance of being in saturation and/or give the best chance of obtaining a promising etch rate. Thickness measurements should be taken at regular intervals to investigate whether the material is etched as illustrated in Figure 2.

Practically, the proto-ALE process can be run for a set number of cycles after which a measurement is taken (optically e.g. through spectroscopic ellipsometry (SE) measurements or by precise measurements in the change in mass of a sample with a quartz crystal microbalance (QCM) to investigate whether material has been removed. A removal rate or etch per cycle (EPC) can be calculated as the mean amount of material removed per cycle given by

$$EPC = \frac{\Delta d}{n}.$$

The top surface may be of different composition than the bulk material because of the deposition process or exposure to air. To reduce influences of a different surface, the process should be repeated sufficiently many cycles to allow the process to reach through a potentially different surface into the bulk material. Since the process has not been optimised in this step, a linear etch rate through the film cannot yet be generally assumed. If no working proto-ALE process can be established, return to step 1.

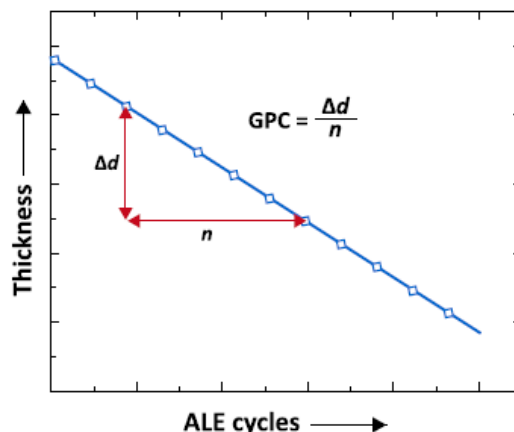


Figure 2: Schematic example of linear thickness decrease and calculation of the etch per cycle (EPC) in a linear regime.



3. Etch Control through Saturation

Are all sub-cycles self-limiting and is accurate etch control achieved?

Now a proto-ALE process has been established, it should be developed into a full ALE process. The next step is to test whether the primary requirement for ALE of self-limitation is sustained by testing for saturation. This may be done by creating saturation curves where the etch rate is measured while one of the sub-cycles is kept at a constant (high) exposure while the other sub-cycle is varied in length and/or composition. A saturation curve in a dosing step should roughly follow the profile illustrated in Figure 3a. The three main points of interest are derived from a saturation curve are the saturating etch rate, the saturating exposure time and the etch rate at no exposure.

Figure 3 curve a, gives a saturation curve for an ideal ALE sub-cycle where a clear plateau is observed at one monolayer of material removed per cycle. A real-world processes can be considered true ALE if the control in the sub-cycle is be maintained meaning that the etch rate must be at or below 1 monolayer/cycle. Three examples are given for a saturation curve, which do not indicate a true ALE sub-cycle. While Figure 3b does saturate, more than one monolayer is removed every cycle, indicating quasi-ALE. Figure 3c does not saturate and thus does not satisfy the self-limitation requirement. From these results, exposure times can be chosen for each of the reactants at saturating values such that no appreciable difference in EPC would be observed if the exposure time were increased.

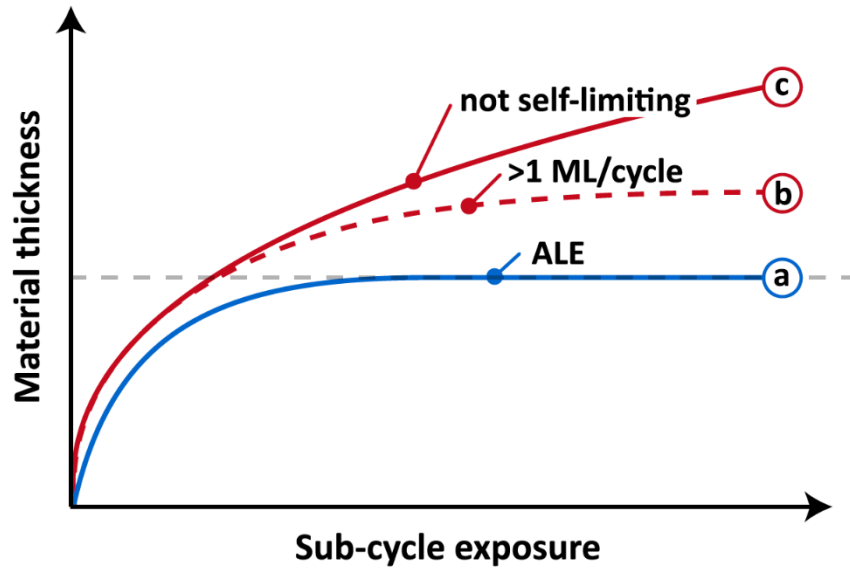


Figure 3: Generalised representation of saturation curves for (a) a true ALE sub-cycle where at most one monolayer of material is removed. (b) gives a sub-cycle which can affect more than one monolayer, (c) does not saturate and is thus not self-limiting. The latter (b) and (c) do not satisfy the self-limiting requirement and are thus not considered as true ALE.



4. Synergy

Does etching only occur because of alternating half-cycles?

When saturating exposure times have been found for all sub-cycles, a synergy test can be performed as a measure for the degree of self-limitation. In a true ALE process, etching only occurs as a synergistic effect from alternating the sub-cycles. This means that no etching should occur as a result of exposures to one of the sub-cycles, synergy looks at the effect of alternating the sub-cycles by comparing the saturated EPC to the etch rates of the sub-cycles individually. Synergy is inherently connected to the saturation investigated in step 3, if a removal step does not saturate, the synergy will be correspondingly low. Non-saturation of a modification step may not exhibit itself as a continuous etch rate and should be identified from saturation curves.

In a synergy test, a sample undergoes consecutive exposures to one of the sub-cycles from which a potential continuous etch rate can be determined as shown in Figure 4. By repeating this for all sub-cycles, continuous etch rates can be determined for each of the sub-cycles, from which the synergy is calculated as

$$S = 1 - \frac{\alpha + \beta}{EPC}$$

For a two-step ALE process with sub-cycles A, with continuous etch rate α , and B, with continuous etch rate β . An ideal ALE process is characterised by $S = 1$ while a process with $S = 0$ indicates that no saturation is found and the process is a chemical vapour etch (CVE) process rather than an ALE process.

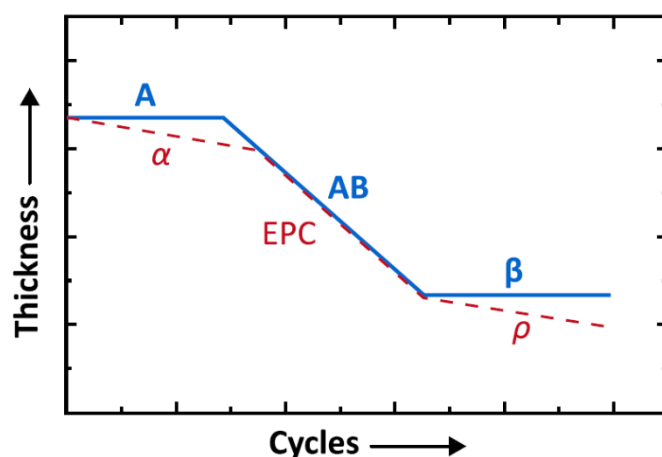


Figure 4: Schematic representation of a synergy test where a sample is first exposed to a repeating sub-cycle A, followed by the full ALE cycle consisting of sub-cycles A and B and repeats of sub-cycle B. Two examples are given where (blue) no etching is observed in the sub-cycles of a true ALE process and (red) where continuous etch component is measured in both of the sub-cycles indicated by α and β .



5. ALE Window

What is temperature and/or ion window or plasma parameter space of the process?

Reactions only take place when it is energetically favourable to do so. In a thermal sub-cycle, the energetics of the reactions are in large parts determined by the temperature at which the process is run as illustrated in Figure 5a. Similar to an ALD temperature window, too low temperatures may result in too low reactivities for reactions to take place. Temperatures above the window may result in reactants breaking apart (or decomposing) before reaching the surface meaning that no etch products are formed. Too high temperatures may also result in unstable bonds between reaction species and the surface resulting in desorption or continuous etching. A temperature window may be determined experimentally by measuring the etch rate for full ALE cycles at different temperatures ranging from, for example, 50 C to 450 C or through a Natarajan-Elliott analysis as outlined in step 1. Different process temperatures may change the saturation point either for the ALE process, thus requiring the runs to be optimised using saturation curves or by running the cycles in over-saturation. Ideally, the EPC is nearly constant in the ALE window but this is not a necessity. The most important aspect of the temperature window is that the sub-cycles self-limit (meaning a saturation point can be found) at all temperatures in the window.

Removal in an anisotropic process uses energy supplied by incoming ions to sputter material from the surface. An ion energy window as illustrated in Figure 5b should be identified experimentally by measuring the etch rate over a range of peak ion energies. Below this window, the ion energies are too low to enable sputtering of the modified layer. Above this window, the ion energies are sufficiently high that bonds in both the modified layer and material can be broken meaning that selectivity is lost, resulting in the sub-cycle no longer self-limiting.

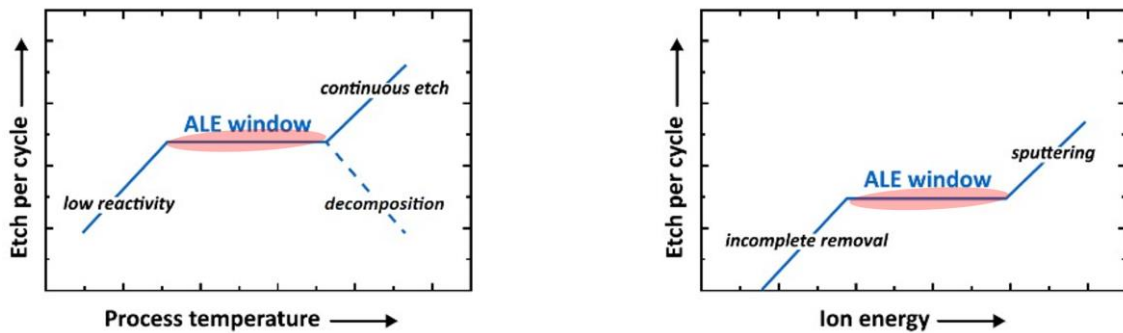


Figure 5: Schematic representations of (a) an ALE temperature window and (b) an ion energy window for anisotropic ALE.



6. Uniformity

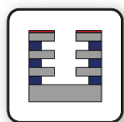
Are the etched thickness and material properties the same across the wafer?

Sequential self-limiting sub-cycles employed in an ALE process should provide good control over the uniformity of the process, both in etch characteristics and material properties of interest. This means that an ALE process in saturation should remove the same amount of material at all points on a wafer. Since a uniformity check calculates the variance in etch rates over a full wafer, it can serve as evidence for a good ALE process. Reactant fluxes may not be uniform throughout the chamber likely resulting in saturation occurring at different exposure times. Although running a process in over-saturation may hurt the efficiency of the process, it should not affect the amount of material etched in a true ALE process thus allowing exposure times to be increased to reach saturation at all points on a wafer.

The non-uniformity of an ALD process is calculated as the ratio between the difference between maximum and minimum thickness and the average thickness, this can be adapted to ALE by taking the difference in etched thickness w.r.t. the average etched thickness \bar{d} as

$$\text{non-uniformity} = \frac{d_{\min} - d_{\max}}{\bar{d}}$$

In addition to the etch rate, material properties such as the roughness and refractive index should be uniform across the wafer.



7. Isotropic or Anisotropic Etching

Is the etch isotropic or anisotropic in nanoscale features?

Whether a choice has been made for an isotropic or anisotropic etch process in step 1, the resulting process should be checked for its isotropy (or directionality) when the process has been optimised for saturation and uniformity. If a choice was made for a thermal process, an anisotropic component is less likely to be present meaning that this step may be of lesser importance. Isotropy can be checked by comparing the etch rates at different parts of a 3D structure as illustrated in Figure 6 through comparison of before etching and after etching TEM images or through analysis of specifically designed structures such as PillarHall™ chips.

Does an isotropic process remove materials on all orientations? Does an anisotropic process only remove material with line of sight to the plasma? If material, is not removed from all desired

surfaces at the same rate, what process parameters may cause this? Too short cycle times may prevent reactants from diffusing into high aspect ratio (deep but narrow) structures during dosing or out of high aspect ratio structures during purging. This may require lengthening of the sub-cycle (far) beyond saturation on a planar substrate to allow species to reach into three-dimensional structures.

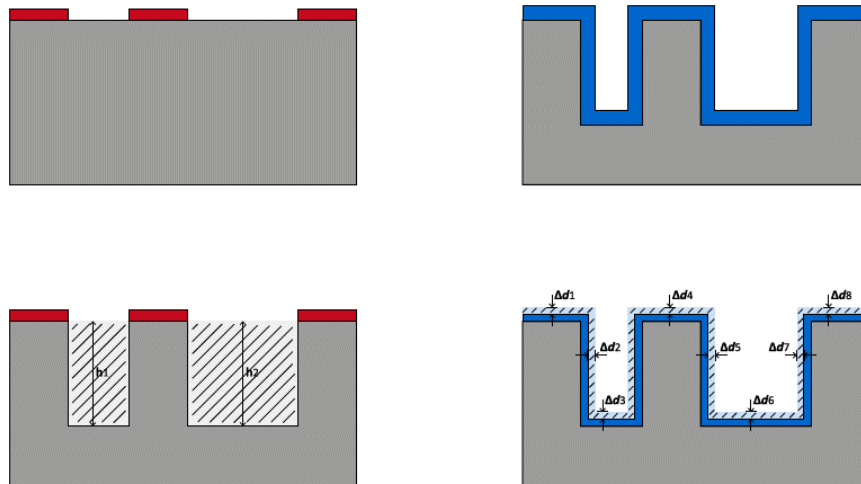


Figure 6: Schematic isotropy check structures where the dashed regions indicate material removed by the ALE process in (red) an anisotropic process and (blue) an isotropic process.

Since the amount of material removed from surface in an ALE cycle is determined by the saturation point, the etch rate is not expected to depend on aspect ratio of a structure as may be the case in reactive ion etching (RIE). This is known as aspect ratio dependent etching (ARDE) or RIE lag. While this is a feature of the etch uniformity in ALE, the 3D nature of ARDE means that it is more practical for it to be checked in this step. ARDE can be quantified by comparing the etch rate at the bottom of trenches of aspect ratios with the etch rate expected to be lower on higher aspect ratio structures if there is an ARDE component.



8. Selectivity

Is the etch selective with respect to other relevant materials?

Knowledge about the selectivity of a proposed process is a determining factor in whether a process can be included in a wider process flow in which a final device is manufactured, thus making it an essential property in an etch process. In principle, selectivity is checked by repeating steps 2, 3, 4 on each material of interest to determine the etch rate of the proposed chemistry on different materials. In practice, this may be done by developing one process for multiple materials in parallel or by performing a single run on a sample composed of multiple materials of interest. Figure 7 schematically shows how a process may affect the materials in such a sample. The selectivity is proportional to the amount of material etched from the materials in the sample as illustrated in Figure 7c.

Since the selectivity of a process is a feature of the process and process conditions, process parameters in step 5 and reactant selection in step 1 must be evaluated if the desired selectivity cannot be obtained. As such, the selectivity of the process may be determined at different temperatures first. In an anisotropic process, the range of ion energies of the species

accelerated towards the surface may exceed the sputter threshold of not to-be-etched materials. If changes in the process parameter space do not yield a desired selectivity, the reactants chosen in step 1 can be re-evaluated.

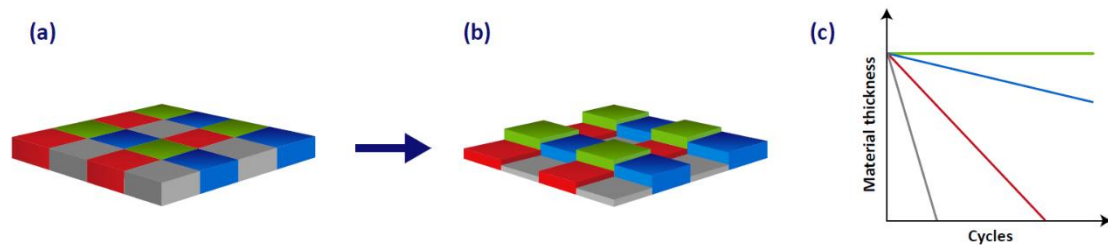
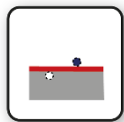


Figure 7: Selectivity of an etch process from an (a) initial film comprised of different types of materials: red, blue, green and grey to (b) a post-etch film. Resulting film thickness as a function of cycles is given in (c) where the process etches grey fully selective to green but shows a lesser degree of selectivity w.r.t. blue and green. Adapted from Carver et al.



9. Post-Etch Surface

Is the ALE process sufficiently damage and residue free?

Not only should the material be etched in a controlled manner, the surface left behind after the process should conform to the process requirements. While ALE is known to cause significantly less roughening to a surface than RIE and multiple cycles can result in smoothing of a surface, the post-ALE surface may not be entirely damage and residue free. A process may inadvertently deposit material or leave a modified surface behind after etching. Sufficiently strong or non-saturating reactants may also cause damage to the film and/or structure. Is the post-etch film of the desired composition? Have no unintended elements been included or removed by the ALE process on the target material and other materials used in the final device? Has the process changed the crystallinity of the material and is this desired? Is the process sufficiently controllable in order for the process not to increase surface roughness?



10. Other Aspects

Are aspects such as safety, cycle times, sustainability, etc. met?

- **Safety:** etch chemistries can be harmful to individuals, the processing equipment or the environment. Precautions should be taken to ensure the safety of individuals in the lab.
- **Placement in a wider process context:** previously reported ALE processes can be grouped in classes, what class does the current process belong to and what insights do the differences and similarities between the processes yield? Are the etch parameters for the current process comparable to those found in literature?
- **Optimisation balance:** a balance may be struck in the process parameter space to optimise for material control, etch rate per cycle/per hour, process cost per wafer or cycle, environmental impact, or other qualities of interest for the process. What considerations apply to the process being developed and have these been met?
- **Throughput and scalability:** whether a process is included in a wider process flow will depend on whether the process can be scaled up. This includes considerations such as the process length and how process parameters compare to the rest of the process flow.

- *Environmental impact:* etching steps are a major contributor to greenhouse gas emissions within semiconductor manufacturing. Therefore, future process development should look to include emission potentials as part of process optimisation. In the reactant choice in step 1, focus can be placed on selection of reactants for low-emission alternatives.