Cremers, Véronique; Puurunen, Riikka L.; Dendooven, Jolien

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Conformality in atomic layer deposition: Current status overview of analysis and modelling

Véronique Cremers,1 Riikka L. Puurunen,2,3 and Jolien Dendooven1,a)

AFFILIATIONS
1Department of Solid State Sciences, Ghent University, Krijgslaan 281/S1, B-9000 Ghent, Belgium
2Department of Chemical and Metallurgical Engineering, Aalto University School of Chemical Engineering, P.O. Box 16100, FI-00076 AALTO, Finland
3VTT Technical Research Centre of Finland, P.O. Box 1000, FI-02044 VTT, Finland

a)Electronic mail: Jolien.Dendooven@UGent.be

ABSTRACT
Atomic layer deposition (ALD) relies on alternated, self-limiting reactions between gaseous reactants and an exposed solid surface to deposit highly conformal coatings with a thickness controlled at the submonolayer level. These advantages have rendered ALD a mainstream technique in microelectronics and have triggered growing interest in ALD for a variety of nanotechnology applications, including energy technologies. Often, the choice for ALD is related to the need for a conformal coating on a 3D nanostructured surface, making the conformality of ALD processes a key factor in actual applications. In this work, we aim to review the current status of knowledge about the conformality of ALD processes. We describe the basic concepts related to the conformality of ALD, including an overview of relevant gas transport regimes, definitions of exposure and sticking probability, and a distinction between different ALD growth types observed in high aspect ratio structures. In addition, aiming for a more standardized and direct comparison of reported results concerning the conformality of ALD processes, we propose a new concept, Equivalent Aspect Ratio (EAR), to describe 3D substrates and introduce standard ways to express thin film conformality. Other than the conventional aspect ratio, the EAR provides a measure for the ease of coatability by referring to a cylindrical hole as the reference structure. The different types of high aspect ratio structures and characterization approaches that have been used for quantifying the conformality of ALD processes are reviewed. The published experimental data on the conformality of thermal, plasma-enhanced, and ozone-based ALD processes are tabulated and discussed. Besides discussing the experimental results of conformality of ALD, we will also give an overview of the reported models for simulating the conformality of ALD. The different classes of models are discussed with special attention for the key assumptions typically used in the different modelling approaches. The influence of certain assumptions on simulated deposition thickness profiles is illustrated and discussed with the aim of shedding light on how deposition thickness profiles can provide insights into factors governing the surface chemistry of ALD processes. We hope that this review can serve as a starting point and reference work for new and expert researchers interested in the conformality of ALD and, at the same time, will trigger new research to further improve our understanding of this famous characteristic of ALD processes.

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I. INTRODUCTION

Atomic layer deposition (ALD) is a gas phase thin film deposition technique which has been discovered and developed independently in the 1960s in the Soviet Union and in 1974 in Finland.1–3 This technique is characterized by exposing the substrate to an alternating sequence of vapor phase reactants. Due to the self-saturating nature of the surface reactions, the film thickness can be controlled at the atomic scale.4–8 A typical ALD process consists of several ALD cycles with each ALD cycle comprising four characteristic steps, which are shown in Fig. 1 for the prototypic4–6 trimethylaluminum (TMA)/H2O process:

1. Step 1: The first reactant A (TMA) reacts in a self-terminating way with the available functional groups on the OH-terminated surface.

FIG. 1. Schematic representation of one ALD cycle of the TMA/H2O process.
2. Step 2: The excess of reactant A (TMAs) and the gaseous by-products (CH₄) are purged or pumped away.
3. Step 3: The second reactant B (H₂O) reacts in a self-terminating way with the adsorbed species (A) on the surface.
4. Step 4: The excess of reactant B (H₂O) and the gaseous by-products (CH₄) are purged or pumped away.

In this review, we will call steps 1 and 3 the first and second reactions of the ALD cycle, respectively. After each ALD cycle, a certain amount of material (coating) is deposited on the surface, which is called the growth per cycle (GPC). The GPC can be expressed in various units such as those of the thickness (e.g., nm), mass gain (e.g., g), and an increase in the areal density (e.g., atoms/nm²).

As opposed to “line-of-sight” deposition techniques such as physical vapor deposition (PVD), ALD has the capability to grow uniform and conformal films in 3D structures with complex shapes and with a large depth to width ratio or in more general terms a large aspect ratio. For deposition techniques that are flux controlled [such as chemical vapor deposition (CVD) and PVD], film growth depends on the local gas flux. Because of the inherent kinetics of gas transport within narrow trenches, the flux of reactant molecules can be several orders of magnitude larger near the entrance as compared to the bottom of the structure. Therefore, the entrance region to narrow trenches tends to get clogged at the beginning of the deposition, making it difficult for reactant molecules to diffuse deeper into the structure. Various approaches exist to improve the conformity of CVD processes, e.g., inhibiting the growth, and using surfactants to catalyze the growth. Also during ALD deposition, the entrance region will receive a higher flux of reactant molecules. However, the self-saturating nature of the surface reactions during ALD results in surface-controlled deposition. Higher flux near the entrance region will result in faster coverage at this location, but once the surface is saturated, no further reaction can take place at this site, avoiding clogging of the trench entrance and allowing the reactant molecules to diffuse deeper into the trench and coat the entire structure.

The miniaturization of semiconductor devices leads to the introduction of more complex 3D geometries with an increasing aspect ratio, often termed high aspect ratio (HAR) structures. Due to the self-limited nature of ALD, ALD is one of the most suitable deposition techniques to deposit thin coatings with an excellent control of the layer thickness onto such structures. ALD is, for example, used for the fabrication of trench capacitors in dynamic random-access memory (DRAM), FinFETs, and 3D NAND structures. Also, outside the field of semiconductor applications, ALD is being considered to deposit films onto 3D substrates, e.g., for surface functionalization and protection of microelectromechanical systems (MEMSs), and coatings for fuel cells, solar cells, batteries, catalytic surfaces, membranes, textiles, and pharmaceuticals.

In this review article, we explore the status of current understanding of the conformity of ALD processes, providing an overview of published experimental and theoretical studies focusing on this topic. First, conformity-related concepts of ALD processes will be introduced in Sec. II. In Sec. III, we discuss methods and dedicated test structures that have been used to quantify the conformity of ALD processes. An overview of experimental reports on the conformity of thermal, plasma-enhanced, and ozone-based ALD processes is presented in Sec. IV. In Sec. V, different models are discussed that have been used to simulate ALD in narrow structures. These models can be used to optimize process parameters towards improved conformity. Fitting of model parameters to experimental data can also provide insights into the ALD surface reactions, e.g., in sticking probabilities and the impact of non-ideal side-reactions during ALD. In Sec. VI, we simulate the influence of different ALD parameters on the conformity with a Monte Carlo model and discuss how one can obtain relevant information on the growth mechanism from the analysis of such thickness profiles.

II. CONCEPTS

A. ALD characteristics: Uniformity and conformity

Due to the self-limited nature of the chemisorption and subsequent surface reactions, it is possible to grow with ALD uniform and conformal films in structures with a large depth to width ratio. Uniform films have an equal thickness and composition (and other properties) at each position along a planar substrate, e.g., along a 300 mm wafer. Conformal films have the same thickness (and properties) inside 3D features (“around-the-corner”). Figure 2 shows a schematic representation of the coating of a 3D structured surface with a non-conformal line-of-sight technique (a) and with the typical conformity of an ALD coating (b). In the absence of the 3D feature, both films could be considered uniform.

B. Gas transport: Molecular to viscous flow

During reactive transport, the reactant molecules penetrate into narrow structures in a certain flow regime. To distinguish the different flow regimes, Knudsen introduced a dimensionless parameter, the Knudsen number Kn, which is defined as the ratio of the mean free path \( \lambda \) (m) and the pore diameter \( d_p \) (m)

\[
Kn = \frac{\lambda}{d_p}. \tag{1}
\]

If the mean free path of the reactant molecules is much larger than the dimensions of the structures \( (Kn \gg 1) \), gas transport takes place in the molecular flow regime. In this regime, the transport is dominated by particle-surface interactions and inter-particle interactions can in most cases be neglected.

The mean free path \( \lambda \) (m) of molecules is given by

\[
\lambda = \frac{k_BT}{\sqrt{2\pi mP}}, \tag{2}
\]

with \( k_B \) (m² kg/(s² K)) being the Boltzmann constant, \( T \) (K) being the temperature, \( P \) (Pa) being the pressure, and \( d \) (m) being the diameter of the molecules. The mean free path depends strongly on pressure, while the molecule size and temperature affect the mean free path to a
minor extent, as illustrated in Fig. 3. At sufficiently low pressure, a molecular flow regime can be obtained in structures with macroscopic (i.e., mm to cm) dimensions, while for near-atmosphere pressures, molecular flow will only be achieved in nanometer scale features.

If the mean free path of the reactant molecules is much smaller than the dimensions of the features \((Kn \ll 1)\), gas transport is governed by viscous flow, also known as continuum flow. In viscous flow, there are frequent particle-particle interactions in the gas phase. The transition flow between molecular and viscous flow takes place when \(Kn \approx 1\) and is often termed Knudsen flow although the latter term is also used as a synonym for molecular flow.

When the gas phase consists of different types of molecules, e.g., when a mixture of reactant molecules (species A) and carrier gas molecules (species B) is used in ALD, one has to adapt the above formula [Eq. (3)] of the mean free path. Chapman et al. derived a specific scattering length \(\lambda_{0,A}(m)\) for a particle of species A taking into account the interaction with particles of species B

\[
\lambda_{0,A} = \frac{k_B T}{\sqrt{2P_A \sigma_{A,A} + \frac{m_A}{m_B} P_B \sigma_{A,B}}}.
\]

with \(k_B\) being the Boltzmann constant, \(T\) being the deposition temperature, \(P_i\) being the partial pressure, and \(m_i\) being the mass of molecules of type \(i\). The cross-section between the molecules \(i\) and \(j\) with radii \(r_i\) and \(r_j\) is represented by

\[
\sigma_{ij} = \pi (r_i^2 + r_j^2).
\]

C. ALD reactor types

One of the distinguishing factors among the different types of ALD reactors is whether they operate in the temporal or spatial ALD mode, with the first mode being the most conventional one. During temporal ALD, the sample is stationary and the different reactants are sequentially injected and removed from the sample cell. In spatial ALD, there is a continuous supply of the reactants in isolated injection regions which are separated by an inert gas curtain, while the substrate moves between the different zones. Suntola developed in 1974 his first ALD reactor where he applied spatial ALD. The reactor comprised a carousel that rotated at several rounds per second and worked at a base pressure of \(10^{-4}\) Pa. In another reactor design, Suntola et al. used a carrier gas to separate the different surface reaction steps from each other in a temporal deposition mode.

As discussed above, the reactant (partial) pressure is a determining factor for the gas transport regime in high aspect ratio structures, influencing in turn the process of conformal coating during ALD. Therefore, we classify the different designs of ALD reactors according to the typical pressure ranges that are applied. Following the classification by George, we define pump-type and flow-type (temporal) ALD reactors. In pump-type reactors, reactants are added into the reactor chamber without the use of a carrier gas and the typical reactant pressure is

\[
s_{ij} = \pi (r_i^2 + r_j^2).
\]
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In this way, high deposition rates can be achieved for certain scenarios. In spatial ALD approaches applying atmospheric pressures for high pressure, a certain minimum amount of time is needed before the ALD reactors take place. In pump-type reactors, it occurs in the viscous flow regime. Flow-type reactors are typically operated at a pressure near 100 Pa, and cycle times are on the order of 10 s. Next to pump-type and flow-type reactors, atmospheric pressure (AP-type) reactors in which ALD processes take place at (or near) atmospheric pressure (∼10^5 Pa) form the third class of ALD reactors. Over the past few years, there has been increasing interest in spatial ALD approaches applying atmospheric pressures for high throughput ALD for a number of applications including photovoltaics. In this way, high deposition rates can be achieved for certain processes, e.g., ∼1 nm/s for ZnO.

As shown in Fig. 3, different flow regimes occur during ALD within high aspect ratio structures, depending on the characteristic size of the 3D features that are present on the substrate and the absolute pressure range, linked to the type of ALD reactor used. For instance, in millimeter-sized features, reactant transport occurs in the molecular flow regime in pump-type reactors, but in flow-type and AP-type ALD reactors, it occurs in the viscous flow regime.

D. Exposure in ALD

Pressure plays a crucial role in the ALD process, as it determines the impinging flux of reactant molecules on the substrate. At a given pressure, a certain minimum amount of time is needed before the sample surface is fully covered with adsorbed reactant molecules and saturation is reached. A useful measure for the reactant exposure is therefore given by the product of the reactant partial pressure and the pulse time. In this way, the exposure is expressed in Langmuir (1 L = 10^3 Torr s = 7500 Pa s). As an example, Gordon et al. estimated that the exposure required to saturate a flat surface with Hf(NMe2)4 molecules during ALD of HfO2 at 200 °C is in the range of 3–43 L. Much larger exposures are commonly required during ALD on high aspect ratio structures to compensate for diffusional limitations. To deposit a conformal coating of HfO2 into holes with a pore diameter of 0.17 μm and a depth of 7.3 μm, an exposure of 9000 L was assumed. Applying sufficiently large exposures is one of the essential conditions to obtain a conformal coating by ALD as will be exemplified later in this review article.

E. Reaction mechanisms and sticking probability

The surface reaction kinetics of ALD processes can be complex and should not be considered as trivial as depicted in Fig. 1. For many processes, even the reaction stoichiometry during an ALD cycle is not necessarily known. To cope with this complexity when modelling the conformity of ALD processes, the reaction chemistry is often simplified by using irreversible Langmuir surface kinetics. The sticking probability s is introduced as the probability that a reactant molecule reacts upon collision with the surface and contributes to film growth. It is often assumed that the sticking probability has a first order dependence with the available surface sites

\[ s = s_0 (1 - \theta), \] (5)

with \( s_0 \) being the initial sticking coefficient (i.e., reaction probability with a bare surface) and \( \theta \) being the fraction of covered sites. This expression implies that the surface reactivity gradually decreases with the increase in the coverage and eventually becomes zero. This simple model thus reflects the self-limiting nature of the surface reactions during ALD, while the reaction kinetics (fast/slow) can be implemented via the initial sticking coefficient \( s_0 \) (high/low values).

Taking a step back and considering in the first instance reversible Langmuir adsorption, the first reaction of an ALD cycle (Reaction A) can be represented by

\[ A_g + \theta \rightleftharpoons A^*, \] (6)

with \( A_g \) being the gaseous reactant, \( A \) a vacant surface site, and \( A^* \) the chemisorbed reactant. A "dumped reaction product" (and not the result of an elementary reaction), containing multiple types of surface species simultaneously.

The adsorption rate \( r_{ads} \) is equal to the product of the adsorption rate constant \( k_{ads} \), the partial pressure of reactant \( A, P_A \), and the fraction of uncovered surface sites, giving the overall second-order surface reaction rate equation

\[ r_{ads} = k_{ads} P_A (1 - \theta). \] (7)

The desorption rate \( r_{des} \) is equal to the fraction of covered sites times the desorption rate constant \( k_{des} \)

\[ r_{des} = k_{des} \theta. \] (8)

The rate of change in the surface coverage \( \theta \) is obtained by subtracting the desorption from the adsorption rate

\[ \frac{d\theta}{dt} = r_{ads} - r_{des}. \] (9)

At equilibrium, \( \frac{d\theta}{dt} \) is zero. In practice, gaseous byproducts are often continuously pumped out, making reverse reactions unlikely and justifying the assumption of irreversibility. When irreversible adsorption is assumed, the second term, \( r_{des} \) in Eq. (9) will be ignored.

The second reaction of the ALD cycle (reaction B) can be described in the lumped way, assuming an "average" reaction product \( AB^* \)

\[ A^* + B_g \rightleftharpoons AB^*. \] (10)

In practice, in many models, reaction B is not modelled separately, and it is only considered that the surface left behind by exposure to reactant \( A \), saturated with \( \theta \approx 1 \), is rendered reactive again in reaction B.

Furthermore, it is often assumed that the total number of adsorption sites for the Langmuir adsorption model is obtained from the number of metal atoms deposited per cycle. GPC. The current authors understand this to be a gross oversimplification, as, e.g., the number of OH groups on alumina, which act as (reactive) adsorption sites in the trimethylaluminum reaction, is known to be 7–9 per nm² at typical ALD Al₂O₃ conditions, while the number of aluminium atoms deposited per cycle is around 4.5 per nm². Despite the fact that this assumption is clearly oversimplified, it
is being repeatedly used as it can give modelling results with a satisfactory fit.

For radical-assisted ALD processes (e.g., plasma-enhanced or PE-ALD) or ozone-based ALD processes, reactant molecules that collide with the surface can undergo recombination processes. For example, an O radical can recombine with an adsorbed O atom and form molecular O2 that leaves the surface. The probability that a species recombines during a collision with the surface is usually defined as the recombination probability \( r_{\text{recomb}} \). Although it depends on the process, the recombined species can often no longer contribute to film growth upon subsequent collisions with the surface, e.g., when the surface is only reactive towards O radicals and not towards molecular O2. Hence, recombination processes are usually considered loss processes.

F. ALD growth types in high aspect ratio structures

Elam et al.\textsuperscript{65} introduced the concepts of a diffusion versus a reaction limited growth type for ALD growth in narrow features in the molecular flow regime.\textsuperscript{1} In the diffusion limited growth type, it is the geometry of the feature that causes the main difficulty in coating.\textsuperscript{2} During deposition, the most accessible sites will be covered first, resulting in a clear front between the accessible (covered) sites and the less accessible (uncovered) sites. During the deposition, this front will gradually penetrate deeper into the feature. In the reaction limited growth type, the difficulty of coating is mainly related to a low sticking probability of the reactant molecules. In this case, there is a less sharp front between coated and as yet uncoated parts of the feature. For plasma-enhanced ALD, Knoops et al.\textsuperscript{66} introduced a recombination limited growth type, where saturation is not limited by the diffusion rate or the sticking probability but by the recombination loss during collisions of the radicals with the side-walls of the feature. These different growth types are illustrated in Fig. 4, which shows unsaturated thickness profiles. Note that both the aspect ratio of the feature and the sticking probability of the ALD reactants will determine the ALD growth type, as will be discussed in Sec. VI B 4 and in Fig. 23.

C. Aspect ratio and equivalent aspect ratio

The Aspect Ratio (AR) of a structure is typically defined as

\[
AR = \frac{L}{w},
\]

with \( L \) (m) being the depth and \( w \) (m) being the width of the structure, as indicated in Fig. 5. Achieving a conformal coating in a structure becomes more difficult with an increase in the AR of the structure. In addition, it will be easier to coat an elongated trench with depth \( L \) and width \( w \) than a cylindrical hole with the same depth \( L \) and diameter \( w \) because the opening through which the reactant can enter will be larger for the trench which facilitates the diffusion. AR is a 2D concept, based on geometrical measures of a cross-section of a 3D object, and is therefore not expected to be sufficient as a parameter to fully describe the difficulty of precursor diffusion into 3D features. Therefore, not only the AR will be important but also the length of the feature along the third dimension will have an impact on the conformality. A schematic representation of a hole and trench structure with equal AR is given in Fig. 5.

Gordon et al.\textsuperscript{62} proposed a generalized expression for the aspect ratio \( a \) of holes

\[
a = \frac{Lp}{4A},
\]

with \( L \) (m) being the depth of the hole, \( p \) (m) being its perimeter, and \( A \) (m\(^2\)) being the cross-sectional area. This expression takes into account the 3D nature (third dimension) of the feature. For cylindrical holes, Eq. (12) reduces to \( L/w \) which is equal to the depth to width AR interpretation from Eq. (11). For trenches, Eq. (12) reduces to \( L/(2w) \), which is a factor of two smaller than the conventionally used AR of Eq. (11). Gordon et al. also showed that for large \( a \), the required exposure for conformal coating scales with \( a^2 \). The difference of \( a \) with a factor of two between trenches and cylinders implies that a four times larger exposure is required to conformally coat a hole in comparison with a trench with the same depth to width ratio (AR) as can be measured in a cross-sectional view. This example of trenches versus holes clearly illustrates that a depth to width ratio of a 3D feature is not a sufficient measure to estimate the difficulty in coating the 3D structure: gas flow into the real structure will depend on the full 3D geometry of the feature.

To facilitate a direct comparison between different structures and literature reports, we propose a new concept to express the aspect ratio in a structure-independent way. Analogous to the "equivalent oxide thickness" which was introduced in the field of high-k oxides to enable a straightforward comparison between different structures and

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Schematic representation of unsaturated thickness profiles: diffusion limited (a), reaction limited (b), and recombination limited growth type (c). Adapted with permission from H. C. M. Knoops et al. J. Electrochem. Soc. 157(12), G241–G249 (2010). Copyright 2010 The Electrochemical Society.}
\end{figure}

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{Schematic representation of a cylindrical hole (a), a square hole (b), and a trench structure (c) with width \( w \) and depth \( L \). The three structures have the same AR; however, the holes [(a) and (b)] have a different EAR than the trench structure (c).}
\end{figure}
materials by expressing their key functional properties with respect to a well-known reference material (SiO₂). We propose to introduce the concept of an Equivalent Aspect Ratio (EAR) by referring to simple cylindrical holes as the reference structure. The EAR of a given 3D feature can then be defined as the aspect ratio of a hypothetical cylindrical hole that would require the same reactant exposure dose during an ALD reaction as the feature of interest.

In Fig. 6, the AR and EAR are compared for arrays of holes, trenches, and pillars. Following expressions for the (E)AR were found:

- For circular holes: \( AR = \frac{L}{w} \) and \( \text{EAR} = \frac{L}{w} \).
- For square holes: \( AR = \frac{L}{w} \) and \( \text{EAR} = \frac{L}{w} \).
- For (infinite) trenches, \( AR = \frac{L}{w} \) and \( \text{EAR} = \frac{L}{(2w)} \).
- For elongated holes, \( AR = \frac{L}{w} \) and \( \text{EAR} = \frac{(L(w + z))}{(2wz)} \), with \( z \) being the length of the hole as indicated in Fig. 6.
- For squares pillars, \( AR = \frac{L}{w} \) and \( \text{EAR} = \frac{L}{(2\sqrt{2}w)} \) (valid for \( L/w \) in the range of 5–50, \( w/w_{\text{pillar}} = 3 \)).

Most expressions follow from Gordon’s definition (12) and were further confirmed via Monte Carlo modelling. For arrays of pillars, the EAR was not derived from analytical equations, but was determined from Monte Carlo simulations, assuming an initial sticking coefficient of unity (see Sec. V). Comparing holes and trenches with the same AR, the EAR of trenches is a factor of two smaller. For (E)AR ratios in the range of 5–50 and \( \frac{L}{w} \) and EAR \( \frac{L}{w} \), we found that the EAR of an array of pillars is a factor of \( 2\sqrt{2} \) smaller than that for holes. It should be noted that this EAR was determined for molecular flow conditions. Additional calculations would be needed to determine the EAR of an array of pillars for viscous flow conditions and hence confirm whether or not the EAR is a flow regime dependent parameter.

H. Ways to express the level of conformality

The 3D uniformity of a film is often discussed either in terms of step coverage or conformality (sometimes conformity). The definition of step coverage may vary from reference to reference.

Typically, Step Coverage (SC) is used for the ratio of the film thickness at the bottom of a feature to the film thickness at the top of the feature. Alternatively, it is calculated as the ratio of the film thickness at the side wall to the film thickness at the top [Fig. 7(a)]. Step coverage is typically expressed as percentage. The term is often used for thin films made by PVD or (PE)CVD. In ALD, the “steps” which may be challenging for PVD and (PE)CVD (e.g., EAR 5:1) are typically coated 100% uniformly, i.e., with 100% SC, and therefore, more demanding (e.g., lateral) test structures are needed for ALD (see Sec. III).

When analysed with vertical structures, conformality of ALD is often defined in a similar manner as step coverage: ratio of bottom-top or sidewall-top film thickness and is given as percentage.

An alternative way to express the conformality of ALD coatings is via the coated (E)AR. This approach is typically used when the ALD coating did not reach the bottom of the feature and is especially useful for lateral, highly demanding test structures (AR > 50:1). If a thickness profile is experimentally obtained, one determines the penetration depth at which the film thickness equals 50% of the film thickness at the top, which we propose to call the half-thickness-penetration-depth or 50%-thickness-penetration-depth, abbreviated PD50%. From the PD50%, one can calculate the coated (E)AR. Alternatively, one can distinguish the coated versus uncoated regions of the feature in cross-sectional electron microscopy or optical images. The transition point is then used to calculate the coated (E)AR. Similar to the PD50%, one can also define the PD50% which stands for the penetration depth at which the film thickness is reduced to 80% of the original film thickness.
thickness. The concepts of step coverage, PD_{50\%} and PD_{80\%}, are illustrated in Fig. 7.

### III. STRUCTURES TO QUANTIFY THE CONFORMALITY OF ALD

When studying the conformality of a certain ALD process, it is important to use test structures in which gas diffusion occurs according to a flow regime that is relevant for the envisioned application and reactor. Most of the high aspect ratio structures on which ALD is used for applications in micro-electronics, batteries, fuel cells, catalytic reactors (because the mean free path of the reactant molecules will be much larger than the structure width). Therefore, the molecular flow regime is most relevant for the majority of 3D substrates, ALD reactors, and targeted applications although viscous flow applies in some specific cases.

Table I and Fig. 8 overview different types of high aspect ratio test structures that have been used for quantifying the conformality of ALD processes, ordered according to a decreasing size. Many types of structures have been used in mm-μm-nm ranges of feature sizes. We classify them here as vertical structures, lateral structures, and porous materials. These structures often differ in the methods typically used to characterize them here as vertical structures, lateral structures, and porous structures with a characteristic width below ca. 1 μm will be determined by molecular flow when the deposition is performed in traditional flow- (low-vacuum) and pump-type (high-vacuum) ALD reactors (because the mean free path of the reactant molecules will be much larger than the structure width). Therefore, the molecular flow regime is most relevant for the majority of 3D substrates, ALD reactors, and targeted applications although viscous flow applies in some specific cases.

A. Vertical structures

Large surface area substrates with vertical features such as arrays of trenches, forests of pillars, carbon nanotubes, or assemblies of pores [e.g., anodized alumina (AAO)] have been used in combination with ALD for applications in fuel cells, batteries, and supercapacitors. Evidently, these substrates can also be used to quantify the conformality of an ALD process. Cross-sectional imaging of the structures [e.g., by scanning electron microscopy (SEM)] allows relatively straightforward visualization of the depth up to which an ALD coating has been deposited. The film thickness can be measured point-by-point; accuracy depends on the sample preparation and skills of the electron microscopy operator.

Trenches etched into silicon have most often a width in the range of 100 nm to several μm and achieve an EAR of >40:1 [Fig. 8(d)]. Vertical trenches are fabricated with an anisotropic etch process which is designed so that a passivated film is deposited on the sidewalls, while the feature is being etched. With the basic Bosch Deep Reactive Ion Etching (DRIE) process, developed in the MEMS industry, one alternates etching and passivation cycles. During the passivation cycle, a protective fluorocarbon film is deposited on all the surfaces. This step is followed by an etching step during which an ion bombardment etches the unprotected parts. The protective film remants etching and passivation cycles during the passivation cycle, a protective fluorocarbon film is deposited on all the surfaces. This step is followed by an etching step during which an ion bombardment etches the unprotected parts. The protective film.

**Table I.** Overview of test structures used to quantify the conformality of an ALD process. The labels (a)-(j) correspond to the labeled images in Fig. 8.

| Structure                                | Characterization method                           | References |
|------------------------------------------|--------------------------------------------------|------------|
| Macroscopic lateral trenches (a)         | Ellipsometry/XRR/XRF/EDX                         | 67, 69, 83, and 84 |
| Capillary tubes (b)                      | Optical microscope                                | 85         |
| Microscopic lateral trenches (c)         | Optical and IR microscope/reflectometry SEM/EDX  | 83 and 86–88 |
| Micron trenches (d)                      | TEM                                               | 89 and 90  |
| Pillars (e)                              | SEM/EDX                                           | 91–94      |
| Anodized alumina (AAO) (f)               | EPMA/TEM                                          | 65, 95, and 96 |
| Nano trenches                            | TEM                                               | 79 and 97  |
| Forests of carbon nanotubes (g)          | SEM/EDX/TEM                                       | 98–100     |
| Opals (h)                                | FE-SEM/TEM                                       | 101–104    |
| Mesoporous thin films (i)                | XRF/porosimetry/TEM/SIMS                         | 47 and 105–108 |
| Mesoporous powders (j)                   | TEM/SEM/EDX                                      | 109–113    |
samples from the AAO template. They also introduced an algorithm to automatically determine the wall thickness and diameter of the nanotube as a function of the depth from the TEM images. The thickness profile of a nanotube obtained out of an AAO pore is shown in Fig. 9(b). Recently, Macak and co-workers\textsuperscript{122} studied the conformity of ALD processes in anodic TiO\textsubscript{2} nanotube layers. The closely spaced nanotubes had a diameter of 110 nm and an EAR of 180:1. By depositing the TiO\textsubscript{2} nanotube substrate on a quartz crystal that can be mounted in a quartz crystal microbalance (QCM), they were able to perform in-situ QCM measurements during the ALD process. This
enabled real-time monitoring of reactant uptake during the ALD reactions. In principle, this approach could be extended to other porous substrates.

Track-etch membranes are another type of micro- or nanoporous materials which are formed by irradiation of polymeric sheets. The diameter of the etched pores can be in the range of a few nm to mm, resulting in an EAR of 10:1–1000:1. SEM and cross-sectional TEM are often used to investigate the conformality of the deposited ALD coating in the membranes. Arrays of (silicon) pillars can be either etched or grown through catalyzed chemical vapor deposition. To ensure mechanical stability, the pillars often have a diameter and spacing of 1–10 \( \mu \)m and a typically height of 50 \( \mu \)m. Forests of carbon nanotubes (CNTs) can be grown by CVD. Multiwalled CNTs can have a diameter of 10–100 nm and a length up...
B. Lateral structures

Dedicated lateral test structures have been designed by several groups to enable easy and accurate quantification of the penetration depth and the composition profile of the deposited coating. Often, the goal is to avoid the need of (time-consuming) cross-sectioning and electron microscopy. In the CVD literature, Yang et al. used macroscopic lateral structures to analyze the CVD growth of $\text{HfO}_2$ thin films. More recently, Shima et al. introduced parallel-plate microchannels to study CVD processes. A patterned Si wafer, fabricated by single step etching, is clamped on a planar Si substrate. In this way, one obtains lateral trench-like features with a microscopic gap size of 1–15 $\mu$m (determined by the depth of the Si etching process) and EAR up to 100:1. The chronological overview below discusses the most important lateral structures that have been used to characterize the conformality of ALD films.

Fused silica capillary tubes with a length of 2 mm and a diameter of 20 $\mu$m were introduced as ALD conformality test structures by Becker et al. [Fig. 8(b)]. After ALD, the coating on the exterior of the tubes was burned off and the inside was filled with a liquid with a similar refracting index as fused silica. In this way, one could visually determine the penetration depth of the ALD coating on the interior of the tubes using an optical microscope.

Macroscopic lateral structures were introduced by Dendooven et al. [Fig. 8(a)] and were created by cutting a rectangular shaped structure (typically 0.5 cm $\times$ 2 cm) from a sheet of aluminum foil (thickness of 100–500 $\mu$m) and clamping the resulting foil in-between two silicon wafers [Fig. 10(a)]. Because of the design of the structure, exposed regions of the clamped Si wafer are effectively turned into the sidewalls of a lateral trench. By using aluminum foils with different thicknesses and by cutting different shapes, one can easily produce structures with EARs in the range of 1:1–100:1. After ALD deposition, the clamped structure can be disassembled, resulting in two planar Si wafers. The penetration depth of the ALD coating can often be observed with the naked eye. Since the lateral size of the structures is on the order of cm, any technique for characterization of the layer thickness or composition with an intrinsic lateral resolution of the order of 1 mm can be used for obtaining an accurate profile of the thickness and composition of the ALD coating along the sidewalls of the test structure. Quantitative thickness profiles can be obtained, e.g., by ellipsometry (SE), x-ray fluorescence (XRF), or Rutherford backscattering spectroscopy (RBS) mapping of the regions of the Si wafers that constituted the sidewalls in the clamped structure. Not only the film thickness as a function of the depth but also the change in the composition of the deposited film can be monitored. This can be particularly important for complex coatings such as, e.g., ternary oxides or LiPON for 3D battery applications. An advantage of the macroscopic lateral structures is that the small thickness of the deposited film ($\text{nm}$) as compared to the total width of the trench ($\text{mm}$) implies that the EAR of the trench remains essentially constant during deposition, which simplifies, e.g., modelling. The main disadvantage is that their use is limited to pump-type reactors working at high vacuum if the molecular-flow assumption needs to be valid.

Air wedge structures were used by Gabriel et al. to quantify the conformality of optical coatings deposited by ALD. These structures consist of two silicon wafer substrates with a side of $7 \text{ cm}$. The two wafers are in contact along one edge and open at the opposite edge with an air gap of 1560 $\mu$m [Fig. 10(b)]. By using such wedge structures, one can simultaneously estimate the penetration depth for a range of EARs (38:1–1410:1).

Musschoot et al. extended the method of Dendooven et al. to investigate the penetration of thermal and plasma-enhanced ALD into fibrous materials. They used a hole, made of Teflon (1 cm $\times$ 1 cm $\times$ 5 cm), and filled it with non-woven polyester. The hole structure was clamped between the substrate holder and a flat Teflon surface. In this way, the ALD reactants could enter the fibrous material from only one side and precursor penetration into the non-woven polyester could be studied in a systematic way.

Puurunen and co-workers fabricated microscopic lateral high aspect ratio (LHAR) trenches, code named PillarHall structures, with a gap height of 200–1000 nm and EARs up to 12 500:1, using microfabrication techniques commonly used for MEMS [Figs. 10(c) and 8(c)]. In recent work, the gap height range was expanded to 100–2000 nm. The lateral structures consist of a Si wafer (as bottom surface) and a suspended polysilicon membrane that is locally supported by a network of Si or $\text{SiO}_2$ pillars. Elongated openings are etched through the top polysilicon membrane to define the access points for the gas into the lateral structure. After ALD, the film penetration can be investigated non-destructively through the membrane using, e.g., infrared spectroscopy or in some cases using a laboratory microscope. After the removal of the membrane, e.g., by using an adhesive tape, one can measure the penetration depth by microscopy and quantify the thickness of the ALD coating deposited onto the Si wafer (i.e., onto the bottom part of the lateral test structures) by using small-spot size techniques such as reflectometry or SEM/EDX. As indicated in Fig. 3, these LHAR structures with a typical 500 nm gap can be used in flow-type ALD reactors in the molecular flow gas transport regime up to pressures of 1000 Pa.

Recently, Schwille et al. studied the conformality of ALD in microscopic rectangular cavities with lateral dimensions of 2000 $\mu$m, a height of 4.5 $\mu$m, and a central access hole with a diameter in the range of 4–60 $\mu$m [Fig. 10(d)]. The centro symmetric nature of the structure slightly complicates the analysis as the equations for trenches do not apply directly because of the different symmetry. These structures resemble those encountered in real MEMS processing.

To tentatively demonstrate that the conformality of an ALD process is indeed determined by the flow type and EAR and not by the absolute dimension, a test was made for this review where a macroscopic lateral test structure reported by Dendooven et al. with EAR of 200:1 and LHAR structures reported by Puurunen and co-workers (Generation 1, Ref. 86) were used to compare the quantification of conformality for the same ALD process in the same ALD run. Both substrates were coated in a pump-type reactor during a TMA/H$_2$O process to deposit an $\text{Al}_2\text{O}_3$ film. The process parameters were identical for both substrates: $T = 100^\circ\text{C}$, $P_{\text{TMA}} = 0.28 \text{ Pa}$, and $P_{\text{H}_2\text{O}} = 0.25 \text{ Pa}$. During the process, 1000 ALD cycles were applied with the following pulse/pump times: TMA (20 s) - pump (60 s) - $\text{H}_2\text{O}$ (20 s) - pump (60 s). The film thickness was measured with SE in the case of the macroscopic lateral structure, while the coating was visualized using an optical microscope for the microscopic LHAR substrate. For
both substrates, a coated EAR of roughly 100:1 was found as can be seen in Fig. 11.

C. Porous materials

Most conformality research has focused on ALD coatings in materials with critical dimensions $> 30$ nm, e.g., using the above-mentioned Si-based trench structures, AAO, and lateral structures. Fewer studies have focused on ALD coatings in sub-30 nm pores. George and co-workers investigated ALD of $\text{Al}_2\text{O}_3$, $\text{TiO}_2$, and $\text{SiO}_2$ in tubular alumina membranes with a pore diameter of 5 nm. After each ALD growth reaction, the pore diameter was derived from in situ $\text{N}_2$ conductance measurements (assuming molecular flow in the pores). The pore size was smaller after a metal reactant exposure than after the subsequent $\text{H}_2\text{O}$ exposure, in accordance with the replacement of the bulkier metal reactant ligands on the pore walls by the smaller OH groups during the $\text{H}_2\text{O}$ step. The pore size was successfully reduced to molecular diameters (estimated in the range of 3–10 Å), demonstrating the potential of ALD in tailoring nanoporous membranes for specific gas separation purposes.

To quantify the penetration of ALD coatings into nanosized pores, Dendooven et al. developed an approach based on mesoporous $\text{SiO}_2$ and $\text{TiO}_2$ films that were deposited onto silicon substrates. The mesoporous $\text{SiO}_2$ films had randomly ordered channel-like pores with an average diameter of ca. 6.5 nm. The mesoporous titania thin films contained ink-bottle shaped pores [Fig. 8(i)], i.e., spherical cages with a diameter in the range of 4–7 nm connected to each other via smaller pore necks (3–5 nm). The amount of deposited material during the ALD process was monitored using in situ XRF and the remaining porosity using in situ grazing incidence small angle x-ray scattering (GISAXS) and ellipsometric porosimetry (EP).

Since the thickness of the deposited film was of the same order as the gap size through which the gas had to enter the pore, the equivalent aspect ratio was not constant, but was gradually increasing as the thickness of the deposited film increased. They demonstrated tuning of the pore size up to near molecular dimensions for both channel-like and ink-bottle shaped mesopores, indicating that the key limiting factor in ALD deposition into nanopores is the diameter of the reactant molecules used during the process, e.g., a TDMAT molecule has a molecular diameter of about 0.7 nm.

Opal structures consist mostly of close-packed silica or polystyrene spheres with a diameter of several hundred nm. With ALD, one can deposit a coating into the void space between the spheres. After the deposition, the original spheres can be removed to obtain an inverse opal structure, with potential applications in photonics. The conformality of ALD in these structures can be evaluated by EDX mapping of cross-sections of the opal structure.
measure the penetration depth. After the removal of the opal template, cross-sectional SEM can be used to measure the thickness and lateral uniformity of the inverse opal structure.

Besides conformality in mesoporous thin films and opal structures, ALD infiltration in mesoporous powders, including silica gel,\textsuperscript{109} Zelite-4\textsuperscript{41,43,51} [Fig. 8(j)], metal organic frameworks (MOFs),\textsuperscript{110,132} and alumina and silica powder with a size of several hundred microns,\textsuperscript{112,133} has also been a subject of research. ALD functionalization of porous powders is mainly explored for applications in the field of catalysis. The diffusion into the interior portions of these materials is considered to be highly challenging, not only because of the high EAR (few nm wide pores of sometimes several microns in length) but also because of the very large surface areas (up to 2500 m\textsuperscript{2}/g)\textsuperscript{110} that need to be covered. Because of these large surface areas, the conformality of ALD is governed not only by the diffusion of the molecules but also by the reactant supply.\textsuperscript{109}

IV. EXPERIMENTS ON CONFORMALITY OF ALD

In this section, we aim to provide a systematic overview of experimental data on the conformality of ALD processes. This overview does not aim to include all reported ALD processes but rather concentrates on those reports in which conformality has been investigated in detail. We distinguish three types of ALD processes: thermal, ozone-based, and plasma-enhanced processes. In thermal ALD, the conformality is influenced by the molar mass and reactivity of the ALD reagents as well as by the partial pressures and exposure times. Reactant decomposition (not occurring in theoretical ALD, but sometimes occurring in real processes) and too short purge/evacuation steps may decrease the conformality. For ozone-based and plasma-enhanced ALD, the conformality additionally depends on the recombination of radicals (or ozone) which causes the flux of radicals (ozone) to decrease inside trenches and hence leads to decreased conformality. Therefore, in general, it is expected that better conformality will be achieved for thermal ALD than for ozone-based or plasma-enhanced ALD processes.

Tables II–IV overview experimental results on the conformality of thermal, ozone-based, and plasma-enhanced ALD processes, respectively, as reported in the literature. The indicated EAR has been calculated according to the definition given in Sec. II based on the feature dimensions reported in the corresponding reference. For AAO pores that are accessible from both sides, the tabulated EAR is calculated using half of the pore length. Unless stated otherwise in the table footnotes, the given exposure corresponds to the metal reactant (reactant A) of the ALD process. The value has been calculated from the reactant partial pressures and pulse times reported in the referenced papers (where available). The coated EAR equals the EAR of the structure in the case of complete coverage or is determined by PD\textsuperscript{50\%} in the case of incomplete coverage as described in Sec. II and indicated with *. If the results were presented in a thickness profile (film thickness as a function of the depth of the structure), “D” is noted after the coated EAR. Not all fields in the tables could be filled because the process parameters were not always reported. For the PE-ALD processes shown in Table IV, the type of plasma configuration is noted. The influence of the type of configuration will be discussed in Sec. IV C.

A. Thermal ALD processes

Table II summarizes experiments on the conformality of thermal ALD processes. According to the mean free path of the molecules as
### TABLE II. Overview of experimental results on the conformality of thermal ALD processes. The coated EAR equals the EAR of the structure in the case of complete coverage or is determined by PD 50% in the case of incomplete coverage and indicated with *. If the results were presented in a thickness profile (film thickness as a function of the depth of the structure), “D” is noted after the coated EAR.

| Film (process) | Substrate | EAR T (°C) | Exposure (10³ L) | Characterization method | Coated EAR | References |
|---------------|-----------|-----------|-----------------|------------------------|-----------|------------|
| Oxides       | Al₂O₃ (TMA/H₂O) | Macro lateral | 100 | 200 | 9 | SE | 50° (D) | 67 |
|              | Trench     | 5 | 300 | | SEM | 5 | 134 |
|              | AAO        | 8.5 | 200 | 300 | SEM/TEM | 8.5 | 135 |
| Nanorods (ZnO) | 300 | 560 | | TEM | Conformal | 99 |
| Pillars (Si) | 125 | | | TEM | Conformal | 93 |
|              | AAO        | 1750 | 177 | | SEM/TEM | 1750 | 96 |
|              | AAO        | 770 | 177 | 4500 | SEM | 770 | 65 |
| LHar         | 10-12500  | 300 | | Reflectometry, optical/IR microscopy, SEM | | |
|              | LHar       | 10-12500 | 110 | | Reflectometry | 130° (D) | 77 |
|              | Trench     | 11 | | | SEM | 11 | 138 |
| Macro lateral | 5 | 75 | 18 | SEM/EDX | 2.5° (D) | 69 |
|              | Hole       | 17 | 200 | 370 | SEM | 17 | 139 |
| TiO₂ (TiCl₄/H₂O) | Pillars (Si) | 110 | | TEM | Conformal | 93 |
|              | AAO        | 7.5 | 200 | | SEM/TEM | 7.5 | 140 |
|              | LHar       | 10-12500 | 110 | | Reflectometry | 90° (D) | 77 |
|              | LHar       | 10-12500 | 110 | | Reflectometry | 65° (D) | 86 |
| TiO₂ (TTIP/H₂O) | VACNT       | 225 | | SEM | (D) | 100 |
| V₂O₅ (VOTP/H₂O) | AAO        | 7000 | 100 | | SEM/TEM/EDAX | 7000 | 96 |
| Fe₂O₃ [Fe₂(O'Bu)₆/H₂O] | AAO | 100 | 140 | | SEM/TEM | 100 | 143 |
| Fe₂O₄ [Fe(Cp)₂/O₂] | AAO | 400 | | | SEM/TEM | 144 |
| ZnO (DEZ/H₂O) | AAO        | 700 | 177 | 2000 | EPMA | 700 (D) | 65 |
|              | AAO        | 5000 | 177 | 60 000 | EPMA | 5000 (D) | 65 |
|              | Opal       | 85 | | | SEM | 102 |
|              | Trench     | 3 | 250 | | SEM | 3 | 90 |
| Nanowire (CuO) | AAO | 150 | | SEM/TEM | | |
|              | AAO        | 10000 | 750 | | SEM | 20 | 149 |
| AlN (TMA/NH₃) | Trench | 17.5 | 420 | | SEM | 17.5 | 150 |
| TiN (TiCl₅/Zn/NH₃) | Trench | 5 | 500 | | SEM | 5 | 134 |
discussed in Sec. II, all experiments were performed with the molecular flow regime inside the structures. To conformally coat a substrate with a large EAR, a large dose of reactant molecules is needed because of the increased coated surface area and due to the increased diffusion time of the molecules. For example, Elam et al. \(^{65}\) used an exposure of \(6 \times 10^8\) L for a conformal ZnO coating of an AAO structure with an EAR of 5000:1. An unusually large exposure time of 10 min, resulting in an exposure of \(6 \times 10^9\) L, was used to achieve a conformal W coating on an AAO structure with an EAR of 1750:1.\(^{166}\) To reduce the deposition time, one can also increase the reactant partial pressure \(^{230}\) to increase the total exposure.

A majority of studies are done on oxides, nitrides, and metals. Only a few studied the conformality of sulfides, \(^{51,225}\) fluorides, \(^{233}\) and phosphates. \(^{92,234}\) The largest coated EAR by conventional (thermal) ALD is in the range of 5000:1,\(^{165}\) in an extreme case an EAR of 7000:1 is achieved.\(^{96}\) All such ultra-high aspect ratio coatings published in scientific journals are oxides and have so far been made with anodic alumina (AAO) structures. The published processes\(^{96}\) are TCl\(_2/\)H\(_2\)O, DEZ/H\(_2\)O, and VOTP/H\(_2\)O\(_2\). For the commonly used TMA/H\(_2\)O process, the record coating so far is EAR 1750:1.\(^{96}\) As seen from Table II, the coated EAR varies greatly for the same process, e.g., 5:1 to 1750:1 for the TMA/H\(_2\)O process, depending on the test structures and process conditions. Also, the purpose of coating high aspect ratio

| Film (process) | Substrate | EAR | T (°C) | Exposure \((10^3 \text{ L})\) | Characterization method | Coated EAR | References |
|---------------|-----------|-----|--------|-----------------------------|------------------------|------------|-----------|
| TaN (TBTDET/NH\(_3\)) | Trench | 11  | -     | 11  | SEM | 11 | 138 |
| WN [(BuN\(_2\))\(_2\)Me\(_2\)N]/NH\(_3\)] | Silica capillary tube | 1000 | 300 | 110 | Optical microscopy | 210 | 85 |
| Metals | Ru [(Pr-Me-Be)Ru(CHD)/O\(_2\)] | Hole | 4.6 | 225, 270, and 310 | TEM | 4.6 | 151 |
| | | Hole | 25 | 270 | TEM | 25 | 152 |
| | | Hole | 24 | 220 | XTEM | 24 | 153 |
| | Ru [(EtCp)Ru(DMPD)/O\(_2\)] | AAO | 20 | 280 | TEM | 20 | 154 |
| | | Hole | 17 | 250 | SEM | 17 | 155 |
| | Ru [(Et-Be)Ru(CHD)/O\(_2\)] | Trench | 2.25 | 225 | TEM | 2.25 | 157 |
| | | Hole | 32 | 225 and 270 | XTEM | 32 | 158 |
| | Ru [(Ru(Me-Me-CHD)/O\(_2\)] | AAO | 166 | 300 | TEM | 100 | 159 |
| | | Hole | 20 | 275 | SEM | 20\(^*\) | 160 |
| | | Trench | 11 | - | SEM | 11 | 138 |
| | Ru [(EtCp)Ru(Py)/O\(_2\)] | Trench | 4 | 270 | SEM | 4 | 161 |
| | AAO | | 10 | 300 | SEM/TEM | 10 | 162 |
| | Ru (RuO\(_4\)/H\(_2\)) | Pillars (Si)\(^{163}\) | 10 | 100 | SEM/EDX | Conformal (D) | 94 |
| | Pd [Pd(hfac)\(_2\)/formalin] | AAO | 1500 | 200 | SEM/EDX electrical conductivity | 1500 | 164 |
| | W (Si\(_3\)H\(_4\)/WF\(_6\)) | AAO | 1750 | 200 | 60 000 000\(^{165}\) | SEM/EDX | 1750 (D) | 166 |
| | Ir [Ir(acac)\(_3\)/O\(_2\)/H\(_2\)] | LHAR | 10-12500 | 250 | EDX optical microscopy | 20\(^*\) (D) | 87 |
| | | LHAR | 10-12500 | 250 | EDX optical microscopy | 15\(^*\) (D) | 87 |
| | | Hole | 142 | 300 | - | - | - |
| | | Trench | 370 | - | SEM | - | 169 |
| | Pt (MeCpPtMe\(_3\)/O\(_2\)) | AAO | 8.5 | 250 | 405 | SEM/TEM | 8.5 | 135 |
| | | AAO | 150 | 250 | SEM/EDX/SANS | 110\(^*\) (D)\(^{170}\) | 171 |
| | | AAO | 200 | 300 | SEM | 94 | 172 |
| | | Trench | 6 | 300 | TEM | 6 | 79 |
| | | AAO | 200 | 300 | SEM/TEM | 50 | 173 |
| | | Hole | 90 | 300 | SEM/TEM | 30 | 173 |
| | PtIr alloy [MeCpPtMe\(_3\)/O\(_2\)/Ir(acac)\(_3\)/O\(_2\)] | AAO | 7.1 | 300 | SEM | 7.1 | 172 |
| | | Trench | 9.5 | 300 | SEM | 9.5 | 174 |
structures can be different: Rose et al.\textsuperscript{180} wanted to determine the slope of the thickness profile, and therefore, they on purpose used an unsaturated exposure.

Besides the exposure, high reactivity (often interpreted as high sticking probability) of the reactant molecules is important to achieve a good conformality in structures with a moderate EAR. In Table V, an overview is given of sticking probabilities that have been reported for specific ALD reactants. There is a large variety in reported sticking probabilities, even in values reported for the same reactant molecule. This variety of values is likely partly caused by the large range of methods used to determine the sticking probability. One can use not only theoretical approaches such as density functional theory calculations\textsuperscript{176} or Monte Carlo modelling\textsuperscript{128,178} but also several experimental methods to measure the sticking probability, e.g., Auger Electron Spectroscopy\textsuperscript{235} and QCM measurements;\textsuperscript{78,236} and more recently, sum frequency generation\textsuperscript{237,238} has been reported in the literature.

### B. Ozone-based ALD processes

The use of ozone in ALD processes has several advantages. Ozone is a strong oxidizer, whereby some metal reactants react with O\textsubscript{3} and not with H\textsubscript{2}O.\textsuperscript{5} Another advantage is that at low deposition temperatures, ozone is easier to purge away than the sticky H\textsubscript{2}O. However, it often proves difficult to achieve a good conformality for ozone-based processes.

In Table III, one observes the best conformality with an ozone-based process for a film growth up to an EAR of 400:1. This result was obtained for a SiO\textsubscript{2} three-steps process from H\textsubscript{2}N(CH\textsubscript{2})\textsubscript{3}Si(OCH\textsubscript{2}CH\textsubscript{3})\textsubscript{3} and water and ozone as reactants.\textsuperscript{177} Also, V\textsubscript{2}O\textsubscript{5} has been deposited conformally in a structure with an EAR of 100:1.\textsuperscript{78} A conformal ZnO coating was achieved in an AAO structure with EAR of 250:1.\textsuperscript{187} In general, most of the other ozone-based ALD processes have a relatively small coated EAR in comparison with the corresponding thermal ALD process. While the largest coated EAR of the thermal Al\textsubscript{2}O\textsubscript{3} process was 1750:1,\textsuperscript{96} for the ozone-based Al\textsubscript{2}O\textsubscript{3} process, the coated EAR was only equal to 20:1.\textsuperscript{176} This difference in coated EAR between thermal and ozone-based ALD processes is caused by the fact that ozone can thermally decompose in recombinational processes on surfaces. The chemical composition of the substrate and the temperature have a large influence on the recombinational probability of ozone. Knoops et al.\textsuperscript{241} studied the recombinational probabilities of ozone by measuring the transmission of ozone through high aspect ratio capillaries (EAR 350:1). The recombinational probabilities from different processes are shown in Table III.

| Film (process) | Substrate | EAR | Exposure (\textsuperscript{10\textsuperscript{3}} L) | Characterization method | Coated EAR | References |
|---------------|-----------|-----|-----------------|----------------------|-----------|------------|
| Oxides | Al\textsubscript{2}O\textsubscript{3} (TMA/O3) | Trench | | | | Ref. 175 176 |
| | SiO\textsubscript{2} ([H\textsubscript{2}N(CH\textsubscript{2})\textsubscript{3}]/H\textsubscript{2}O/O3) | AAO | 400 | | SEM/TEM | 400 | 177 |
| | Si(OCH\textsubscript{2}CH\textsubscript{3})\textsubscript{3}/H\textsubscript{2}O/O\textsubscript{3} | Hole | 20 | 180 | TEM | 20° (D) | 178 |
| | TiO\textsubscript{2} (TDMAT/O\textsubscript{3}) | CNT\textsuperscript{179} | 100 | 4500 | TEM/SEM/EDX | 98 |
| | TiO\textsubscript{2} [Cp\textsuperscript{Ti}OMe\textsubscript{3}]/O\textsubscript{3} | Hole | 15.3 | 270 | SEM/TEM | (D) | 180 |
| | V\textsubscript{2}O\textsubscript{5} (VOTP/O\textsubscript{3}) | AAO | 100 | | SEM/EDX | 100 | 150 |
| | Fe\textsubscript{2}O\textsubscript{3} [Fe(Cp\textsubscript{2})/O\textsubscript{3}] | AAO | 185 | 170 | SEM/TEM | 44 | 159 |
| Silica aerogel | | | | | | |
| | Fe\textsubscript{2}O\textsubscript{3} [CpFeC\textsubscript{2}H\textsubscript{2}CH\textsubscript{2}CNH(CH\textsubscript{3})\textsubscript{3}]/O\textsubscript{3} | Trench | 2 | 250 | SEM | | 181 |
| | Co\textsubscript{2}O\textsubscript{3} (CoCp\textsubscript{2}/O\textsubscript{3}) | Anodisc\textsuperscript{183} | 375 | 167 | SEM/EDX | 375 (D) | 184 |
| | NiO [Ni(CpEt)\textsubscript{2}/O\textsubscript{3}] | AAO | 70 | 250 | TEM/SEM/EDX | 70 | 185 |
| | | | | | | |
| | TiO\textsubscript{2} (TDMAT/O\textsubscript{3}) | Hole | 15.3 | 180 | SEM | 2 (D) | 189 |
| | | | | | | |
| Metal | Ru [Ru(EtCp\textsubscript{2})\textsubscript{2}/O\textsubscript{3}] | Hole | 16 | 275 | TEM | 16\textsuperscript{193} | 194 |
| | | | | | | |
| | Ir [Ir(acac\textsubscript{3})\textsubscript{2}/O\textsubscript{3}] | LHAR | 10-12500 | 185 | EDX\textsuperscript{190} optical microscopy | 15° (D) | 87 |
| | PtO\textsubscript{2}[Pt(acac\textsubscript{2})\textsubscript{2}/O\textsubscript{3}] | Trench | 3.5 | 120 | FE-SEM | 3.5 | 191 |
| | PtO\textsubscript{2} (MeCpPtMe\textsubscript{3}/O\textsubscript{3}) | Trench | 5 | 120 | SEM | 5 | 192 |
| | Fe\textsubscript{2}O\textsubscript{3} [CpFeC\textsubscript{2}H\textsubscript{2}CH\textsubscript{2}CNH(CH\textsubscript{3})\textsubscript{3}]/O\textsubscript{3} | Anodisc\textsuperscript{183} | 375 | 167 | SEM/EDX | 375 (D) | 184 |
| | | | | | | |
| | NiO [Ni(CpEt)\textsubscript{2}/O\textsubscript{3}] | AAO | 238 | 300 | TEM/SEM | 238 | 186 |
| | | | | | | |
| | ZnO (DEZ/O\textsubscript{3}) | AAO | 250 | 50 | SEM/EDX | 250 (D) | 187 |
| | | | | | | |
| | HfO\textsubscript{2} (TEMAHf/O\textsubscript{3}) | Hole | 15.3 | 180 | SEM/TEM | 9.6° (D) | 180 |
| | | | | | | |
| | IrO\textsubscript{2} [Ir(acac\textsubscript{3})\textsubscript{2}/O\textsubscript{3}] | LHAR | 10-12500 | 185 | EDX\textsuperscript{190} optical microscopy | 15° (D) | 87 |
| | PtO\textsubscript{2}[Pt(acac\textsubscript{2})\textsubscript{2}/O\textsubscript{3}] | Trench | 3.5 | 120 | FE-SEM | 3.5 | 191 |
| | PtO\textsubscript{2} (MeCpPtMe\textsubscript{3}/O\textsubscript{3}) | Trench | 5 | 120 | SEM | 5 | 192 |
| | Ru [Ru(EtCp\textsubscript{2})\textsubscript{2}/O\textsubscript{3}] | Hole | 16 | 275 | TEM | 16\textsuperscript{193} | 194 |
| | | | | | | |
| | Ir [Ir(acac\textsubscript{3})\textsubscript{2}/O\textsubscript{3}] | LHAR | 10-12500 | 185 | EDX optical microscopy | 45°(D) | 87 |
| | Pt (MeCpPtMe\textsubscript{3}/O\textsubscript{3}) | AAO | 150 | 150 | SEM/EDX | 35° (D) | 195 |
| | Pt (Pt(acac\textsubscript{2})\textsubscript{2}/O\textsubscript{3}) | AAO | 120 | 150 | SEM | 50 | 196 |
| Film (process) | Substrate | EAR | T (°C) | Plasma configuration | Exposure (10^3 L) | Characterization method | Coated EAR | References |
|---------------|-----------|-----|--------|----------------------|------------------|------------------------|------------|------------|
| Oxides        | Al₂O₃ (TMA/O₂) | Macro lateral | 10 | 200 | RI | 27 | SE | 10 (D) | 70 |
|               |           | Hole | 8 | 200 | RI | 8 | SEM | 197 |
|               |           | Trench | 13.5 | 250 | RC | 13.5 | 198 |
|               |           | Macro lateral | 5 | 75 | RI | 5 | EDX | 0.75° (D) | 69 |
|               |           | Hole | 10 | 225 | 30 | FE-SEM | 10 | 200 |
|               |           | Trench | 2 | 250 | C | TEM | 2 | 201 |
|               |           | Trench | 15 | 0 | R | SEM | 15° | 202 |
|               | SiO₂ (3DMAS/O₂) | Trench | 30 | 250 | RC | 30 | 198 |
|               | SiO₂ (H₂Si[N(C₂H₅)]₂/O₂) | Trench | 15 | 0 | R | 15 | 202 |
|               | TiO₂ (TTIP/O₂) | Trench | 13.5 | 150 | RC | 13.5 | 198 |
|               | Ti (TiCl₄/O₂) | Trench | 4.5 | 200 | RI | 75 | FE-SEM/FEI | 4.5 | 205 |
|               | HfO₂ (TEMAHf/O₂) | Trench | 30 | 250 | RC | 30 | 198 |
|               | Ta₂O₅ (Ta(OEt)₅/O₂) | Trench | 2.5 | 150-250 | RE | 2.5 | 206 |
|               | TiN (TDMAT/NH₃) | Trench | 10 | 200 | RC | 10 | 198 |
| Nitrides      | AlN (TMA/NH₃) | Macro lateral | 10 | 200 | RI | 40 | SE | 2.5° (D) | 70 |
|               | Si₃N₄ (SiCl₆/NH₃)| Trench | 2.5 | 400 | C | TEM | 2.5 | 208 |
|               | Si₃N₄ (DTDN₂-H₂/N₂) | Trench | 2.75 | 300 |  | TEM | 2.5 | 208 |
|               | TiN (TDMAT/NH₃) | Hole | 10 | 250 | R | 10 | FE-SEM/AES | 10 | 210 |
|               | TiN (TDMAT/NH₃) | Trench | 10 | 180 | C | 10 | FE-SEM | 10 | 80 |
|               | TiN (TDMAT/H₂) | Hole | 10 | 250 | R | 10 | FE-SEM/AES | 10 | 210 |
| Metals        | Co ((C₈H₇)₂CO/NH₃) | Trench | 5.5 | 300 | HW | 20 | FE-SEM | 5.5 | 219 |
|               | Ni (Ni(Cp)₂/H₂O/H₂) | Hole | 3.3 | 165 | C | 3.3 | 221 |
|               | Cu (Cu(acac)₂/H₂) | Trench | 1.75 | 85 | C | 1.75 | 222 |
|               | Ru (Ru[EtCp]₃/NH₃) | Trench | 4.5 | 85 |  | 4.5 | 222 |
|               | Ag ((Ag(O₂CtBu)(PEt₃))/H⁺) | Trench | 4.5 | 140 | RE | 4.5 | 225 |
|               | ((Ag(O₂CtBu)(PEt₃))/H⁺) | Trench | 4.5 | 140 | RE | 4.5 | 225 |

TABLE IV. Overview of the experimental results on the conformality of PE-ALD processes. The plasma configuration is indicated as C (capacitive), I (inductive), R (remote), and RE (radical enhanced). The coated EAR equals the EAR of the structure in the case of complete coverage or is determined by PD > 50% in the case of incomplete coverage and indicated with "C". If the results were presented in a thickness profile (film thickness as a function of the depth of the structure), "D" is noted after the coated EAR.
Table VI. There are low-loss oxides (silica and alumina), high-loss oxides (MnO$_2$ and Ru$_2$O$_3$), and high-loss noble metal surfaces (Pt). Liu et al.\textsuperscript{150} reported that during ALD of HfO$_2$ using O$_3$, the decomposition rate increased for increasing substrate temperature, leading to a reduction in the step coverage. This temperature effect is also shown in Table VI for the ZnO process. Besides the temperature and the chemical nature of the surface, other parameters can also influence the recombination coefficient of ozone. For Pt\textsuperscript{242} and Fe$_2$O$_3$,\textsuperscript{243} it has been reported that humidity can decrease the decomposition rate of ozone. In these cases, a co-dosing of ozone and H$_2$O could lead to a higher conformality, as earlier suggested by Knoops et al.\textsuperscript{241} Also, the addition of N$_2$ could in some cases decrease the recombination probability of ozone; however, this can also influence the growth process (increase or decrease the film thickness, depending on the ALD process) and the material properties, e.g., N impurities in the TMA/O$_3$ process.\textsuperscript{244}

| Film (process)         | Substrate | EAR | T (°C) | Plasma configuration | Exposure (10$^3$ L) | Characterization method | Coated EAR | References |
|------------------------|-----------|-----|--------|----------------------|--------------------|------------------------|------------|------------|
| Ir(Ir(acac)$_3$/O$_2$) | Hole (elongated) | 370 | I      | SEM                  |                    |                        |            |            |
|                        | Trench    | 370 | I      | SEM                  |                    |                        |            |            |
| Pt(MeCpPtMe$_3$/O$_2$) | Trench    | 17  | 300    | I                    | SEM                | 17 (D)                 |            |            |
| Ta(TaCl$_5$/H$_2$)     | Trench    | 3   | 250    | I                    | SEM                |                        |            |            |

Table V. Sticking probabilities for several ALD reactants and the method how they were derived, as reported in the literature. Updated from H. C. M. Knoops et al., J. Electrochem. Soc. 157(12), G241–G249 (2010).

| Species       | Deposited material | Method                                      | T (°C) | Sticking probability | References |
|---------------|--------------------|----------------------------------------------|--------|----------------------|------------|
| Al(CH$_3$)$_3$ | Al$_2$O$_3$        | Monte Carlo model                            | 177    | 0.001                | 65         |
|               |                    | Ballistic model                              | 225    | 0.026                | 200        |
|               |                    | Semi-Analytical model                        | 200    | 0.1                  | 67         |
|               |                    | DFT                                          |        | 0.1-0.9              | 176        |
|               |                    | Continuum model                              | 300    | 0.00572              | 77         |
|               |                    | Monte Carlo model                            | 200    | 0.02                 | 128        |
|               |                    | Sum-frequency generation                     | 100-300| 0.002-0.005          | 237        |
|               |                    | Auger electron spectroscopy                  | 25     | 0.01                 | 235        |
| Hf(NEtMe)$_4$  | HfO$_2$            | Monte Carlo model                            | 180-270| 0.03-0.6             | 180        |
| Ti(NMe$_2$)$_4$| TiO$_2$            | Monte Carlo model                            | 180    | 0.02 ± 0.005         | 178        |
| Ti(O/Pr)$_3$   | TiO$_2$            | Ballistic model                              | 125-225| 0.04-0.1             | 204        |
| Cp*Ti(OMe)$_3$ | TiO$_2$            | Monte Carlo model                            | 270    | 0.01                 | 180        |
| TiCl$_4$      | TiN                | QCM                                          | 25-125 | 0.006 ± 0.002        | 236        |
|               |                    | Continuum model                              | 110    | 0.1                  | 77         |
| ZnEt$_2$      | ZnO                | Monte Carlo model                            | 177    | 0.007                | 65         |
| SiCl$_4$      | SiO$_2$            | Monte Carlo model                            | 10$^{-8}$|                            | 65 and 239 |
| H$_2$Si[N(C$_2$H$_5$)$_2$]$_2$ | SiO$_2$ | Monte Carlo model                            | 300    | 3 × 10$^{-5}$        | 128        |
| Zr(NMe$_2$)$_4$| ZrO                | QCM                                          | 200    | 0.07                 | 78         |
| Co(C$_6$H$_5$)$_2$ | Co      | Monte Carlo model                            | 300    | 0.002                | 220        |
| H$_2$O        | Al$_2$O$_3$        | DFT                                          | 100    | 0.000001             | 238        |
|               |                    | Sum-frequency generation                     | 300    | 0.0001               | 238        |
|               |                    | Auger electron spectroscopy                  | 25     | 0.25; 0.009$^{240}$  | 235        |
| O$_3$         | Al$_2$O$_3$        | DFT                                          |        | 0.001-0.01           | 176        |
| O$^+$         | Al$_2$O$_3$        | DFT                                          |        | 0.1-0.9              | 176        |
| H$^+$         | TiN                | QCM                                          | 25-125 | 0.0003 ± 0.0001      | 236        |
| N$^+$         | TiN                | QCM                                          | 25-125 | 0.01 ± 0.002         | 236        |
C. PE-ALD processes

In PE-ALD processes, one uses plasma excitation during the reactive exposure step, to create reactive species, such as electrons, ions, and radicals. In some cases, PE-ALD offers a higher GPC, higher film density, and lower deposition temperature than those obtained with thermal ALD. A lower deposition temperature can be useful for thermally fragile samples such as biological substrates or polymers.

The main disadvantages of PE-ALD include potential plasma damage to the substrate, more challenges in batch processing for higher throughput, and a limited conformality in high aspect ratio structures due to the recombination of the radicals by collisions with the surface. Note that, during two-particle collisions in the gas phase, recombination will not occur because of preservation of energy and impulse.

When coating deep holes or trenches with PE-ALD, the reactive species undergo multiple wall collisions during which they may be lost through surface recombination before they can reach the surfaces deeper in the hole. The elimination of radicals through recombination on the sidewalls of high aspect ratio structures will inevitably limit the conformality of PE-ALD. This is clear from Table IV, where the highest achieved conformally coated EAR for PE-ALD is only equal to 30:1, compared to the much higher conformally coated EAR of thermal ALD (7000:1).

Table VII lists recombination probabilities for O, N, and H atoms on various surfaces. The r values span a large range from 0.0000094 for the recombination of O atoms on Pyrex to 0.8 for the combination of H atoms on silicon. In general, higher recombination rates are measured on metallic surfaces, which explains the lower EAR values for PE-ALD of metals listed in Table IV. The largest coated EAR for metals coated with PE-ALD is 17:1, for a Pt coating in a trench structure. In contrast, the largest PE-ALD coated EAR for metals coated with PE-ALD is 17:1, for a Pt coating in a trench structure.

The conformality of a PE-ALD process depends on the recombination probability and therefore on the type of radical, on the type of material on which it collides (the deposited material), and on the process parameters, such as deposition temperature, gas pressure, and plasma configuration. Varying the gas pressure or the plasma set-up will not only affect the recombination probability but also affect the radical density which has an influence on the conformality.

Dendooven et al. used macroscopic test structures to study the influence of the gas pressure, the RF power, the plasma exposure time, and the gas composition on the conformality of PE-ALD.
V. SIMULATION MODELS ON CONFORMALITY OF ALD

A number of models for simulating the conformality of ALD processes, based on different theoretical and numerical approaches, have been developed in recent years. In this section, we aim to provide an overview of the (semi)analytical and computational models that are available in the literature. First, a classification for the models is proposed in Sec. VA, while multiscale approaches are addressed in Sec. VB. Next, attention is given to the key assumptions that are used and how these differ for different models. Finally, typical model output results are discussed. An overview of the reported models focusing on the conformality of ALD is given in Table VIII. In Table IX, an overview of the multiscale models is presented (see also Sec. VB). For each model, the main modeling approach, the key assumptions, simulation space, simulated structures, and the most important conclusions are listed.

A. Overview

1. Analytical models

In 2003, Gordon et al.102 introduced a kinetic model to describe the diffusion and deposition of reactant molecules into holes with aspect ratio \( a \). Gordon et al. defined the aspect ratio as

\[
a = \frac{Lp}{4A},
\]

with \( L \) (m) being the length, \( p \) (m) being the perimeter, and \( A \) (m\(^2\)) being the cross-section of the hole.

Gordon et al.102 obtained an analytical expression, based on conductance formulae for cylindrical holes, for the exposure required to conformally coat a hole with a certain aspect ratio \( a \)

\[
P_T = K_{max} \sqrt{2m k_B T \left(1 + \frac{19}{4} a + \frac{3}{2} a^2\right)},
\]

In this equation, \( K_{max} \) is the saturated coverage of the reactant molecule per unit surface area (molecules/m\(^2\)), in practice, calculated from the GPC value of the process, \( m \) (kg) is the mass of the reactant molecules, \( k_B \) is the Boltzmann constant, and \( T \) (K) is the temperature. For large EARs, the required exposure increases approximately quadratically with \( a \). The model assumes that reactant molecules react upon their first collision with an unsaturated part of the substrate wall, implying a sticking probability of unity. Therefore, the model is especially powerful in the diffusion limited growth type, where the exposure time strongly depends on the value of \( a \) and much less on the value of the sticking probability (see also Sec. VI B 4 and Fig. 24). Alternatively, in the reaction limited growth type, the model predicts a minimum exposure for the reactant (with a sticking probability of less than one for any real ALD reaction) to coat a structure with a certain \( a \). The predictions of the model agreed with the experimentally determined minimum exposure for coating holes with H2O (EAR 36:1).103

Inspired by the model of Gordon et al., several analytical models on the conformity of ALD processes have been derived. Dendooven et al.104 used a similar approach based on conductance formulae to study the effect of sticking probability on the thickness profile. Ylilammi et al.105 used diffusion equations to study the propagation of ALD growth in narrow channels. Yazdani et al.106 and Cremers et al.107 extended the Gordon model for other geometries being forests of CNTs and arrays of pillars, respectively. Also in these papers, closed-formulae were obtained to calculate the required exposure for conformal coating.

2. Computational models

In addition to the (semi)analytical models, models that require computational effort have been introduced to simulate the conformity of ALD processes. Following the classification suggested by Yanguas-Gil et al.,108 these models can be categorized as ballistic, continuum, and Monte Carlo models.
| References         | Main modelling approach | Key assumptions                                                                 | Simulation space | Geometry | Conclusion                                                                 |
|-------------------|--------------------------|---------------------------------------------------------------------------------|------------------|----------|-----------------------------------------------------------------------------|
| Gobbert282        | Ballistic                | Molecular flow                                                                  | 2D               | Trench   | Predict optimal pulse durations Simulation results for both ALD reactions and purge steps |
| Gordon62          | Analytical (conductance formulae) | Reversible adsorption during first ALD reaction, irreversible reaction during second ALD reaction Species fluxes constant over small time scales | 3D               | Hole Trench | Formula to estimate the minimum exposure required for conformal coating of a hole/trench with an aspect ratio a |
| Elam65            | Monte Carlo              | Molecule is irreversibly adsorbed if random number < s Re-emission of the molecule over a distance of ± di289 with di the diameter of the pore at the i-th position All nanopores identical and molecules are entering the pores from both ends with equal rate | 1D               | AAO      | Predict minimum exposure for conformal coating s ≫ H diffusion limited growth type integrated coverage ∼t1/2 s ≪ H reaction limited growth type integrated coverage ∼t |
| References | Main modelling approach | Key assumptions | Simulation space | Geometry | Conclusion |
|------------|-------------------------|----------------|-----------------|----------|------------|
| Rose\textsuperscript{178} | Monte Carlo | Molecular flow Adsorption if random number \(< s\) Re-emission according a random direction | 2D | Hole | Predict thickness profile Method to determine \(s\) |
| Dendooven\textsuperscript{67} | Semi-analytical (conductance formulae) | Molecular flow Irreversible Langmuir adsorption Cosine distributed re-emission direction Surface reactions occur at a much faster time scale than gas transport into the hole Incoming flux at pore entrance constant in time | 1D | Cylindrical hole | Predict coverage as a function of depth Extension Gordon model: Sticking probability different from unity |
| Lee\textsuperscript{290} | Continuum | Molecular flow Sticking probability of unity “Outer” transport of molecules is much faster than transport into the pores Only radial diffusion Concentration of reactant molecules is constant Irreversible adsorption | 3D | Cylindrical, spherical, and planar monoliths with tortuous pores | Calculate minimum exposure time for conformal coating. This exposure is largely dependent on the shape of the substrate. |
| Dendooven\textsuperscript{70} | Monte Carlo | Molecular flow Irreversible Langmuir adsorption Cosine distributed re-emission direction Recombination probability | 3D | Hole | Predict coverage as a function of depth of the feature, for PE-ALD |
| Knoops\textsuperscript{46} | Monte Carlo | Molecular flow \(s, r\) constant\textsuperscript{291} Cosine distributed re-emission direction | 2D | Trench | Simulate PE-ALD Introduction of recombination limited growth type |
| Adomaitis\textsuperscript{266} | Ballistic | Molecular flow Irreversible Langmuir adsorption Cosine distributed re-emission direction Reactant in – reactant out = reactant consumed Steady-state fluxes | 3D | Circular hole | Derive reactant transmission probability functions for intra pore feature fluxes |
| References         | Main modelling approach | Key assumptions                                                                                                                                                                                                 | Simulation space | Geometry                      | Conclusion                                                                                     |
|-------------------|-------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|-------------------------------|-----------------------------------------------------------------------------------------------|
| Musschoot69       | Monte Carlo             | Molecular flow  
Irreversible Langmuir adsorption  
Re-emission according inverse reflection  
Particles in the medium are at rest, and  
the moving particle is small  
Neglect multiple collisions in a cell  
Transport equations (transmission, loss,  
and reflection probability)         | 1D               | Hole filled with non-woven polyester                                                   | Simulate thermal and PE-ALD  
Predict coverage as function of depth in porous/fibrous substrate |
| Yanguas–Gil272    | Continuum               | Molecular flow  
Irreversible Langmuir adsorption  
The surface coverage changes concurrently with the diffusion process²⁹²  
Time-dependent reaction equation | 1D               | Via                                         | Predict saturation exposure times and thickness profiles  
Suitable for high tortuosity structures (high number of wall collisions)  
Can be extended for viscous flow, 3D,… |
| Shimizu220        | Monte Carlo             | Molecular flow  
Irreversible Langmuir adsorption  
Cosine distributed re-emission direction                                                | 2D               | Trench                                | Determine sticking probability                                                             |
| Yazdani100        | Continuum               | Molecular flow  
Quick equilibrium within and outside the CNT arrays  
Fast distribution of carrier gas  
Adsorption rate \(\gg\) diffusion rate  
(Semi-)analytical  
Analytic approximation for \(s = 1\)  
Exclude discrete nucleation phase²⁹³ | 3D               | CNT                                        | A larger precursor supply is needed with increasing film thickness due to the increasing diameter of CNTs in combination with a larger surface area, which results in a limited penetration depth and non-uniform thickness |
| Keuter294         | Continuum               | Based on the model by Yanguas–Gil²⁷²  
Including second-order kinetics  
Transport to the substrate is not considered  
Pores are not taken individually into account (mean porosity, tortuosity, pore size, and Knudsen diffusion coefficient)  
Only reaction sites which are not shielded are taken into account | 1D               | Porous substrate                                      | Predict thickness profile                              |
| References  | Main modelling approach | Key assumptions | Simulation space | Geometry    | Conclusion                                                                                                                                 |
|------------|--------------------------|-----------------|-----------------|-------------|---------------------------------------------------------------------------------------------------------------------------------------------|
| Cremers    | Monte Carlo              | Molecular flow  |
|            |                          | Irreversible Langmuir adsorption |
|            |                          | Cosine distributed re-emission direction |
|            | Analytic                 | Molecular flow  |
|            |                          | Initial sticking coefficient of unity |
|            |                          | Cosine distributed re-emission direction |
| Schwille   | Monte Carlo              | Molecular and viscous flow |
|            |                          | Cosine distributed/specular re-emission direction |
|            |                          | Coverage if random number $< s$ |
| Jin        | Monte Carlo              | Molecular and viscous flow |
|            | Analytic                 | Molecular flow   |
| Poodt      | Monte Carlo              | Molecular and viscous flow |
|            |                          | Irreversible Langmuir adsorption |
|            |                          | Simplified diffuse reflection model |
|            | Analytic                 | Molecular and viscous flow |
| Ylilammi   | Continuum                | Molecular flow   |
|            |                          | Reversible Langmuir adsorption |
|            |                          | Irreversible successive surface reaction |

The required exposure for conformal coating of an array of pillars is a factor of 2-30 times smaller than an array of holes with equal surface area.

Predict film thickness in 3D structures.

Extraction of the sticking probability of the reactant.

Predict pulse time for conformal coating.

Predict exposure for 95% coverage.

Predict the saturation dose for complete coverage (only valid in the diffusion limited growth type).

Calculate the thickness profile in high-aspect ratio trenches.

Extract kinetic growth information.
TABLE IX. Overview of multiscale modelling works describing the conformality of ALD, listed in the chronological order.

| References      | Scale  | Model               | Key assumptions                                      | Space | Geometry | Conclusion                                                                 |
|-----------------|--------|---------------------|------------------------------------------------------|-------|----------|---------------------------------------------------------------------------|
| Prechtl         | Feature| Ballistic           | B3LYP gradient corrected DFT functional             | 2D    | Trench   | Derive the activation energy of the initial adsorption and $s$            |
|                 | Reactor|                     | Molecular flow                                       |       |          | For low $s$, depletion on the reactor scale is small; filling time $\sim 1/s$ |
|                 |         |                     | Viscous flow                                         |       |          | For high $s$, filling time independent of $s$                            |
| Lankhorst       | Feature| Continuum           | Molecular flow                                       | 1D    | Trench   | Predict minimum exposure for conformal coating                           |
|                 | Reactor|                     | Viscous flow                                         |       |          | Deposition time for conformal coating of trenched wafers $\gg$ than for flat wafers |
| Adomaitis       | Feature| Continuum           | Molecular flow                                       | 1D    | Nanopore | Observe GPC, film density, and surface roughness with varying ALD cycles and reactant dose |
|                 | Reaction| Monte Carlo         | Molecular flow                                       | 2D    |          |                                                                           |
| Yanguas-Gil     | Feature| Ballistic           | Markov chain                                         | 3D    | Circular pores| Track the probabilities as a function of the number of collisions          |
|                 | Reaction|                 | Molecular flow                                       |       |          | General expression for the absorption, escape, and effective reaction     |
|                 |         |                     | Cosine distributed re-emission direction             |       |          | probability of the feature                                               |
|                 |         |                     | Multiple reaction channels each with a specific probability |     |          | Predict total exposure required to cover the substrate                  |
| Miyano          | Reactor| Continuum           | Flow rate of the gas below the inlet is uniform over the plane | 2D    | Showerhead reactor | Predict the thickness profile in a hole                                 |
|                 | Feature|                     | Molecular flow                                       |       | Hole     | Precursor partial pressure and feeding time can be estimated for a hole with a given $a$ |

a. Ballistic models. The derivations for collisionless flow in cylindrical tubes made by Clausing et al.\textsuperscript{265} in the 1930s provide the basis for the ballistic transport models that are used nowadays. Ballistic models\textsuperscript{264,266} inherently imply particle transport in the molecular flow regime. One uses the balance of particles to compute fluxes at different locations in the high aspect ratio structure. More specifically, the flux of reactant molecules reaching section $i$ ($\phi_i$) is expressed as the sum of the flux of reactant molecules coming from other sections in the structure ($\phi_j$) and the flux of molecules coming from outside ($\phi_0$)

$$S_i \phi_i = \sum q_{ij} (1 - s_i - r_j) S_j \phi_j + q_{0i} S_0 \phi_0,$$  \hspace{1cm} (15)

with $S_i$ being the surface area of the discrete section $i$ and $q_{ij}$ and $q_{0i}$ being the probabilities that the molecules coming from section $j$/0 (outside the trench) can reach section $i$. $s_i$ and $r_j$ represent the reaction and surface recombination probabilities. The ballistic transport models used in the ALD literature are based on the earlier work of Cale and co-workers on low-pressure CVD.\textsuperscript{267,268}

b. Continuum models. In continuum models,\textsuperscript{230,269–273} one uses a diffusion equation to simulate the transport inside a high aspect ratio structure. When the transport of the precursor molecules is described as a diffusion process without an additional flow, the diffusion can be described by Fick’s second law

$$\frac{\partial n(t,z)}{\partial t} = D \frac{\partial^2 n(t,z)}{\partial z^2} - x(t,z),$$  \hspace{1cm} (16)

with $n(t,z)$ being the precursor density, $z$ being the axial position along the depth of the high aspect ratio feature, $t$ being the time, $D$ being the diffusion coefficient, and $x(t,z)$ being a loss term representing the adsorption of precursor molecules (chemisorption). Assuming that the cross-sectional area of the pore is independent of the position, particle conservation in a section of the feature reduces Eq. (16) to

$$\frac{\partial n(t,z)}{\partial t} = D \frac{\partial^2 n(t,z)}{\partial z^2} = s(\theta) A \Delta A_{iwall},$$  \hspace{1cm} (17)

with $\Delta A_i$ being the surface area per unit volume, $s$ being the reaction probability, $\theta$ being the fraction of available sites, and $A_{iwall}$ being the reactant flux per unit area to the walls. The change in surface coverage is given by

$$\frac{\partial \theta}{\partial t} = s(\theta) A \Delta A_{iwall},$$  \hspace{1cm} (18)
with $A_b$ being the average surface area of an adsorption site. One can use Eqs. (16) and (17) both in the viscous flow regime and in the molecular regime by using the corresponding diffusion coefficient valid in that regime, as explained in Sec. V.C.2. This is an important advantage of continuum models. In addition, the geometry of the substrate is only incorporated via two parameters, the diffusion coefficient and the surface area per unit volume, which makes this type of model suitable for simulation of more complex substrates.

c. Monte Carlo models. In Monte Carlo models, one particle at a time is simulated based on an algorithm, as is exemplified in the flowchart in Fig. 12. Each particle typically represents a certain number of reactant molecules. Following the path of the particle, the intersection of the path and one of the boundary walls of the substrate feature is calculated. A random number $x$ in the range of 0–1 is generated, and a sticking probability $s$ of the reaction is assumed. If $x < s$, the particle will be adsorbed and another particle will be simulated. Otherwise, the particle will be re-emitted according to a certain type of re-emission mechanism. The simulation stops if a predefined number of particles are simulated or if the predefined integrated coverage of the high aspect ratio structure is achieved.

B. Multiscale approach

By modelling the conformality of ALD, one can focus on different length scales, being the reactor, feature, and molecular scale. In Fig. 13, a schematic representation of the different scales in the simulation space is shown. Multiscale approaches aim at combining the transport and/or reactions taking place at two (or more) different length scales.

1. Reactor and feature scale

Several models focus on the feature scale and do not take into account transport at the reactor scale. One assumes that the pressure at the opening of the feature or in the reactor, in general, is constant, while, in practice, the pressure will vary during a reactant pulse. For relatively small surface area structures, it can be correct to assume a constant flux of molecules at the feature entry during the ALD reaction. However, if one simulates high surface area materials like porous powders (e.g., SBA-15 powder can have a BET value larger than 300 m$^2$/g) or batches of multiple trenched wafers (e.g., 100 V-NAND wafers yield a surface area of 1450 m$^2$ in a batch reactor), saturation will no longer be limited by the diffusion of the molecules but also by the limited availability of precursor molecules in the reactor.

Lankhorst et al. developed a multiscale model in which continuum reactor scale simulations and 1D feature scale simulations of trench structures were combined. They simulated the HfO$_2$ coating of high aspect ratio trenched wafers loaded in a multi-wafer vertical batch reactor. They found that the exposure time required for saturating all trenched wafers with TEMA$\text{H}_2$ was mainly governed by the timescales corresponding to the following three processes: (1) supply time needed to saturate the gas phase with the reactant, (2) supply time needed to provide sufficient reactant molecules to achieve full coverage, and (3) deposition time needed to coat the trench structures. The latter one can be estimated using the expression of Gordon et al., yielding a value of 6 s for a trench with an EAR of 60:1 and a reactor pressure of 93 Pa. However, the total required exposure time for coating all trenches was found to be a factor of 10 higher, showing that depletion effects in the batch reactor, characterized by large required supply times, have a considerable impact.

Prechtl et al. derived the sticking probability by ab initio calculations of the first adsorption step and fed that data as input into a feature scale simulator, coupled with a fluid dynamics based reactor simulator. With this model, they could predict the step coverage and saturation pulse time of an Al$_2$O$_3$ deposition, for a given deposition temperature, ALD tool, trench geometry, and oxygen partial pressure. Prechtl et al. performed TMA/H$_2$O depositions in a trench and these experimental results confirmed the validity of their multiscale simulation model.

2. Feature scale and molecular scale

Besides the multiscale approach of the coupling between feature and reactor scale, one can also study the coupling between the transport in the high aspect ratio structure and detailed reaction simulations at the surface. Vanguas-Gil et al. used a Markov chain approach to decouple the transport from the complex chemical surface reactions. In a Markov chain approach, the trajectory of a molecule is represented by a series of transitions between different states. A state represents a certain geometrical position in the simulated feature.
Figure 14 shows a schematic representation of a Markov chain. A molecule in state $i$ can undergo different transitions each with a characteristic transition probability. The molecule can react via a surface reaction pathway or be re-emitted outside the feature (state 0) or re-emitted to position $j$. Adapted with permission from A. Yanguas-Gil and J. W. Elam, Theor. Chem. Acc. 133, 1465:1–1465:13 (2014). Copyright 2014 Springer.

C. Key assumptions used in modelling

1. Flow regime: Molecular or viscous flow

A majority of models assume a molecular flow regime where particle-particle interactions can be neglected. This is especially true for the listed ballistic25,26,28 and Monte-Carlo based models.29,30,31,32,33,34 As already discussed in Sec. II, one can only obtain a molecular flow regime if the mean free path of the molecules is much larger than the limiting dimensions of the studied features ($Kn > 1$). An important characteristic of the molecular flow regime is the scale invariance of the reactive transport process.35 The same model to simulate the transport of molecules at a reactor scale can be used to model the transport of molecules inside high aspect ratio structures. However, in the limit of very small pore sizes, i.e., micropores with pore diameter $< 2 \text{ nm}$, the diffusion is, in principle, governed by molecular flow but also surface diffusion and the interaction potential between molecules and the walls will affect the reactant transport.36

Due to the high pressure in atmospheric pressure-type reactors, there is no molecular flow but a viscous flow regime where intermolecular collisions control the diffusion. To be able to describe ALD processes in atmospheric pressure reactors and to get a better insight into the effect of the process parameters, one needs other models which assume a viscous instead of a molecular flow regime. Yanguas-Gil et al. developed a continuum formulation model in which the same formulae can be applied for molecular and viscous flow as further detailed. Poo et al.,37 Schwillche et al.,38 and Yilammi et al. developed simulations models, which can be used in both the molecular and viscous flow regimes.

2. Diffusion coefficient in continuum and analytical models

The transport of reactant molecules can be described by a diffusion coefficient. In the molecular flow regime, some models use a diffusion coefficient $D_{\text{Kn}}$ derived for a cylindrical geometry with pore diameter $d_p$ (m)29,30

$$D_{\text{Kn}} = d_p \sqrt{\frac{8k_BT}{\pi m_p}}$$

where $k_B$ is the Boltzmann constant, $T$ (K) is the temperature, and $m_p$ (kg) is the mass of the reactant molecule.

Yazdani et al.39 developed a model to simulate an ALD process on CNTs. The different geometry required an adaptation of the diffusion coefficient, which was approximated as

$$D_{\text{Kn}} = \left( \frac{1}{\sigma_{\text{CNT}}} - 2r \right) \sqrt{\frac{8k_BT}{\pi m_p}}$$

with $r$ (m) being the radius and $\sigma_{\text{CNT}}$ ($\text{m}^2$) being the areal density of the CNTs. Other models assume an approximated diffusion coefficient for other geometries such as square holes or pillars.31

In the continuum based model of Yanguas-Gil et al.,40 simulations in the viscous flow regime are achieved by replacing $D_{\text{Kn}}$ by an effective diffusion coefficient $D$ which represents the overall resistance to molecular motion given by

$$\frac{1}{D} = \frac{1}{D_{\text{gas}}} + \frac{1}{D_{\text{Kn}}}$$

with $D_{\text{Kn}}$ being the Knudsen diffusion coefficient (molecular flow contribution) and $D_{\text{gas}}$ being the gas phase diffusion coefficient (viscous flow contribution) given by the Chapman-Enskog approximation.36

3. Simulation space in Monte Carlo models

Monte Carlo models offer the possibility for modelling complex geometries. However, most models neglect the 3D nature of the experimentally used structures and simulate features in one or two dimensions for simplification and to reduce the computational time. One assumes that the transport of reactant molecules in the structure is
largely determined by only one of the dimensions of the cross-section, implying a trench structure instead of a hole structure. Elam et al. used a 1D Monte Carlo model, to simulate a TMA/H₂O and DEZ/H₂O process into an AAO structure. The pores of the AAO structure were modelled as a 1D array with array elements representing the diameter of the nanopore at a specific distance of the opening of the tube. If an element of the array becomes coated, the diameter of the given segment decreased. Other models use a 2D structure. However, with a 2D model one cannot distinguish between, e.g., a trench and a cylindrical hole. A 3D MC simulation model was recently developed by Cremers et al. They gained insights into the required exposure for conformal coating of an array of pillars versus holes and found that the required exposure to coat an array of pillars is a factor of 2–30 times smaller than the exposure needed to coat an array of holes with equal dimensions. Figure 15 shows a schematic representation of a simulated structure by a 1D, 2D, or 3D model.

4. Reaction mechanism

In several models, surface dynamics are related to reactant impingement fluxes, which are computed using the kinetic theory of gases. The Langmuir adsorption kinetics are often used as a simplification to model the complex reaction chemistry as was discussed in Sec. II E. Different models introduce a sticking probability s to model the conformality of ALD. In Sec. VI, we will further look into the effect of the sticking probability on the thickness profile. Gobbert et al. combine reversible and irreversible reactions to describe an ALD cycle. When a particle hits the surface but is not adsorbed, it will be re-emitted according a cosine distribution. This mechanism was first suggested by Maxwell and was later experimentally verified in the work of Clausing and Hurlbut. Knudsen et al. used the cosine re-emission mechanism in the derivation of the diffusivity coefficient for low-density gases in narrow tubes. This assumption is often used in models of ALD. When the particle undergoes a diffuse elastic re-emission mechanism, the re-emission direction of colliding particles is random: the particles have an equal probability to be re-emitted in any direction above the surface. The latter mechanism was used by Rose et al. in their simulation model. In the specular re-emission mechanism, the re-emission angle is equal to the angle of incidence, and the surface acts as a perfectly reflecting wall. This mechanism is often used for the modelling of CVD processes. Kim et al. compared their simulation results with the experimental results of the coverage of a hole with TiO₂ to fit several parameters including the re-emission mechanism, and they concluded that the cosine re-emission mechanism produced the best fit to the experimental data.

5. Re-emission mechanism

When a particle hits the surface but is not adsorbed, it will be re-emitted (i.e., bounced back) in a certain direction. Three re-emission mechanisms are typically reported in the literature: cosine re-emission, specular re-emission, and diffuse elastic re-emission. The different re-emission mechanisms are illustrated in Fig. 16. In the cosine and diffuse elastic re-emission mechanisms, the particle experiences a strong interaction with the surface and loses all information of the incoming trajectory. Following the cosine re-emission mechanism, particles are re-emitted according a cosine distribution. This mechanism was first suggested by Maxwell and was later experimentally verified in the work of Clausing and Hurlbut. Knudsen et al. used the cosine re-emission mechanism in the derivation of the diffusion coefficient for low-density gases in narrow tubes. This assumption is often used in models of ALD. When the particle undergoes a diffuse elastic re-emission mechanism, the re-emission direction of colliding particles is random: the particles have an equal probability to be re-emitted in any direction above the surface. The latter mechanism was used by Rose et al. in their simulation model. In the specular re-emission mechanism, the re-emission angle is equal to the angle of incidence, and the surface acts as a perfectly reflecting wall. This mechanism is often used for the modelling of CVD processes. Kim et al. compared their simulation results with the experimental results of the coverage of a hole with TiO₂ to fit several parameters including the re-emission mechanism, and they concluded that the cosine re-emission mechanism produced the best fit to the experimental data.

6. Simulating one or multiple ALD cycles

To simplify the simulations, models do not typically simulate the entire ALD cycle, but simulate the first ALD reaction, assuming the second ALD reaction to be fully saturated. A difference between the various models is including or neglecting the film growth. Some models simulate only one ALD reaction. The simulated profile is taken as the thickness profile obtained after a multiple cycle deposition. This interpretation is correct as long as the film thickness is small in comparison with the dimensions of the high aspect ratio feature.
Otherwise, the EAR experienced by the molecules will increase with an increasing number of ALD cycles, which will have an additional effect on the thickness profile.

Several models include film growth and can simulate multiple ALD cycles. In these models, one simulates multiple times the first ALD reaction, assuming the second ALD reaction to be saturated. The film growth is determined by the entire ALD cycle (first reaction + second reaction) and the film thickness equals a multiple of the GPC.

During ALD in a nanoscopic hole, such as an AAO pore, the coating deposited during each ALD cycle decreases the pore diameter, while the EAR increases. This was also demonstrated by Gordon et al. with a deposition of HfO2 into patterned holes. The EAR of the holes increased from 36:1 to 43:1, after the deposition. Consequently, for a fixed unsaturated exposure, the Gordon model predicts a decrease in the penetration depth with each ALD cycle deposited. Perez et al. showed good agreement between the slope obtained in the thickness profiles for HfO2 ALD in AAO pores and the slope predicted by iteratively applying Gordon’s model to a pore that is gradually getting narrower as the ALD process progresses. Similarly, Yazdani et al. observed the influence of the film thickness on the exposure required to coat a forest of CNTs. The increasing film thickness leads to an increasing hindrance of the precursor molecules.

In some cases, an additional coating will influence not only the transport of the precursor molecules but also the surface area which has to be coated. When coating nanopores, the pores will gradually shrink, as discussed in Sec. III C. When coating nanowires or CNTs as done by Yazdani et al., the effective surface area which has to be covered will, in fact, increase as the coating thickens.

D. Model output

1. Exposure and EAR

Based on the simulations, one can predict the required exposure to conformally coat a structure with a certain geometry. In addition, systematic simulations can provide valuable insights into the effect of specific simulation parameters on the required exposure time, such as the effect of sticking probability, geometry, and recombination probability.

As an example, Fig. 17 shows the calculated required TMA exposure for holes, trenches, and two arrays of pillars as a function of depth to width ratio using a 3D Monte Carlo model. If we compare the $L/w$ ratios that can be obtained for a given exposure time, for example, for the value indicated by the dashed line in the figure, the $L/w$ ratio that can be coated in a trench is 2 times larger than in a hole, and $2\sqrt{2}$ times larger in a pillar structure with $w/w_{\text{pillar}} = 3$. These factors of 2 and $2\sqrt{2}$ are valid in the plotted range of $L/w$ values, being 5–25.

These results confirm the earlier proposed definitions of EAR for trenches and illustrate how simulations can be used to calculate the corresponding EAR of a given structure, as done here for square pillars with $w/w_{\text{pillar}} = 3$. Note that, for square pillars with $w/w_{\text{pillar}} = 1$, it is not possible to derive a general expression for the EAR as a function of $L/w$ that is valid for a large $L/w$ range. Instead, the EAR should be calculated for a particular $L/w$ value. For example, for $L/w = 25$, we find that the required exposure for an array of pillars with $w/w_{\text{pillar}} = 1$ is equal to the required exposure for an array of holes with $L/w = 10$, yielding an EAR of 10 for the array of pillars with $L/w = 25$ and $w/w_{\text{pillar}} = 1$.

2. Thickness profile and sticking coefficient

In addition to knowledge about the required exposure, which is a critical parameter in the experimental optimization of the conformality of ALD processes, fundamental insights into the ALD process can be obtained by simulating detailed thickness profiles as a function of depth in the feature. Figure 18 shows some typical thickness profiles obtained from simulations, published in the literature. To evaluate the models, one often compares the simulated thickness profiles with the experimentally obtained thickness profiles. A distinct feature often observed in both experimental and simulated profiles is the slope near the end of the thickness profile. For nanoscopic features, this slope has been partly attributed to the evolution of the EAR of the structure as the deposited film thickness has the same order of magnitude as the width of the structure, as already discussed in Sec. V C 6.

However, the slope observed, e.g., in the thickness profiles for Al2O3 ALD in macroscopic holes, cannot be explained by an increasing EAR during the deposition because the deposited film thickness (~nm) is negligible compared to the width of the hole (~100 µm). In this case, the observed slope is interpreted to be related to a sticking probability which is less than one. By comparing experimental and simulated thickness profiles, one can determine the initial sticking coefficient as will be explained in more detail in Sec. VI B 3. To give the reader more insights into the effect of the sticking probability on the thickness profiles and, in
turn, how an experimentally observed profile can provide information on the chemistry of the ALD process, a systematic simulation study is presented and discussed in Sec. VI.

3. Other output

In addition to exposure and thickness profiles, some models can also explicitly provide information on the pressure profile inside the structure during the deposition, providing information on the reactant molecule distribution and on gas diffusion within the structure. 66,114 Yanguas-Gil et al.264 reported statistical information such as the average interaction time, the trajectory of individual reactant molecules, and the average number of wall collisions.

VI. INSIGHTS INTO ALD THICKNESS PROFILES BY MONTE CARLO SIMULATIONS

One can obtain fundamental insights into the factors governing the surface chemistry of an ALD process by simulating thickness profiles along the depth of high aspect ratio structures. A schematic figure of a typical experimental thickness profile inside a high aspect ratio feature is shown in Fig. 19. In this review paper, we will focus on the slope at a 50% thickness (PD 50%), which we will simply call the slope of the thickness profile. In this section, the effect of the initial sticking coefficient, feature size, and contributions of possible secondary CVD-type reactions on the thickness profile will be investigated by 3D Monte Carlo simulations. The effect of recombination probability has been previously discussed by Knoops et al.66 and will not be considered here.
B. Theoretical ALD cases

1. Model of Gordon et al.: Sticking probability of unity

Assuming a constant sticking probability of unity, the thickness profile consists of a fully covered part and an almost uncovered part, separated by a distinct and abrupt front (a step function). Gordon et al. suggested that the top part of the trench, where all active surface sites have been saturated, can be considered as a "vacuum tube" because impinging molecules simply bounce back. The bottom part of the trench, which presents a surface covered with reactive sites, acts as a "vacuum pump" because all impinging molecules will stick to the wall. Based on this representation of the problem as a vacuum system, Gordon et al. derived an expression to calculate the exposure required to saturate a hole with given dimension, as already discussed in Sec. V A 1. For an unsaturated exposure, the Gordon model predicts complete coverage of the pore walls up to a depth \( l \):

\[
l = \frac{4w}{3} \left( 1 + \frac{3}{8} \frac{Pt}{k_{\text{max}} \sqrt{2 \pi n k_B T}} - 1 \right). \tag{24}
\]

Step profiles calculated with Eq. (24) are shown in Fig. 20(a).

2. Irreversible Langmuirian adsorption: Influence of sticking probability on the thickness profile

Thickness profiles simulated assuming Langmuir-type irreversible adsorption with different values of the initial sticking coefficient are shown in Figs. 20(b)–20(e). If one introduces Langmuir's adsorption assumption to describe the sticking probability, \( s = s_0(1 - \theta) \), still assuming the initial sticking probability to be one, one observes a more gentle slope in the thickness profile compared to the step function of Gordon et al. With the decrease in \( s_0 \), the profile becomes smoother. For very low initial sticking probabilities, the unsaturated thickness profiles do not necessarily show the initial plateau as shown in Fig. 20(e). This situation corresponds to the sketch in Fig. 4(b). Similar thickness profiles were also observed in the simulations of Rose et al., Dendooven et al., and Knoops et al.

3. Determining the initial sticking coefficient through comparing simulation with experiment

By comparing simulated thickness profiles with experimentally obtained profiles, one could quantify the initial sticking coefficient of a given ALD reactant. This approach was suggested by Rose et al., who obtained a value of 0.02 ± 0.005 for TDMAT on TiO₂. Shimizu et al. obtained a sticking probability of 0.002 for a \( \text{C}_6\text{H}_{13}\text{Co} \) reactant. However, one should realize that a high density of data points along the depth profile, and especially in the slope region, are needed in order to make a fair conclusion about the sticking probability, as illustrated in Fig. 22. In this respect, the recent development in experimental test structures and analysis methods to extract depth profiles, e.g., by the microscopic LHAR structures or the recently introduced methods by Schwille and co-workers might allow for a more detailed investigation of the initial sticking coefficient. By comparing experimental and simulation results, Bartha and co-workers could extract an initial sticking coefficient of \( 2 \times 10^{-2} \) for TMA and \( 3 \times 10^{-3} \) for the BDEAS reactant. Ylilammi et al. compared experimental results, obtained using the microscopic LHAR structures, with simulation results, obtained using their diffusion model, to extract an initial sticking coefficient of 0.00572 for TMA.

4. Influence of the initial sticking coefficient on the required exposure

In addition to the influence of sticking probability on the thickness profile, it is of interest to understand the effect of sticking probability on the reactant exposure required for creating a conformal coating up to a certain EAR. In Fig. 23, the exposure is shown as a function of the EAR, simulated by the Monte Carlo code of Cremers et al. Similar simulation results were earlier published by Knoops et al. For small EAR (up to EAR 30:1), one observes an increasing exposure for decreasing \( s_0 \) in the range of 1 to 0.01. With the increase in EAR, the exposure becomes independent of \( s_0 \). As already discussed in Sec. II, these two behaviors correspond to the reaction limited (low EAR) and diffusion limited (high EAR) growth types, respectively. The exposure required to obtain a fully covered trench with high EAR (100:1) is equal for different initial sticking coefficients, in the range of 1–0.01; however, the thickness profile for unsaturated doses differs with the initial sticking coefficient due to differences in the ALD reaction kinetics. Figure 23 shows the difference in the thickness profile for an unsaturated coating of a trench structure with EAR of 100:1 and for an initial sticking coefficient of 1 and 0.01, respectively.
5. Influence of the bottom of the feature

The existence of a bottom in the structure is expected to have an impact on the thickness profile for an unsaturated exposure dose. In Monte Carlo simulations, we observe that for each case listed in Fig. 20, in general, the bottom of the structure is covered faster than the adjacent walls. This phenomenon of a faster coverage of the bottom of the structure has been observed in other Monte Carlo simulations and was also reported in ballistic models which can be explained by the contribution of the direct pore-opening to pore-bottom flux, leading to a higher coverage of the bottom in comparison with the pore walls.
C. Contribution of secondary CVD-type reactions

In a typical flux-controlled CVD process, film growth depends on the local gas flux and lacks the characteristic self-limited behavior of ALD. To simulate the contribution of a CVD-type process, the same simulation program was used for the ALD processes, omitting the limit on the number of adsorbed reactant molecules per unit area and with an adapted sticking probability \( s \). We reduce the chemistry of the CVD process to one parameter \( p_{\text{reaction}} \) which represents the reaction probability and which is independent of the local coverage \( h \). In the schemes in Fig. 24, the CVD contribution is represented by the orange curve. The ALD contribution during the process is similar as in the theoretical ALD case, assuming the irreversible Langmuir adsorption (blue curve). The total probability that a reactant molecule sticks on the surface (green curve) is given by the sum of the probability for ALD reaction and \( p_{\text{reaction}} \) of the irreversible CVD process, leading to

\[
s = s_0 (1 - h) + p_{\text{reaction}}.
\]
In Fig. 24, we show two cases of an ALD reaction with a small CVD contribution described with a \( p_{\text{reaction}} \) of 0.0002. In (a) and (b), the initial sticking probability for the ALD reaction is considered 0.1 and 0.01 so that the simulation results can be compared to the ideal ALD cases in Figs. 20(c) and 20(d), respectively. The main impact of the CVD contribution can be observed in the thickness profile near the feature opening. A coverage degree of more than 100% can be observed at the entrance of the structure, with a value of ca. 160% for the highest simulated exposure. As expected due to the flux controlled nature of the CVD contribution, the coverage degree increases with exposure time, surpassing the value of 100%, meaning that more than one saturated ALD layer is deposited. Instead of the initial plateau typically observed in the ideal ALD simulations for \( s_0 \) above 0.01 (Fig. 20), the CVD contribution gives rise to a decreasing contribution because the flux decreases inside the feature. With the increasing exposure time, the slope of this initial part of the thickness profile increases, ultimately leading to clogging of the feature mouth. This first part of the thickness profile is in agreement with the classical CVD profile.297 Deeper in the trench, where the coverage drops below 100%, we recognize the characteristics of the typical ALD profile, with a marked slope. This slope decreases with the decrease in the initial sticking probability, as for the ideal ALD case, and the slope and its position (PD50%) are only slightly affected by the CVD component. The PD50% is a bit lower because the reactant molecules that are consumed in the CVD reactions near the feature entrance are no longer available to contribute to deposition deeper in the structure. The effect of the presence of a feature bottom is comparable to the ideal ALD case.

To the best of our knowledge, simulated profiles including a CVD contribution have not been studied in detail before nor have they been compared to experimental data. A more extended study of simulations could be instructive on how even a minor CVD component can impact the conformality of an ALD process. Moreover, comparing those thickness profiles with experimental thickness profiles can potentially give a hint on the possible contribution of a CVD-like component in the ALD process. To this end, it would also be useful to extract experimental thickness profiles for processes where intentionally a CVD component is present, e.g., by selecting a deposition temperature slightly above the decomposition temperature of the metal ALD reactant.

D. Other reactions potentially influencing the thickness profile

The position of the slope and the gradient of the slope of the simulated profiles are often in good agreement with the experimental results.87,178 However, there are also examples of experimental data which cannot yet be explained by the simulations. For example, there are experimental profiles in which no initial plateau is observed114 (e.g., experimental profile in Fig. 22), or which show a more gradual decrease lacking a well-defined slope,69 or a long tail following the slope.69 Although irreversible Langmuir adsorption can often
satisfactorily describe the thickness profile, real processes are more complex, and the assumptions of the Langmuir model likely oversimplify the reactions. Moreover, additional reactions might contribute in real ALD processes:

- The more complex real surface chemistry may also include reversible reactions, which would affect the observed thickness profile. Then, some surface groups left behind after one reaction of the ALD process may desorb during the purging/pumping step, resulting in less reaction sites for the next ALD reaction. Indeed, when coating demanding 3D structures, the purging/pumping time is typically prolonged to allow excess reactants and reaction by-products to diffuse out of the structure. This prolonged evacuation time may affect the possible desorption of surface species.

- Real gas-solid reactions used in ALD may involve multiple surface reaction pathways that occur simultaneously or consequently. For example, for the TMA/H2O process, the existence of multiple reaction pathways has been proposed on the basis of experimental evidence. Simulations have been made to illustrate possible coverage profiles with a theoretical two-site model with different reaction probabilities.

- With this Monte Carlo code, the simulations are limited to the first reactant exposure of the ALD process, assuming the second reaction to be saturated. However, in the experimental cases, it is possible that both reactions are unsaturated and both limit the conformal nature of the coating. In this case, both reactions will contribute in their own particular way to the profile, which may lead to more complex profiles.

- As already discussed in Sec. V C6, by deposition of more cycles, the EAR of the coated structure increases and the deposited film gradually limits the diffusion on molecules. As a consequence, the steepness of the slope of the thickness profile will decrease.

- In the growth of composite films by ALD, etching reactions of one of the reactants can occur. This etching effect may be dependent on the flux of one of the reactants and may therefore have an influence on the corresponding thickness profile of the ALD process.

- Metal ALD on oxide supports usually suffers from nucleation difficulties. Islands form at the start of the process, which in turn act as catalysts for the ALD reactions, speeding up the growth. However, in 3D structures, due to differences in local reactant pressure along the feature, the nucleation process will likely be delayed deeper in the trench. In that way, the catalytic enhancement of the ALD growth will be affected and as such also the conformality. Also for applications in catalysis where one is mainly interested in nanoparticles grown by ALD, the diffusional limitations may cause an uneven nucleation over a 3D porous structure.

- Gaseous by-products (e.g., HCl) may not be inert, but they can occupy the same sites as the reactant. Therefore, less sites will be available for the reactant molecules, potentially leading to a decrease of the GPC deeper in the structure.

VII. SUMMARY AND OUTLOOK

In this review, an overview was given on the analysis and modelling of the conformality of ALD processes. Vertical, lateral, and (meso)porous substrates can be used to quantify the conformality of ALD processes. In general, a higher conformality is obtained for substrates coated with thermal ALD processes than with energy-assisted processes, such as plasma-enhanced and ozone-based ALD where surface recombination inevitably leads to a decrease in the impinging flux of radical/ozone species at an increasing penetration depth. To gain more insight into the process parameters influencing the conformality of ALD, several models (classified as analytical, ballistic, continuum, Monte Carlo) have been reported in the literature. Models can predict the exposure required to conformally coat a certain substrate and can simulate detailed thickness profiles as a function of the penetration depth. These profiles for unsaturated exposures are characterized by a slope, the steepness of which increases with the increasing initial sticking coefficient. The steepness of the slope can also be influenced by an increasing aspect ratio of the coated feature during deposition due to the comparable dimensions of the feature and the film thickness. Besides ALD, also other reactions can influence the profile. CVD type contributions lead to growth beyond the ALD GPC and clogging at the entrance of the feature. An interesting potential direction of future work concerns investigating how more complex effects, such as etching, nucleation, and undersaturation, contribute to the thickness profile.

To define the achieved conformality, in the literature, one often focuses on the conformality as percentage or on the penetration depth of the deposited film along the high aspect ratio substrate. However, also the properties of the film could change along the depth of the structure. It would be interesting to extend the work on conformality to the observation of differences in the composition, crystallinity, morphology, and functional properties (e.g., dielectric constant, electronic conductivity, or Li ion conductivity) of the deposited coating.

Experiments on the conformality of ALD films have been performed on a variety of test structures for which often the height to width ratio (AR) is reported. This diversity of substrates and the lack of a standard definition of a geometry-independent aspect ratio often complicate a direct comparison of the reported results. In this article, we propose a geometry independent equivalent aspect ratio (EAR), to facilitate comparison. For benchmarking purposes, it would be interesting to investigate a specific process with different types of conformality test structures and cross-compare the results. In the future, it might be beneficial if a consensus could grow within the ALD community on the use of standardized test structures which could be used to validate conformality across a wide range of ALD reactor types, pressure ranges, and ALD processes.

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NOMENCLATURE

- **A** Cross-sectional area
- **a** Aspect ratio according to Gordon et al. \(^{62}\)
- **3DMAS** Tris(dimethylamino)silane
- **\(\pi(t, z)\)** Loss term representing the adsorption of precursor molecules
- **\(\varphi\)** Vacant surface site

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The term diffusion limited may cause some confusion, because the estimated time scales for diffusion in an inert tubular structure or trench are much smaller than the exposure times typically needed to conformally coat a high aspect ratio structure by ALD. However, one should realize that in the case of ALD the reactants need to diffuse in a reactive or sticky tube instead of an inert tube meaning that the surface of the high aspect ratio structure acts as an additional loss channel in particular for reactions with a high sticking probability.

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