Atomic Layer Deposition Process Development

10 steps to successfully develop, optimize and characterize ALD recipes

Atomic layer deposition (ALD) is a surface-controlled thin film deposition technique that can enable ultimate control over the film thickness, uniformity on large-area substrates and conformality on 3D (nano)structures.[1–5] Each ALD cycle consists at least two half-cycles (but can be more complex), containing a precursor dose step and a co-reactant exposure step, separated by purge or pump steps (see Figure 1). Ideally the same amount of material is deposited in each cycle, due to the self-limiting nature of the reactions of the precursor and co-reactant with the surface groups on the substrate. By carrying out a certain number of ALD cycles, the targeted film thickness can be obtained.

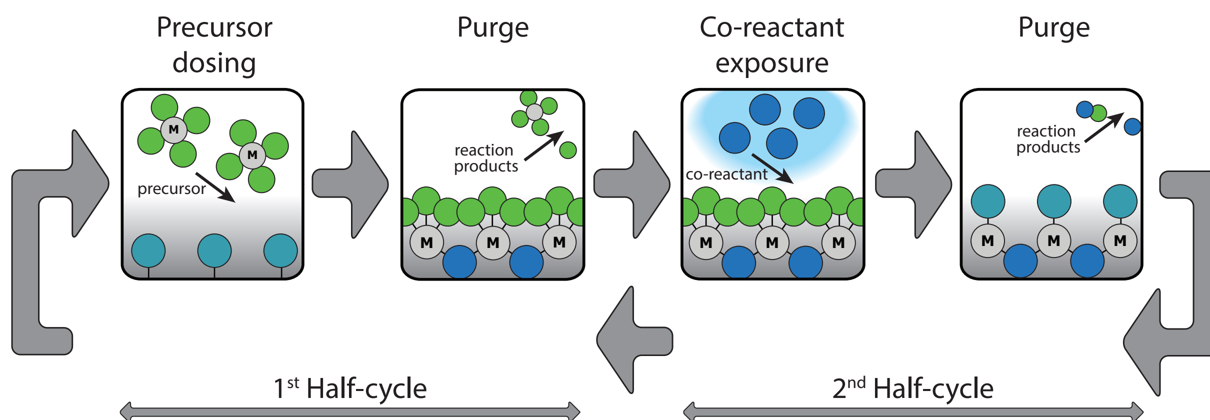
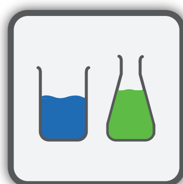


Figure 1. Schematic illustration of a typical ALD cycle consisting of two half-cycles. Sequential precursor and co-reactant doses are separated by purge or pump steps, leading to self-limiting film growth. 'M' indicates the metal atom, which can for instance be bound to oxygen or nitrogen atoms (in blue), to form a metal oxide or metal nitride, respectively. Precursor ligands are colored green and are eliminated by reaction with the co-reactant before being purged away.

Although the principle of ALD appears to be relatively simple, developing an ALD process is not necessarily a trivial task and it requires careful attention.[6] Here, steps are suggested and described to successfully set up an ALD process. Although the steps are roughly ordered chronologically, repetition of some of the steps might be needed at a later stage. In summary, it is advised that the following steps are taken when developing an ALD process:

1. Reactant selection: Which precursor and co-reactant will be used for the process?
2. Composition: Is the deposited film of the expected material composition?
3. Thickness control: Does the film thickness proceed linearly with cycles?
4. Saturation: Are the precursor, co-reactant and purge steps in saturation?
5. Properties: Does the material have the desired material properties?
6. Temperature: Is ALD behavior observed for a range of deposition temperatures?
7. Uniformity: Does the film have the same thickness everywhere on the substrate table?
8. Conformality: Is the film thickness the same everywhere along 3D-structures?
9. Nucleation: Does the initial growth on the substrate differ from the steady-growth regime?
10. Other aspects: Are aspects such as safety, stability, reproducibility, etc. met?

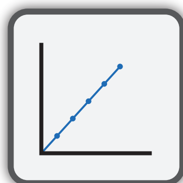


1. Precursor and co-reactant selection

Before setting up an ALD process, a suitable combination of precursor and co-reactant has to be decided on. Most importantly, the precursor and co-reactant molecules should consist of the appropriate elements, to obtain a material of the desired composition. In addition, they need to be reactive towards the surface groups present after the preceding subcycle, and in turn result in reactive surface groups after dosing.[7] Moreover, volatility, thermal stability and reactivity need to be sufficiently high.[8] Other requirements include availability and safety of the chemicals. Furthermore, reactor constraints and the application of the ALD film have to be considered, since they can limit the choice of possible chemicals. In addition to selecting the precursor it has to be determined how the precursor will be delivered to the chamber: vapor drawn, carrier gas assisted (i.e. carrier gas flowing over the precursor), bubbling (i.e. carrier gas flowing through the precursor), etc.

2. Chemical composition

Soon after deposition of the first ALD film, it is valuable to check if the grown material consists of the intended elements. Common ways to investigate the chemical composition are X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS), although XPS is typically more readily available. In case the material should be conductive, a simple four-point probe conductivity measurement can tell if the material is of high purity. Furthermore, a quick assessment of the refractive index can also indicate whether the desired material is obtained. If the deposited material is very different from the expectation, it might be good to reconsider **Step 1**, since proceeding can be a waste of time. However, in many cases, optimization of the deposition temperature or dosing and purge times can lead to improvement of the material composition. It is important to realize that the chemical composition and stoichiometry will determine the final material properties.



3. Thickness control

An important characteristic of ALD is the deposition of the same amount of material in each cycle, allowing for ultimate thickness control.[9] To confirm this, the thickness or material increase is to be determined per cycle, which is called the growth per cycle (GPC). Determining the GPC can be done both *in situ*, by following the material increase during deposition, as well as *ex situ*, by depositing multiple samples with varying number of cycles. Typically, the film thickness is measured (e.g. by spectroscopic ellipsometry), although alternative ways to check for linear growth are by determining the number of deposited atoms (e.g. by Rutherford backscattering spectroscopy) or deposited mass (e.g. by a quartz-crystal microbalance). Figure 2 shows a typical example of the film thickness increasing linearly with the number of ALD cycles. Note that the initial growth on the substrate might occur differently than at a later stage, as will be discussed in **Step 9**. For this reason the focus should lie on relatively thick films, with thicknesses over ~15 nm.

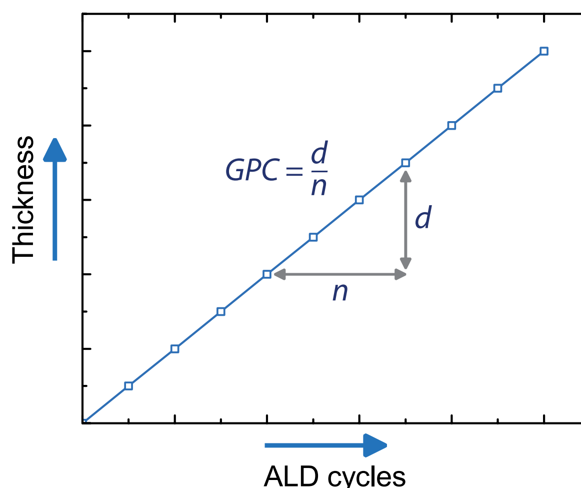
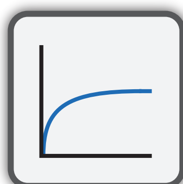


Figure 2. Typical example showing the film thickness as a function of number of ALD cycles, illustrating the linear growth behavior which is typical for ALD. The growth per cycle (GPC) can be defined as the slope of the thickness as a function of cycles. In case the deposited atoms or mass is measured as function of cycles, the GPC is given in terms of atoms per unit area or grams per unit area deposited per cycle.



4. Saturation

To confirm self-limiting growth, one of the key characteristics of ALD, the growth per cycle (GPC) has to be determined as a function of dosing and purge times. In the case of a standard AB-type (i.e. two-step) process, the precursor dosing time, precursor purge time, the co-reactant exposure time and co-reactant purge time need to be optimized. This is done by choosing a relatively long time for three of the four times and keeping those constant, while varying the fourth. This needs to be done for every step and, logically, the first step would be to confirm saturation of the precursor dosing time (See Figure 3a). After this the saturation of the other dosing times can be investigated, and perhaps the whole procedure has to be reiterated with slightly different dosing and purge times based on the findings.

Ideally, a clear plateau is observed when investigating saturation, meaning that the GPC does not increase or decrease when more precursor/co-reactant is dosed, or the purge time is extended.[9] Certain phenomena can however cause deviation, such as precursor condensation and precursor decomposition in the case of the precursor saturation curve. In addition, too short co-reactant dosing times can cause impurity incorporation, while too short purge times (See Figure 3b) can lead to a parasitic CVD component (i.e. reaction of the precursor and co-reactant molecules in the gas phase or at the surface), which can impact conformal and uniform deposition. Too long dosing and purge times, on the other hand, can significantly slow down the experiment, or in the case of industrial application, fabrication time. Note that it can also be insightful to perform experiments where only the precursor or co-reactant is dosed, to see if this leads to film deposition or modification of the substrate. Furthermore, saturation should also be confirmed at other process conditions, such as different table temperatures, as will be addressed later.

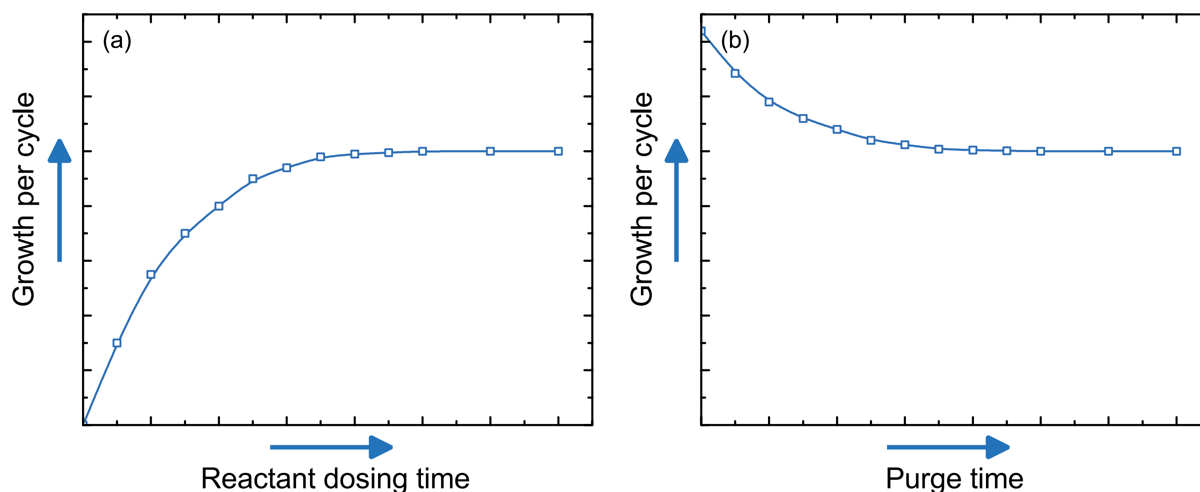
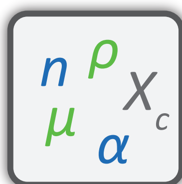
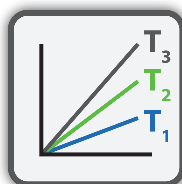


Figure 3. Idealized growth per cycle (GPC) as a function of (a) reactant (precursor or co-reactant) dosing time and (b) purge time, illustrating the self-limiting ALD behavior. After saturation is reached, dosing additional precursor, or prolonging the purge time does not lead to a change in GPC. Note that it is important to include a measurement for the data point corresponding to 0 s precursor (or co-reactant) dosing time. When purge times are too short, parasitic CVD can occur, leading to a higher GPC.



5. Material properties

Apart from the desired chemical composition, several other material properties are highly important. Depending on the application of the ALD films, it can be of interest to check the following: optical properties (refractive index n, absorption coefficient α), electrical properties (resistivity ρ, carrier density N_e and mobility μ), film and surface morphology (roughness, crystallinity X_c), et cetera. Note that the material properties are strongly linked to the chemical composition of the films, which should be investigated in detail first, and that tuning of the chemical composition can enable different material properties.



6. Temperature dependence

Varying the deposition temperature can have a significant effect on both the growth behavior and the material properties. For this reason, it is advised to deposit films over a range of substrate temperatures, for example between 50 °C and 350 °C. ALD researchers often speak about an ALD window, i.e. a region where the GPC is (nearly) constant, allowing for reliable and repeatable results despite slight temperature variations (See Figure 4).[10] However, this constant GPC is not a necessity for an ALD process, and it is mostly important that saturation behavior is found for all temperatures. Effects such as precursor condensation (at low temperature) and precursor decomposition (at high temperature) can namely become visible by verifying saturation at various temperatures. While a constant GPC is a desirable feature, numerous reports actually exist of ALD processes that demonstrate a temperature dependent GPC, but do show saturating ALD behavior over a wide temperature range.

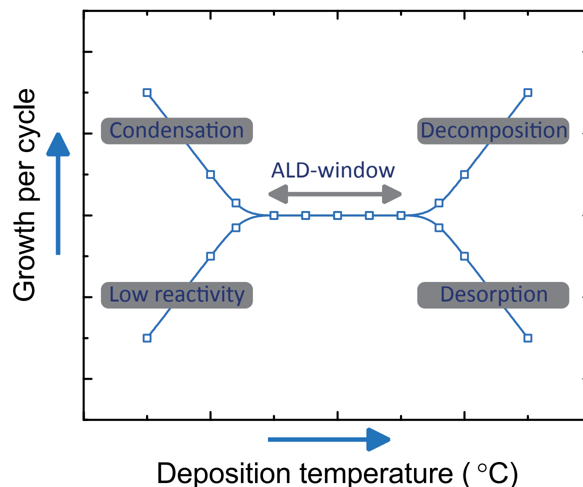


Figure 4. Growth per cycle (GPC) as a function of deposition temperature, showing the idealized ALD window. In addition, precursor related phenomena which can occur at high or low temperature are indicated.

It should be noted that the actual temperature of the sample can be significantly lower than the set temperature of the substrate table, especially when working with a warm (instead of hot) wall reactor at high vacuum. This difference in temperature can be due to the poor thermal contact between the table and the sample, which is pressure dependent.

7. Uniformity

Another important merit of ALD is the uniformity of the film over large area substrates.[11] Often, saturation is verified using coupon samples at the center of the substrate table, which doesn't mean that precursor or co-reactant dosing is sufficient everywhere. Moreover, non-uniformity is generally a clearer signal of a CVD component than obtained through saturation curves. Hence, a good uniformity is evidence that the process is a well-behaving ALD process. Therefore, it is a recommended that a film is deposited on the largest substrate that fits in the ALD reactor. Most importantly, the thickness variation can easily be determined, either manually, or using an automated mapping stage. However, certain material properties such as composition and resistivity can also be important with respect to uniformity. It might for example be that the thickness uniformity of the deposited film is good, while the resistivity of the film varies significantly over the substrate.

8. Conformality

Although often disregarded during ALD process development, the conformality of the ALD film should be taken into account. Conformality is the ability to conformally deposit a film on 3D structures, i.e. with (ideally) no variation in thickness along the structure.[12] Instead of the conventional planar coupons, specific samples are required to assess the conformality, which contain trenches or vias. A way to quantify the conformality is to deposit in a vertical trench or via with a certain aspect ratio (AR), and, after preparation of a cross-section, calculate the ratio between the thickness at different locations (See Figure 5). Another approach is to use a specifically designed structure with a lateral via, such as Pillar Hall,[13] allowing for assessment of the thickness profile without the need of a cross-section. In addition to conformality in terms of film thickness, variations in material properties along the 3D structure can also be significant.

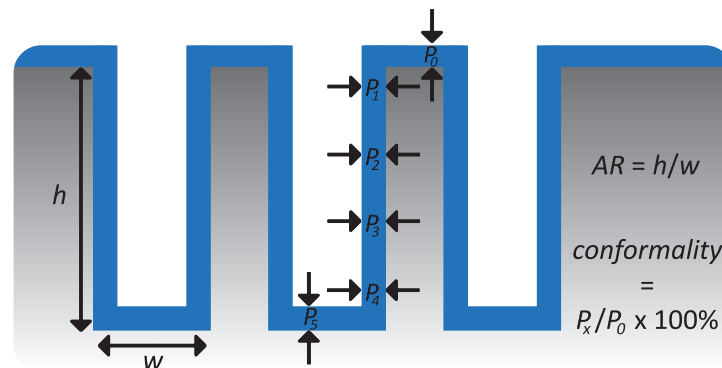
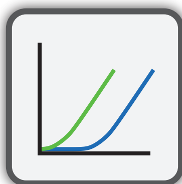


Figure 5. Schematic explaining conformality, which can be defined as the film thicknesses at different positions in the trench relative to the thickness at the top of the trench. The trench has an aspect ratio (AR), defined as the height of the trench divided by the width.



9. Nucleation behavior

The film growth during an ALD process might initially show a different behavior than at a later stage of the deposition (See Figure 6). The reason for this is that reactions of the precursor with the material and the chemical groups present on the substrate will probably occur differently than reactions with surface groups on the deposited film. As is shown in Figure 6, it is generally possible to distinguish three cases that can manifest themselves during the initial cycles: linear growth, accelerated or enhanced growth, and delayed growth.[14] The nucleation behavior can affect material properties, such as defect or pinhole density, crystalline structure, and film resistivity. Moreover, sometimes differences between growth on various substrates can be observed, which can be the starting point for an area-selective ALD process. This means that a delayed growth can be beneficial in certain cases, although usually fast nucleation is desired for regular applications

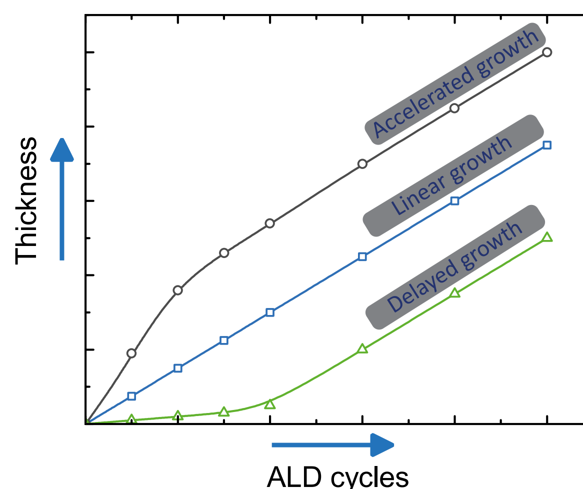


Figure 6. Example of the thickness as a function of number of ALD cycles, illustrating the difference between accelerated, linear, and delayed growth during the initial ALD cycles.

The nucleation behavior is strongly dependent on the growth mode of the ALD material. ALD of a metal on a metal oxide often starts with island growth, also Volmer-Weber-type growth, before a closed films is obtained, while certain other materials growth in a layer-by-layer fashion or Frank-Van Der Merwe mode.[15] Note that the growth mode depends on the difference in surface energy between the substrate and the deposited film. After investigating the nucleation behavior, it is important to realize that specific thickness effects may start playing a role in the growth behavior after the initial nucleation phase. For instance, crystallization of the film after a certain film thickness is reached might lead to an increase of the GPC.

10. Other important aspects

Several other aspects are also important during ALD process development, although they are not necessarily specific to ALD.

i. Safety: Apart from considering the safety of the used chemicals, it is a very good idea to inform yourself whether any poisonous or potentially harmful reaction products are produced during the ALD reactions, or upon contact with the environment. Moreover, it should be checked if the film material itself is not creating any safety risk.
ii. Film stability: The stability of the deposited films over time and their sensitivity to the environment (e.g. the ambient) need to be taken into account. Especially in case the film is intended for use in a certain environment, it should be confirmed if it can withstand these conditions (e.g temperature, humidity, etc.).
iii. Reproducibility: It should be confirmed that the same film thickness and film properties can be obtained by repeating the same deposition recipe. Conditioning of the reactor wall can play a role in this context, although variations in substrate temperature or reactor pressure can also be responsible for unwanted effects.
iv. Precursor consumption: Efficient use of the precursor becomes more significant for expensive precursors and can for instance be achieved by minimizing the size of the reactor chamber and by avoiding overdosing. Note that the required precursor dosing typically depends on the total surface area of the substrate, which is larger when working on 3D substrates.
v. Precursor stability: Prolonged heating of the precursor, which is usually needed to obtain a certain vapor pressure, can sometimes cause degradation of the precursor. For this reason it might be needed to turn off the precursor heating during periods that no deposition runs are being performed.
vi. Literature comparison: It is advised to verify whether the obtained results are in agreement with previous reports on the same (or very similar) ALD process, especially in terms of chemical composition and growth behavior. If this is not the case, an explanation for the distinctions should be found.
vii. Device performance: The real test for the developed ALD process will be the application in a working device, such as a transistor or solar cell. Certain phenomena, for instance the presence of defect states or film pinholes or incorporation of particles, might not be detected by basic characterization techniques and might only become visible when testing the film in a device.

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