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Area-selective atomic layer deposition of Al2O3

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Master thesis

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Abstract

Alignment between subsequent patterning steps has become challenging for the *top-down* patterning strategies currently employed in the fabrication of nanoelectronics. As a result, innovative *bottom-up* fabrication strategies, such as area-selective atomic layer deposition (ALD), have been drawing a lot of attention. Area-selective ALD enables deposition on specific areas on a substrate and can, for example, be applied on a predefined pattern. In this work, Al₂O₃ area-selective ALD is investigated, that uses chemoselective inhibitor molecules to block precursor adsorption. The primal goal was to gain deeper understanding into the underlying mechanisms of Al₂O₃ area-selective ALD, and thereby, develop a process with high selectivity.

Optimization experiments with acetylacetone (Hacac) as an inhibitor, trimethylaluminum (TMA) as a precursor, and either H₂O or O₂ plasma as a co-reactant revealed that the dose time and partial pressure of TMA are the dominant factors that influence the precursor blocking. These findings suggest that the precursor dose should always be set to the minimum dose that is sufficient for saturation on the growth area.

Precursor blocking was enhanced at high temperatures, as shown by *ex-situ* spectroscopic ellipsometry (SE) measurements. The effect of temperature can be attributed to multiple factors and was further investigated here by researching three contributions: (I) surface dehydroxylation, (II) higher Hacac coverage with increasing temperature and (III) temperature-dependent Hacac removal by TMA. Contributions from (I) and (II) were observed with *in-situ* Fourier transform infrared spectroscopy (FTIR) experiments on Al₂O₃ samples, where a temperature increase from 100 °C to 200 °C resulted in 13±2 % decreased TMA absorbance signal and 37% increased Hacac signal. The *in-situ* FTIR measurements on Hacac-functionalized samples for contribution (III) showed only a marginal increase in Hacac removal from 100 °C to 200 °C. This result indicates that most of the additional Hacac adsorbates found at higher temperatures are strongly bonded to the surface, and therefore can contribute to better TMA blocking. In the same experiment, TMA blocking increased by 36±3 % from 100 °C to 200 °C, which is significantly larger than the decrease in TMA absorbance signal measured in contribution (I) (13%). This difference suggests that enhanced precursor blocking at higher temperatures should be assigned to multiple contributions, rather than a single factor.

Dimethyl-aluminum isopropoxide (DMAI) and tris(dimethylamido)aluminum (TDMAA) were explored as alternative Al precursors, to investigate the effect of precursor choice on area-selective ALD. *In-situ* FTIR studies on Al₂O₃ samples indicated that the ALD reactions take place in a self-limiting way for TMA and DMAI, while TDMAA decomposed on the Al₂O₃ surface. Additional *in-situ* FTIR experiments on Hacac-functionalized samples revealed that precursor blocking is inefficient when using TMA as precursor (22% blocked), but very effective for DMAI and TDMAA (96±4 % blocked). In the same experiment, 24% of Hacac adsorbates was removed upon dosing TMA, while Hacac removal was limited to 3% and 1.7% for DMAI and TDMAA, respectively. Lastly, TMA and DMAI were compared in terms of nucleation delay obtained on Hacac-functionalized CoOₓ and HfO₂ substrates. The x-ray photoelectron spectroscopy (XPS) and *in-situ* SE analysis showed that the use of DMAI allowed for Al₂O₃ area-selective deposition of ∼3 Å and ∼7.4 Å on SiO₂, with CoOₓ and HfO₂ as non-growth areas, respectively. In contrast, no nucleation delay was achieved with TMA, indicating that the Hacac-DMAI combination results in higher selectivity.

Finally, aniline was investigated as an alternative inhibitor by using a three-step process with aniline (step A), TMA or DMAI (step B) and H₂O (step C). The *in-situ* SE and XPS analysis showed that the aniline-TMA combination enabled selective deposition of ∼9 Å Al₂O₃ on SiO₂, when considering Co as non-growth area. The aniline-DMAI combination was less effective, since it resulted in selective deposition of ∼6.5 Å. Interestingly, the inhibitor and precursor comparative studies showed that DMAI should be employed with Hacac, while TMA is preferred with aniline, thereby indicating that the precursor choice is coupled with the inhibitor selection. Overall, this work enabled selective deposition of Al₂O₃ by utilizing small inhibitor molecules, and provided insights into the underlying mechanisms of area-selective ALD.
A  FTIR measurements for ALD processes using TMA, DMAI and TDMAA

B  XPS measurements for A+BC type cycles with Hacac

C  XPS measurements for ABC type cycles with aniline
1 Introduction

Since the introduction of integrated circuits (ICs) in the 1950's [1], the semiconductor industry has succeeded in the continuous down-scaling by reducing the size of the components comprising the electronic devices. The fabrication of ICs is currently based on top-down patterning methods [2]. Top-down fabrication can be compared to sculpting from a block of stone, where the base material is removed from where it is not required. Similarly, various deposition, lithography and etching steps are carried out during IC fabrication to produce features of controlled shape and size. Currently, fabrication of sub-5 nm node chips is required, which is challenging by using exclusively top-down strategies [3]. Smaller features require an increasing number of processing steps, which rockets the manufacturing costs, and at the same time, feature alignment has become problematic [4]. These issues have become the prime bottleneck in the progress towards smaller device features. In order to tackle them, the conventional top-down patterning techniques need to be replaced by innovative bottom-up fabrication schemes [5, 6, 7]. Bottom-up fabrication can be compared to building a brick house, where building blocks are combined to make larger structures. Similarly, bottom-up fabrication in nanoelectronics utilizes atoms and molecules as building blocks, thereby enabling fabrication with accuracy at the atomic-level. One of the most promising bottom-up fabrication candidates is area-selective atomic layer deposition [8], in which film deposition takes place selectively only on a predetermined area.

In this chapter, a conventional patterning approach is firstly introduced along with the current issues that restrain further down-scaling. Furthermore, the concepts of atomic layer deposition (ALD) and area-selective ALD are explained. Moreover, the basic differences between temporal and spatial ALD are discussed, since reactors of both ALD concepts have been employed in this project. Lastly, the goals of this work are presented.

1.1 Patterning

ICs manufacturing requires the fabrication of high-density features on an already existing pattern. Typically, the desired features are fabricated by using lithography, as illustrated in Figure 1.1. In this example, deposition is needed only on the area depicted in blue. Patterning starts with a uniform deposition of the material that needs to be structured (red layer). Then, a photoresist layer, depicted in grey, is spin coated on the whole surface (not shown here). The photoresist is a photo-sensitive material that experiences a change in its chemical and structural properties when exposed to the radiation source. The desired pattern is transferred to the photoresist by using masks that protect specific areas of the photoresist from radiation exposure. The exposed and unexposed photoresist sites differ chemically, and can therefore be selectively removed with the proper solvent. This process is generally known as photoresist development and results in a patterned photoresist film, as depicted in Figure 1.1b. An alignment error during the photoresist patterning resulted in a misplaced photoresist film, with respect to the underlying blue surface on the patterned sample. As the patterning proceeds, regions of the deposited film that are not covered with the photoresist are removed by (wet or dry) etching. Finally, the process is completed by the resist strip, resulting in the desired structure. As shown in Figure 1.1c, the alignment error in the photoresist film has been passed on to the deposited layer, which is now misplaced. The difference between the intended and the printed feature position is known as edge placement error (EPE). An example of such a case is depicted in Figure 1.2, where a scanning electron microscopy (SEM) and transmission electron microscopy (TEM) cross-section image of an Intel 3D Xpoint memory chip is shown. The vertical line connections within the dashed blue circle suffer from an EPE.

In contrast, area-selective ALD can enable self-aligned fabrication by allowing for selective deposition on the intended area, as illustrated in Figures 1.1e and 1.1f. In this way, the alignment issues can be eliminated, and at the same time less patterning steps are required [4].

1.2 Temporal Atomic Layer Deposition

ALD is based on cyclic and alternating exposure of a substrate surface to gas-phase reactants that undergo self-limiting adsorption reactions, as shown in Figure 1.3. The cycle typically starts with the precursor dosing step. In the case of metal oxide ALD, a precursor is a molecule with a metal atom in its center, surrounded by chemical functional groups called ligands. The precursor adsorbs on the surface sites and/or surface chemical groups, as long as these are available and accessible. The precursor reacts neither with itself in gas-phase, nor with the surface sites it creates. As a result, the surface saturates and the reactions are finished as soon as the the precursor molecules fully cover the surface. In temporal ALD, a purging step is required after each exposure such that the remaining compounds in gas phase and the reaction products are removed from the reactor. In this way, a chemical vapor deposition (CVD) component can be avoided. During the second half-cycle, the surface is exposed to the co-reactant, which is typically an
Figure 1.1: (a, b, c) Schematic representation of the process flow in conventional patterning. (a) Patterned sample, representing a multilayered device structure under fabrication. Deposition is needed only on the blue colored region. (b) Patterning starts with a uniform deposition of the desired layer, followed by patterning and development of the resist layer. Due to alignment issues, the resist film has been misplaced. (c) The resulting substrate after etching of the deposited film that is not covered by the photoresist, and removal of the photoresist. The misplaced photoresist layer resulted in a misalignment between the deposited film and the underlying surface, known as edge placement error [9]. (d, e, f) Self-aligned fabrication based on area-selective ALD. Material deposition takes place selectively on the intended area, thereby eliminating the EPE.

Figure 1.2: Cross-sectional SEM and TEM image of Intel’s 3D XPoint Memory Array. Edge placement errors (EPEs) can be identified in the top-right image, indicated by the blue dashed circle [10].

An oxidizing agent (e.g. H₂O, O₂ plasma) in the case of metal oxide ALD. The co-reactant reacts with the precursor ligands present on the surface, again in a self-limiting way. Lastly, the cycle ends with another purging step. After completion of the last step, the first layer of the (desired) material has been deposited.
and the cycle can be repeated.

Figure 1.3: Schematic of a typical ALD process. In the first half-cycle, the substrate is exposed to a saturated precursor dose, followed by a purge step. Then, a co-reactant dose is applied, where the co-reactant molecules react with the adsorbed precursor in a self-limiting way, resulting in the desired layer. Finally, the cycles ends by removal of the reaction products with a purge step [11].

As a typical example of an ALD process, Al₂O₃ deposition by using trimethylaluminium (TMA) and water is discussed here [12]. In the first step, TMA undergoes a Brønsted acid-base ligand exchange reaction with the OH surface groups, as described in equation 1.1. The hydroxyl group (-OH) acts as a Brønsted acid by donating a H to the methyl (CH₃) of TMA, which is the Brønsted base [11]. This reaction results in formation of a surface Al-O bond and the release of volatile methane (CH₄) as reaction product. The reactions cease as soon as the surface is fully terminated with CH₃ groups. In the second-half cycle, a hydrolysis reaction takes place, as given in equation 1.2. The H₂O molecule reacts with the adsorbed TMA molecule, where the volatile CH₄ product leaves the surface, and a new Al-OH bond is formed. The hydrolysis reactions are finished when all TMA ligands are removed and the surface is again hydroxylated.

\[\text{n} - \text{OH} + \text{Al(CH}_3)_3 \rightarrow \text{n} - \text{Al(CH}_3)_3 \text{n} + n \text{CH}_4 \uparrow, \text{where } n = 1, 2 \quad (1.1)\]

\[\text{O} - \text{Al(CH}_3)_3 + \text{H}_2\text{O} \rightarrow \text{O} - \text{Al} - \text{OH} + \text{CH}_4 \uparrow \quad (1.2)\]

The saturation of both half-cycles leads to a characteristic growth per cycle (GPC), which differs for each ALD process. The GPC depends on the substrate material [11] and the reactants used, but not on their corresponding doses, since the ALD reactions take place in a self-limiting manner. Moreover, changes in temperature can have a large impact on GPC. In fact, an ALD process takes place in a self-limiting manner only within a specific temperature region, called the temperature window [11]. The temperature window differs for each ALD process depending on the employed precursor, and should be investigated when characterizing a new process.

To conclude this section, ALD enables layer-by-layer material deposition, thereby allowing for thickness control at the atomic-level. Moreover, ALD facilitates the deposition of uniform, conformal and pinhole-free layers, even on high aspect ratio structures [13], as illustrated in Figure 1.4. High-quality film deposition can be also achieved at low substrate temperatures, by using a plasma as the co-reactant [8, 14, 15]. This process is referred to as plasma-assisted ALD, and can be employed to prevent damage to temperature-sensitive device components during the fabrication process. These key merits have been imperative in various fields, such as the semiconductor industry [16, 17], catalysis [18, 19] and photovoltaics [18, 19].

1.3 Spatial atmospheric-pressure Atomic Layer Deposition

As discussed in section 1.2, in conventional ALD the precursors are dosed one after the other, separated in time by purge steps. In spatial ALD, however, the precursors are separated in space and they are supplied simultaneously and continuously. A schematic illustration of this concept is depicted in Figure 1.5. The setup consists of two dosing inlets (precursor 1 and 2), which are utilized to dose the precursor and co-reactant. Material deposition is achieved by horizontally oscillating or rotating the substrate underneath the different gas inlet sections, in close proximity to the injectors (typically 20-100 µm). The dosing inlets are separated by inert gas-bearing inlets, where high flow of non-reactive gas (e.g. N₂) is applied. The gas-bearing inlets not only function as a bearing between the injector and the substrate, but also restrict the precursors and the reaction products in their corresponding dosing zones. In this way, the time consuming purging steps needed in temporal ALD can be omitted, thereby allowing for very
short cycle duration, high throughput deposition, while maintaining the required high film quality [20]. For example, \( \text{Al}_2\text{O}_3 \) deposition rates larger than 1 nm/s have been demonstrated with spatial ALD [21], while the corresponding rate for temporal ALD is \( \sim 1 \) nm/min. Finally, isolation of dosing zones from the surrounding environment enables deposition under atmospheric pressure, which can effectively reduce the manufacturing costs [20, 22].

In spatial ALD, the dose time is defined as the time a fixed point at the substrate is exposed to a precursor. It depends on the geometry and dimensions of the spatial ALD setup, but also on the relative movement speed of the substrate with respect to the injectors. Since the geometry and dimensions (e.g., the injector size) are fixed, the exposure time can be modified only by the relative substrate speed. For instance, higher relative speed results in shorter exposure time, since the substrate spends less time underneath the precursor inlet. The relative speed is fixed during the process, and therefore the exposure time is coupled for all recipe compounds. Nevertheless, the dose (or exposure), which is defined as the product of the gas pressure and the exposure time can differ for each recipe compound, since the gas pressure can be altered independently.

Owing to its aforementioned key merits, spatial ALD reactors have emerged in the past few years as a very promising tools for ALD commercialization. Spatial ALD has been successfully demonstrated in printed electronics for thin-film transistor (TFT) fabrication [23, 24], in passivation layers for c-Si solar cells [21, 25] and in deposition of barrier layers against moisture and oxygen [21].

### 1.4 Principle of area-selective ALD

As mentioned in section 1.1, alignment challenges can be eliminated or mitigated by replacing conventional top-down fabrication schemes with bottom-up schemes, such as area-selective ALD. Ideally, in area-selective ALD the key merits of ALD are combined with a precise growth in the lateral dimensions, thereby allowing for accurate deposition only on the intended area. Typically, the area where deposition occurs is labeled as the growth area, while the area on which no growth should take place is referred as non-growth area (blue and green regions, respectively, in Figure 1.1a). Area-selective deposition can be achieved by exploiting differences in local surface chemistry. Particularly, the growth area should be active towards the applied ALD chemistry, thereby allowing for fast nucleation of the deposited film. In contrast, deposition should
not readily initiate on the non-growth area, resulting in a nucleation delay. This difference in nucleation behaviour could be utilized to deposit selectively on desired surface. Characteristic examples of that concept are a) TiCl$_4$ (Ti precursor), and tetrakis(diethylamino)hafnium (TDEAH, Hf precursor), that show selective adsorption on OH-terminated surfaces, rather than on H-terminated surfaces [26, 27], and b) the selective Co growth on metal substrates between 160 °C and 220 °C [28]. The Co precursor undergoes exothermic reactions with Pt and Cu surfaces, whereas the reaction with the SiO$_2$ surface is endothermic, hence not favorable [29].

In practice, after a number of ALD cycles, undesired material deposition typically initiates on the non-growth area. One of the most common ways to observe all stages of selective deposition, is to examine the thickness evolution as a function of the number of ALD cycles for both surfaces, as shown in Figure 1.6. On the left, a typical thickness trend corresponding to the growth area is given. The thickness starts increasing from the first cycle onwards and follows a linear trend, which indicates immediate film nucleation and controlled layer-by-layer deposition. The slope of this curve corresponds to the GPC. In contrast, on the right an example of a nucleation delay on the non-growth area is given. At first, no deposition takes place (i.e. there is a nucleation delay), but after repeated exposure to the precursor, material starts accumulating in the form of islands on the surface. Finally, the islands coalesce and fully cover the starting surface. At this point, there is no difference in surface chemistry between the growth and the non-growth area and therefore the thickness increases in the same linear manner in both cases.

Figure 1.6: Film thickness as a function of number of ALD cycles for two different starting surfaces: (a and a1-a3) On the growth area, film growth readily starts with the thickness following a linear trend. (b and b1-b3) On the non-growth area, film growth does not start immediately (nucleation delay). Then, island formation takes place, indicated by a small increase in thickness. Finally, the islands coalesce and cover the starting surface. Beyond this point film growth follows the same linear trend as on growth-area [30].

From Figure 1.6, it becomes evident that a larger nucleation delay results in larger selectivity. Here, the selectivity term is defined as:

$$S = \frac{\theta_1 - \theta_2}{\theta_1 + \theta_2}$$  \hspace{1cm} (1.3)

where $\theta_1$ and $\theta_2$ correspond to the surface coverage of material on the growth area and non-growth area, respectively [31].

The selectivity window corresponds to the number of cycles in which material can be deposited on the growth area, while the thickness on the non-growth area ideally remains zero. Extension of the selectivity window to a larger number of ALD cycles, without affecting deposition on the growth area, is the primary goal in every area-selective ALD process.

### 1.5 Strategies to enable area-selective ALD

In many cases, precursor and/or co-reactant adsorption occurs on both the growth and the non-growth area, and therefore nucleation takes place in the same manner on both surfaces. To achieve area-selective deposition in such cases, the surface of the non-growth area needs to be functionilized to prevent adsorption...
of precursor and/or co-reactant. This approach is known as area-selective ALD by area deactivation. The most extensively studied case of this approach is deactivation by using self-assembled monolayers (SAMs) [32, 33, 34]. SAM monomers are long organic molecules that consist of mainly three parts, a head group, a long alkyl chain as backbone, and a tail group (Figure 1.7a). The head group expedites the binding on the surface, and since it is chemically active only to specific surfaces or surface species it allows for selective adsorption on the non-growth area. The alkyl chain contributes to the formation of an ordered monolayer via the Van der Waals interactions with the neighboring chains. Finally, the surface is terminated with the tail groups, which modify the surface properties according to their chemical properties. Therefore, by selecting a tail group that is inactive towards the ALD precursors, material deposition can be blocked on the non-growth area.

![Figure 1.7: (a) An octadecyltrichlorosilane (ODTS) molecule, as a typical example of a molecule that can form a SAM (b) a SiO$_2$ surface covered with a SAM of ODTS. The hydrophilic SiO$_2$ surface is transformed to hydrophobic surface [35].](image)

Although area-selective ALD has been successfully demonstrated with SAMs on many different materials [5], SAMs have some limitations. First of all, the formation of a well-packed and defect-free SAM layer, which is essential for effective blocking [5], typically requires more than 24 h, especially when SAMs are prepared by sample immersion in a solution [36]. Moreover, SAMs degrade upon plasma exposure, and therefore they are not compatible with plasma-enhanced processes [5, 37]. Lastly, SAM degradation can also take place during high temperature processes, due to their relatively low thermal stability [38]. The above limitations suggest that SAMs would be difficult to implement in an IC fabrication scheme.

An alternative option for area deactivation is the use of smaller organic molecules, which are here referred as inhibitors [39]. Inhibitors open up new possibilities for area-selective ALD, since their small size allows them to exhibit high volatility. As a result, they can be dosed in vapor phase as an additional ALD step and therefore enable fast deposition with a much higher throughput, as compared to the case of SAMs. Moreover, inhibitors are compatible with plasma-enhanced processing, since they can be dosed in every cycle. This concept has been successfully demonstrated for SiO$_2$ area-selective ALD [8] by adopting an ABC-type process, where steps A, B and C correspond to the inhibitor, precursor and co-reactant dose, respectively, as depicted in Figure 1.8.

![Figure 1.8: Schematic illustration of an ABC-type area-selective ALD process with inhibitor molecules. Grey and yellow areas on the pattern correspond to the growth and the non-growth area respectively. The successive process steps are: A) inhibitor, B) precursor, and C) co-reactant (O$_2$ plasma) [8].](image)

Although the inhibitor was removed from the non-growth area during the co-reactant dose (O$_2$ plasma),
it was easily re-applied in the beginning of each cycle. To conclude, the capability for fast exposure, paired with their compatibility with either thermal or plasma ALD processes, makes inhibitors very promising candidates for area-selective ALD. Thus, this work is dedicated to investigating their potential.

1.6 Mitigation of EPE effects using area-selective ALD

As discussed in section 1.1, area-selective ALD could replace top-down patterning techniques to reduce the required patterning steps [7] and enable the fabrication of EPE-free features. In this work, the application of area-selective ALD in fabrication of ICs aims at the mitigation of the effects caused by EPE, rather than tackling EPE itself. In order to fully appreciate the potential of such an application, the use of area-selective ALD in the ICs fabrication is discussed in this section.

First and foremost, more information regarding the architecture of an integrated circuit (IC) are required. A schematic representation of a typical IC is given in Figure 1.9a. It consists of the so-called front-end-of-line (FEOL) and the back-end-of-line (BEOL). The FEOL is the first part of the IC fabrication, where all the individual devices (transistors, capacitors, resistors) are patterned (also shown in Figure 1.9b). A patterned surface, consisting of millions of isolated transistors, is the outcome of a complete FEOL fabrication process. In the BEOL, the individual devices of the FEOL are connected with metal wiring, for signal distribution. The BEOL consists of stacked horizontal dielectric layers into which the metal lines are patterned. As an example, a schematic of the first two horizontal metal layers (Line 1, Line 2) connecting the individual devices can be seen in Figure 1.9b. In today’s complex ICs, ten or more metal layers are required [40].

![Figure 1.9: Schematic of (a) a typical modern chip architecture. Each isolated device in the FEOL is connected with metal wiring in the BEOL. (b) A closer look at the devices in the FEOL and the first patterned metal layers in the BEOL. [40]](image)

The metal lines in the BEOL must be connected vertically through layers of interconnects, which are called vertical interconnect accesses (VIAs) and allow signal to be transmitted between the layers. A schematic of a VIA connecting the first two metal lines is also shown in Figure 1.9b, while a cross-sectional SEM image of the BEOL of an actual device is given in Figure 1.10. Typically, low-k carbon-doped oxide (e.g. carbon-doped SiO\(_2\)) is employed as isolation material, which can mitigate the capacitive coupling ("cross-talk") between the neighboring metal lines. This layer is referred to as interlayer dielectric, or ILD. The lower level interconnects, called local interconnects, are thin and densely packed (approximately 24-32 nm [41, 42, 43] in the 7 nm node), while the upper levels, called global interconnects, are thicker and more widely separated (300 nm [43] in the 7 nm node). Cu is currently employed for the global interconnects, while Co or Co-capped Cu VIAs are fabricated for local interconnects [44].

The starting surface in VIA fabrication consists of patterned, conducting metal lines, separated by the interlayer dielectric, as shown in the left-most image in Figure 1.11a below. The center-to-center (or edge-to-edge) distance between the lowermost metal lines is referred to as metal pitch. In modern ICs, an increasingly smaller metal pitch is required, and therefore VIAs need to be placed more accurately on the metal line. However, this has become a real challenge and in many cases, the VIA partially lands on the dielectric (i.e. EPE), as depicted in Figures 1.11 and 1.2. Currently, fabrication of smaller metal pitch is limited by the variation control of EPE. For instance, transition to the 5 nm node requires a 24 nm metal pitch, and therefore the maximum tolerated EPE (EPE\(_{\text{max}}\)) should not exceed 6 nm [43], which is
Figure 1.10: Cross-sectional SEM image of 32 nm interconnects. Carbon doped oxide (shown in dark) is employed as an isolation layer between the metal lines (light gray). The lower level interconnects need to be thin and densely packed to fit with the aggressive scaling of the front end of line, while the upper levels are wide, since they connect devices [45].

extremely challenging. EPEs exceeding this limit can be detrimental for the device performance, reliability and durability. Particularly, misplaced VIAs have a reduced contact with the underlying metal line, which increases the contact resistance (R). The reduced contact area also lowers the electromigration (EM) reliability\(^1\), which can lead to eventual failure of the device [46]. Moreover, proximity to the neighboring metal lines results in higher capacitance (C) between the VIA and the corresponding metal line. In ICs, the product R·C needs to be kept as low as possible, in order to switch the transistors rapidly on and off. The delay in the signal speed through the circuit wiring, due to increased resistance and/or capacitance caused by EPE, is known as RC-delay. The RC-delay has become the main bottleneck in further downscaling, and therefore mitigation of the effects caused by EPE has become essential for the semiconductor industry.

To mitigate these effects, the fabrication of fully self aligned vias (FSAV) is currently investigated in the semiconductor industry [47]. FSAV can be considered as an extension of the self aligned via scheme (SAV), which is discussed in [45]. In the FSAV, a recess etch of the metal lines is applied prior to the VIA fabrication, resulting in the topography illustrated in the first image of Figure 1.11b. To achieve that, a H\(_2\)O\(_2\) solution is first employed to oxidize the metal, which is subsequently removed with an HF-based solution [16], thereby forming trenches approximately 10 nm deep. This topography provides an additional spacing between the VIA and the neighboring metal line, even when the VIA is patterned with the same EPE, as illustrated in the right-most image of Figure 1.11b. The increased spacing can result in a lower parasitic capacitance, compared to the case in Figure 1.11a, and therefore mitigate the RC-delay. Moreover, this scheme allows for patterning of vias with larger dimensions, which can increase the contact area between VIA and the underlying metal line. Thus, EM reliability can be improved and a decrease in contact resistance (R) can be achieved. However, wet etching (i.e. etching by utilizing solutions) does not provide high reproducibility and accurate thickness control. Moreover, it results in increased metal roughness due to increased etch rate at grain boundaries [48].

A similar topology can be fabricated by using area-selective ALD, as depicted in Figure 1.11c. An area-selective deposition of a dielectric barrier on the dielectric line can be utilized to increase spacing between the VIA and the neighboring metal line, and thereby mitigate the effects of EPE. In this case, ALD allows for excellent control over the dielectric barrier thickness, and at the same time, metal roughening can be avoided.

As mentioned earlier, minimizing the RC-delay is pivotal for the fabrication of efficient ICs, and therefore the choice of material for the dielectric-on-dielectric area-selective ALD process is essential. A SiO\(_2\) layer is considered as promising candidate [49], since its low dielectric constant (k\(_{\text{SiO}_2}\sim4\) [49]), results in small capacitance, and therefore it has only a small contribution to the RC-delay. However, SiO\(_2\) is easily removed by the subsequent etching steps applied during the VIA fabrication [16]. Partial removal of the SiO\(_2\) film would result in a thinner dielectric barrier layer, and therefore smaller spacing between VIA and the neighboring metal line. In contrast, an Al\(_2\)O\(_3\) layer is chemically more resistant against the etch steps, and it will not be removed. However, due to its high-k value (k\(_{\text{Al}_2\text{O}_3}\sim8-9\) [49]), it could also significantly contribute to the RC-delay [49].

A combined solution to this complication could be provided by the scheme given in Figure 1.12. A SiO\(_2\)

\(^{1}\)As current flows through a conductor, the metal anions are exposed to two opposing forces. The first is the electrostatic force caused by the electric field in the metallic interconnect, while the second is caused by momentum transfer during electron-ion collisions. The latter is typically dominant and results in inhomogeneous material transport in the direction of the electron motion. This causes atom accumulation and/or accumulating vacancies in the conductor and can lead to failure of electronic devices. EPEs can enhance this effect, since they result in reduced contact area between the VIA and the underlying metal line. This increases the current density passing through the VIA, thereby enhancing EM and reducing the device reliability.
Figure 1.11: (a) Schematic representation of the BEOL, consisting of patterned metal lines (yellow) and horizontal dielectric lines (blue). Fabrication of the interconnect was performed with the self aligned via (SAV) scheme, which is discussed in [45]. Alignment issues during the interconnect fabrication resulted in an EPE. (b) FSAV scheme with recess etch. Etching of the metal lines prior to the VIA fabrication allowed for increased distance between the VIA and the neighboring metal line. This can reduce the effects caused by EPE, but results in increased roughness on the metal surface. (c) FSAV scheme based on area-selective ALD. Selective deposition of dielectric-on-dielectric prior to the VIA fabrication can also mitigate the effects on EPE, without roughening the metal [47].

dielectric barrier could be selectively grown on the dielectric line, thereby increasing the spacing between the VIA and the neighboring metal line. Next, an Al$_2$O$_3$ layer is deposited with area-selective ALD on SiO$_2$, to protect the underlying SiO$_2$ from the subsequent etching steps during the VIA fabrication. The accurate thickness control provided by ALD allows for deposition of a very thin Al$_2$O$_3$ layer (~3 nm), thereby avoiding significant contributions to RC-delay [16].

Figure 1.12: Combined solution for mitigation of the EPE effects. The spacing between the fabricated VIA and the adjacent metal line is increased by an area-selective deposition of a SiO$_2$ barrier. The latter is protected by a thin Al$_2$O$_3$ etch-stop layer [47].
1.7 Research questions

The primary goal of this project was to develop an Al\textsubscript{2}O\textsubscript{3} area-selective ALD process by utilizing small inhibitor molecules to block deposition on a metal non-growth area. As discussed in the previous section, area-selective deposition of dielectric-on-dielectric, while considering a metal surface (e.g. Co) as the non-growth area can mitigate the EPE effects, thereby improving device performance and reliability. To achieve deposition with high selectivity, the following research goals/questions were set.

The first goal was to identify the parameters that can influence selectivity and optimize them to obtain a more effective process. To achieve that, the effect of dose and purge times of the inhibitor, precursor and co-reactant on precursor blocking was investigated with \textit{in-situ} spectroscopic ellipsometry (SE). The optimized processes that resulted from this analysis were subsequently utilized in studies focused on the application of area-selective ALD.

Moreover, the effect of substrate temperature on precursor blocking was researched in detail. \textit{Ex-situ} SE was employed to study the GPC as a function of temperature, in order to identify a temperature region where precursor blocking is enhanced. Deeper understanding of the temperature effect was obtained by \textit{in-situ} Fourier Transform Infrared Spectroscopy (FTIR) measurements. In these experiments the inhibitor adsorption mechanisms and the precursor interaction with substrates with and without inhibitor were studied at various temperatures.

To further improve area-selective ALD of Al\textsubscript{2}O\textsubscript{3}, investigation of alternative Al precursors (TMA, DMAI and TDMAA) and inhibitors (Hacac, aniline) was performed. Particularly, \textit{in-situ} FTIR experiments were carried out to gain more insight into the fundamental interactions between the different inhibitors and substrates with and without inhibitor. Furthermore, the Al precursors were compared in terms of the nucleation delay measured with X-ray photoelectron spectroscopy (XPS) on CoO\textsubscript{x} samples, and with \textit{in-situ} SE on HfO\textsubscript{x} samples. XPS and \textit{in-situ} SE measurements were also performed to compare the two inhibitor candidates. The goal in these experiments was not only to compare the inhibitors’ performance towards a single Al precursor, but also to investigate different precursor-inhibitor combinations. This could provide additional insight into the effect of inhibitor/precursor choice and potentially lead to improved selectivity.

To conclude, the sub-topics discussed above are summarized by the following research questions:

1. Which parameters can influence the selectivity of Al\textsubscript{2}O\textsubscript{3} area-selective ALD?
2. How does the substrate temperature affect the Al\textsubscript{2}O\textsubscript{3} area-selective ALD process?
3. How is the selectivity affected by the inhibitor/precursor choice?
2 Experimental details

In this chapter, experimental details on the ALD reactors, and the diagnostics used for substrate characterization are given. Moreover, the adopted dosing strategies are discussed.

2.1 ALD setups

The investigation of Al₂O₃ area-selective ALD was carried out in two temporal ALD reactors located at TU/e, and a spatial atmospheric-pressure ALD at TNO-Holst Centre. The first temporal ALD reactor is an Oxford Instruments FlexAL reactor, equipped with in-situ spectroscopic ellipsometry (SE) for thickness measurements. Moreover, a home-built temporal ALD reactor was employed, known as ALD-I, where in-situ Fourier Transform Infrared Spectroscopy (FTIR) was used to study surface reactions that take place during area-selective ALD and quantify surface species. Lastly, a lab-scale rotary spatial ALD reactor was utilized for fast depositions under atmospheric pressure.

2.1.1 FlexAL reactor

Figure 2.1 shows a schematic of the Oxford Instruments FlexAL reactor. It consists of a 10 liter main chamber with a substrate table, a vacuum pump providing low pressure during deposition (10⁻⁶ mbar), an inductively coupled plasma (ICP) source with plasma power up to 600 W and various precursor inlets. Gasses such as Ar, N₂, H₂, O₂, NH₃, SF₆, can be dosed from the inlet located on top of the ICP source. The precursors are kept in bubblers and they are dosed in gas phase (vapor drawn) from separated precursor lines. The bubblers can be independently heated to increase the vapor pressure, and Ar can be employed as carrier gas to increase the precursor flow in the chamber. Moreover, substrate heating is available within the range of 25 °C - 400 °C. Lastly, precise thickness monitoring is enabled by in-situ SE (J.A. Woollam M2000D ellipsometer) with a photon energy range of 1.3-5 eV.

Experimental details regarding the chemicals investigated in this project are summarized in Table I. The dose times listed in the table correspond to the total exposure time in one cycle. Due to the relatively low vapor pressure in the case of dimethylaluminumisopropoxide (DMAI), the corresponding bubbler was heated to 60 °C to increase DMAI vapor pressure. The delivery lines were always kept at equal or higher temperature compared to the bubbler temperature in order to avoid precursor condensation in the lines. For Hacac (inhibitor), three doses of 5 s were applied in each cycle. These doses were separated with a reaction step, where the dosed gas was trapped in the chamber to react with the substrate surface. Lastly, for aniline (inhibitor) three doses of 500 ms each were employed in every cycle and for H₂O three doses of 100 ms each. The same reaction step of 1 s in between the three doses was used for aniline and H₂O as well.

The experiments in this setup were all performed at 250 °C and therefore sample heating was required, which was done with a 15 minute heating step applied prior to the beginning of each experiment. During sample heating, a mixed gas of O₂ and Ar was introduced in the chamber to facilitate the heating process. Next, the sample was exposed to O₂ plasma (100 sccm O₂ at 400 W plasma power) for 5 minutes, to remove any contamination from the substrate surface (e.g. adventitious carbon). Particularly for the Co
Table I: Experimental details of employed inhibitors, precursors and co-reactants (RT = room temperature).

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Bubbler temperature (°C)</th>
<th>Vapour pressure (Torr)</th>
<th>Dose time (ms)</th>
<th>Line temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylaluminum (TMA)</td>
<td>RT</td>
<td>12.2 (at RT)</td>
<td>40</td>
<td>RT</td>
</tr>
<tr>
<td>Dimethyl aluminum isopropoxide (DMAI)</td>
<td>60</td>
<td>9 (at 66 °C)</td>
<td>400</td>
<td>60</td>
</tr>
<tr>
<td>Acetylacetone (Hacac)</td>
<td>RT</td>
<td>0.98 (at 20 °C)</td>
<td>3x500</td>
<td>80</td>
</tr>
<tr>
<td>Aniline</td>
<td>80</td>
<td>20 (at 80 °C)</td>
<td>3x100</td>
<td>100</td>
</tr>
<tr>
<td>Water</td>
<td>RT</td>
<td>23.8 (at RT)</td>
<td>3x100</td>
<td>40</td>
</tr>
</tbody>
</table>

samples, this means that the substrate is oxidized, and therefore the experiment is performed on a CoOₓ surface. In the experiments with aniline, the O₂ plasma was substituted with a H₂ plasma (100 sccm O₂ at 400 W plasma power), to reduce the CoOₓ surface.

2.1.2 ALD-I reactor

A schematic for the ALD-I reactor is depicted in Figure 2.2. It is a home-built ALD setup that functions similarly to FlexAL, which means that it is also a temporal ALD reactor, equipped with a turbo pump and an ICP source. ALD-I offers the possibility of *in-situ* Fourier transform infrared spectroscopy (FTIR), which enables qualitative and quantitative monitoring of surface reactions during ALD (see more details in section 2.3). Similarly to the FlexAL experiments, the inhibitor, precursors and co-reactants were vapor-drawn from the corresponding bubbler and introduced into the reactor through the precursor deliver lines. The bubbler settings shown in Table I were used also in this case. During dosing, the lines between the chamber and the ICP, FTIR and pump were kept closed in order to protect these areas from precursor exposure and also to prevent any unnecessary precursor loss.

![Figure 2.2: Schematic representation of the ALD-I setup, equipped with a turbo pump, an ICP source, as well as an *in-situ* FTIR apparatus. The light beam passes through the sample, and the transmitted signal is guided to the detector.](image)

The accuracy of FTIR measurements depends on the signal-to-noise ratio. This can be maximized by employing a powder as the substrate, instead of a planar wafer, since the available surface area for adsorption is much larger in the former case. In this way, more species adsorb on the surface, thereby resulting in a more pronounced absorbance signal. The powder samples were prepared by pellet-pressing non-porous AEROSIL OX 50 SiO₂ powder into a tungsten mesh (Alfa Aesar, woven from a 0.05 mm diameter wire with a 0.2 mm opening width). Sample heating was enabled by passing an electrical current through the tungsten mesh, while the temperature was monitored by a thermocouple, which was welded onto the sample. Lastly, it is important to mention that all FTIR experiments were performed having Al₂O₃ surface as a starting surface and Hacac as inhibitor. Based on earlier studies, Hacac demonstrates good adsorption on Al₂O₃, and therefore this surface was ideal for investigation of the fundamental interactions between the inhibitor and precursor. To obtain an Al₂O₃ powder, the SiO₂ powder was coated using 30 cycles of the thermal Al₂O₃ ALD process prior to the start of each experiment.

2.1.3 Spatial ALD reactor

For the experiments conducted at atmospheric pressure, a rotary spatial ALD reactor was employed, as illustrated in Figure 2.3. It consists of a reactor head and a rotating substrate table, which are placed in
an oven for temperature uniformity and stability. Different gas inlets (inhibitor, metal-organic precursor, plasma or H$_2$O) are installed in the injector head, as shown in Figure 2.3b. The plasma is provided by an atmospheric pressure dielectric-barrier-discharge (DBD), operating at voltage of 105 V and a pulsed frequency of 56 kHz. The inlets (or dosing zones) are separated by gas bearing regions, which allow for a small and controllable distance between the reactor and the substrate, in the order of 20-100 micrometers [21]. Moreover, the gas bearings completely isolate the dosing zones from the environment and also confine the dosed gasses and reaction products within the corresponding dosing zones. In this way, parasitic chemical vapor deposition can be avoided and at the same time, the time consuming purge steps can be omitted. Lastly, it should be noted that the spatial ALD apparatus is not equipped with in-situ SE, and therefore thickness measurements were performed ex-situ. A HORIBA UVISEL 2 spectroscopic ellipsometer was employed, which has a spectral range of 0.6-6.5 eV [56].

![Figure 2.3](image_url)

Figure 2.3: (a) Schematic drawing of the rotary spatial ALD reactor. It consists of the substrate table and the reactor gas injection head, where a plasma slit and different precursor inlets are installed. The reactor is placed in an oven that provides temperature uniformity and stability. Deposition takes place by rotating the substrate underneath the reactor head, thereby exposing it sequentially to the different gasses. (b) Schematic bottom view of the reactor head, consisting of the gas inlets, surrounded by exhaust zones. High N$_2$ flow is applied around the exhaust zones, and therefore all precursor gases and reaction products are confined within these dosing areas [57].

The substrate has a diameter of 150 mm and is placed on the substrate table, which rotates below the head with rotational frequency up to 600 rotations per minute (rpm) [21]. During each rotation, the sample is exposed sequentially to all components of an ALD recipe, and therefore a full rotation corresponds to one ALD cycle. The tangential speed is proportional to the radial position, and therefore it is higher further away from the wafer center. Due to the rectangular shape of the inlets, this results in shorter exposure time at higher radii. Moreover, the exposure time is coupled for all compounds, since the rotational speed is fixed during the process. Nevertheless, the dose of each compound, defined as the product of gas pressure and exposure time, can be accurately controlled by changing the corresponding gas pressure with mass flow controllers. In this way, the dose is sufficient for saturation for all compounds at all radii.

This precise control over the exposure time and gas pressure allows for excellent recipe optimization, since the GPC can be easily studied as a function of the inhibitor, precursor and co-reactant dose. Particularly the pressure control enables the investigation of precursor blocking at different inhibitor and precursor pressures, which was challenging in the temporal ALD setups. In this project, the impact of the parameters given in Table II on GPC was investigated in the spatial ALD reactor.

Table II: Studied parameters with spatial ALD experiments, and their investigation range.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Bubbler temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylaluminium (TMA)</td>
<td>10-75 sccm</td>
<td>RT</td>
</tr>
<tr>
<td>Acetylacetone (Hacac)</td>
<td>100-500 sccm</td>
<td>RT-55</td>
</tr>
<tr>
<td>Water</td>
<td>500 sccm</td>
<td>RT</td>
</tr>
<tr>
<td>Rotation speed</td>
<td>10-60 rpm</td>
<td>-</td>
</tr>
<tr>
<td>Reactor temperature</td>
<td>100-250 °C</td>
<td>-</td>
</tr>
</tbody>
</table>
2.2 Dosing strategies in ALD

The primary inhibitor requirement is selective adsorption on the non-growth area, which allows for material deposition solely on the growth area. If that requirement is met, after some cycles the patterned surface will consist of the non-growth area and the deposited layer (i.e. the non-growth area is covered). An additional requirement would be that inhibitor adsorption does not take place on the deposited layer. In this section, the dosing strategies enabled by an inhibitor meeting either the former, or both requirements are discussed.

If both requirements are met, the inhibitor can be applied in every cycle, since it adsorbs only on the non-growth area and it hinders material deposition exclusively on that surface. Inhibitor application in each cycle is done with the ABC-type type cycles, where step A, step B and step C correspond to the inhibitor, precursor and co-reactant respectively, as shown in Figure 2.4a. This strategy enables the use of plasmas as co-reactants, since the inhibitor molecules removed by the plasma exposure are restored in the next cycle \[5, 8\]. In this project, both plasma and thermal ABC-type cycles were used, where \(\text{O}_2\) plasma and \(\text{H}_2\text{O}\) doses were employed respectively, during the C step.

However, for some inhibitors only the first requirement is met. For instance, although Hacac shows selective adsorption on the non-growth area (\(\text{CoO}_x\)) and not on the growth-area (\(\text{SiO}_2\)) \[8\] (illustrated in Figure 2.5a), it has also been reported that it readily adsorbs on \(\text{Al}_2\text{O}_3\) surfaces \[8\]. Since \(\text{Al}_2\text{O}_3\) is the material that was deposited in this project, \(\text{Al}_2\text{O}_3\) area-selective deposition on \(\text{SiO}_2\) results in a patterned area consisting of \(\text{CoO}_x\) and \(\text{Al}_2\text{O}_3\) after a couple of cycles, instead of \(\text{CoO}_x\) and \(\text{SiO}_2\). At this point, an Hacac dose will result in inhibitor adsorption on both \(\text{CoO}_x\) and \(\text{Al}_2\text{O}_3\), as illustrated in Figure 2.5b, which will significantly hinder film deposition on the growth-area. To address this, a dosing strategy illustrated in Figure 2.4b was adopted for the experiments focused on nucleation delay measurements. A saturated Hacac dose was applied at the beginning of the recipe (step A), followed by consecutive BC-type cycles, where B and C correspond to the Al precursor and \(\text{H}_2\text{O}\) respectively. Water was preferred instead of \(\text{O}_2\) plasma in this case, since plasma would result in inhibitor removal after the completion of the first BC cycle. This dosing strategy is referred as A+BC type cycles in the following chapters. In this project, either the ABC or A+BC type cycles were employed, depending on the goal of each experiment. The process used in each particular case is discussed in the results sections.

Figure 2.4: Schematic of the adopted dosing strategies. (a) ABC-type cycles with A, B, C corresponding to inhibitor, Al precursor and \(\text{O}_2\) plasma dosing respectively. The inhibitor must be applied in each cycle, since \(\text{O}_2\) plasma can remove it. (b) Thermal process, where the non-growth area is covered with a saturated dose of the inhibitor, followed by consecutive BC cycles.

Figure 2.5: Schematic illustration of (a) Hacac adsorption on \(\text{CoO}_x\) (non-growth area) and not on \(\text{SiO}_2\) (growth area). (b) Hacac adsorption on both \(\text{CoO}_x\) and \(\text{Al}_2\text{O}_3\) (deposited layer). Color code: Si atoms or \(\text{SiO}_2\) surface, grey; O atoms, brown; H atoms, white; \(\text{CoO}_x\) surface, blue; Hacac molecules, orange; Al atoms or \(\text{Al}_2\text{O}_3\) surface, green.
2.3 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a widely used technique to probe the chemical bonds in materials (gas, liquid, and solid) by using an infrared light (IR) beam. The IR region of the electromagnetic spectrum is specifically selected, since it energetically matches the transitions between the molecular vibrational or rotational energy states.

A typical FTIR spectrometer is depicted in Figure 2.6. It consists of an IR light source, Michelson interferometer, sample chamber, detector, amplifier and computer. The generated light enters the interferometer (Bruker Optics Vector 22), where it is split into two parts by the beam splitter. One part is transmitted through the beam splitter to the fixed mirror, while the second is reflected, and guided to the moving mirror. Subsequently, both parts are reflected back to the beam splitter, where they recombine resulting in an interference pattern due to the difference in optical paths introduced by the moving mirror. In this way, spectral information of all wavelengths can be acquired at the same time, thereby making FTIR measurements very time efficient. Afterwards, part of the recombined beam transmits through the pressed powder and reaches the detector, which is a liquid-nitrogen cooled Mercury Cadmium Telluride (MCT) detector (Bruker D316, 10000-550 cm\(^{-1}\)). There, the signal is amplified and converted to digital signal (interferogram). Finally, the Fourier transform algorithm is applied to the interferogram, translating it to the corresponding spectrum.

![Figure 2.6: Schematic of a typical FTIR setup](image)

To study the surface interactions and the adsorbed species on the pressed powder during one dosing step, the transmission spectra before and after the dose are required. The measurement before the dose is considered as the background measurement, and it is labelled here as \(l_A\), while the measurement after is labelled as \(l_B\). Typically, an FTIR spectrum shows the absorbance \((A)\) as a function of the corresponding wavenumber \((\text{cm}^{-1})\), where:

\[
A = - \log \left( \frac{l_B}{l_A} \right)
\]  

(2.1)

According to equation 2.1, any positive peaks in the spectrum correspond to species added on the surface after the dose, whereas negative peaks correspond to consumed or removed species. In contrast, persisting surface groups are not shown in the calculated spectrum, since \(l_A\) and \(l_B\) are equal in this part of the spectrum and cancel out. In this way, information about the adsorbed and removed species can be extracted, while the rest is filtered out. As an example, the FTIR spectrum of TMA adsorbed on \(\text{Al}_2\text{O}_3\) coated powder is given in Figure 2.7. The positive peaks in the region of 2800-3000 cm\(^{-1}\) correspond to symmetric and asymmetric C-H stretches of a methyl group \((\text{CH}_3)\) and therefore indicate TMA adsorption on the powder [59, 60, 61]. On the other hand, the negative peaks around 3050-3800 cm\(^{-1}\) suggest consumption of OH groups [62, 63, 64, 65]. The reaction of TMA with OH groups on alumina surfaces is consistent with the reaction mechanism discussed in equation 1.1.

In this project, the saturated doses of the inhibitor (Hacac) and the Al precursors were studied with FTIR. The dose required for saturation depends on the molecule used and the powder sample employed in each particular case. The use of large amounts of powder can provide more surface sites available for precursor/inhibitor adsorption, and therefore a larger dose is required for saturation. Moreover, the samples were prepared by pellet-pressing the powder into a mesh, which does not allow for accurate control
of the powder dimensions and aspect ratio. Therefore, even samples that are prepared with the exact same amount of powder would not have the same amount of available surface sites. As a result, the doses required for saturation were not known for the FTIR experiments. This complication was encountered by the following procedure: First, a background measurement was taken, which corresponds to \( l_A \) in equation 2.1. Then, small doses (pulses) of the molecule under investigation were applied, with an FTIR measurement in between \( (l_{B1}, l_{B2}, \ldots, l_{BN}) \). By plotting all measurements with respect to the background, accurate monitoring of the positive/negative peaks was enabled. The surface was considered saturated when dosing had no impact on the surface (i.e. the measurement \( l_{B(N-1)} \) was found (approximately) the same with \( l_{BN} \)). To conclude, it should be noted that the FTIR spectra discussed later in the results were plotted by using the last FTIR measurement \( (l_{BN}) \), the background \( (l_A) \), and equation 2.1, unless stated otherwise.

![Figure 2.7: FTIR signal of TMA adsorbed on Al_2O_3 surface.](image)

2.4 Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) is an optical measurement technique, where the change in the polarization state of incident light upon reflection from a substrate surface is measured, to determine the film thickness and optical properties. It is a fast and non-destructive technique, which can easily be employed for in-situ measurements, and therefore it is a versatile tool for studying area-selective ALD [8, 15, 66, 67].

2.4.1 Principle of spectroscopic ellipsometry

As shown in Figure 2.8, the incident light during an SE measurement consists of the \( s \) and the \( p \) components. The former is polarized perpendicular to the plane of incidence, while the latter is polarized parallel. Ellipsometry measures the complex reflectance ratio \( \rho \), which is parameterized with the amplitude component \( \psi \) and the phase difference \( \Delta \) as follows:

\[
\rho = \tan \psi \exp i\Delta = \frac{r_p}{r_s}
\]  

(2.2)

where \( r_p \) and \( r_s \) are defined by the ratios of reflected electric fields to incident electric fields, hence \( r_p = E_{rp}/E_{ip} \) and \( r_s = E_{rs}/E_{is} \) [68]. Thus, \( \tan \psi \) corresponds to the amplitude ratio upon reflection, while \( \Delta \) is the phase shift. By measuring \( \psi \) and \( \Delta \) over a range of wavelengths and fitting them with an optical model, the film thickness, roughness and optical constants can be extracted. More details on the models employed in this project are discussed in the following section.

2.4.2 Ellipsometry modeling

In SE, the thin film thickness and/or optical properties are not provided directly by the measurement. Instead, an optical model is required to fit \( \psi \) and \( \Delta \), in order to determine these film properties.

A simple approach is to describe the sample as a stack of several layers with different optical properties. Then, various models such as Cauchy, Tauc-Lorentz, B-Spline and others [68] can be employed to convert
the measured $\psi$ and $\Delta$ into the thickness of film under investigation. The simplest case used in this project is schematically shown in Figure 2.9a, where $\text{Al}_2\text{O}_3$ was grown on a SiO$_2$ surface (growth-area). The model includes a crystalline silicon substrate (c-Si), with a native oxide, which is a well-studied case [69, 70] and therefore modelled easily. The native oxide thickness was fixed at 1 nm for all models and fits. On top of that, the $\text{Al}_2\text{O}_3$ layer under investigation is added. $\text{Al}_2\text{O}_3$ has a band gap higher than the energy range of our measurements [71] and therefore it can be considered transparent within this range. Thus, the $\text{Al}_2\text{O}_3$ layer can be described by a Cauchy model [72], which describes the refractive index ($n$) of transparent materials as follows:

$$n(\lambda) = B + \frac{C}{\lambda^2} + \frac{D}{\lambda^4}$$

where $\lambda$ is the wavelength, and B, C, and D are the coefficients determined by the fitting. During the fitting process, which is explained in more detail below, only parameter B was allowed to vary since C and D had almost no impact on the fit.

For the experiments focused on the application of area-selective ALD, the growth of $\text{Al}_2\text{O}_3$ film on Hacac-functionalized CoO$_x$ samples had to be monitored. However, modelling of a CoO$_x$ surface is in general considered a challenging task. Thus, a HfO$_2$ layer was employed as non-growth area for the SE measurements, since area-selective ALD of SiO$_2$ with Hacac as inhibitor has been demonstrated on that substrate [7]. This indicates that Hacac is able to adsorb on HfO$_2$ and demonstrate efficient precursor blocking. The HfO$_2$ layer was deposited with 200 thermal ALD cycles on a c-Si layer at 250 °C. Typically, HfO$_2$ can be accurately described by either Tauc-Lorentz [73], or Cody-Lorentz [74] oscillators. In our case, both approaches resulted in the same layer thickness. The former case was employed, since this concerns a simpler model with a lower number of parameters involved. On top of this layer, the $\text{Al}_2\text{O}_3$ Cauchy layer was placed, as illustrated in Figure 2.9b.

For the experiments focused on more fundamental studies and recipe optimization, $\text{Al}_2\text{O}_3$ was employed as substrate. The Hacac inhibitor has shown good adsorption on the $\text{Al}_2\text{O}_3$ surface [7], and therefore the use of this substrate was a fast and effective way to investigate the effect of different parameters on the selectivity. The sample was prepared by performing 300 $\text{Al}_2\text{O}_3$ plasma ALD cycles at 200 °C on a c-Si wafer. Since the $\text{Al}_2\text{O}_3$ substrate and the $\text{Al}_2\text{O}_3$ deposited layer are fabricated by using different processes (i.e. grown by plasma/thermal processing, on different substrates and at different temperatures), their optical parameters should not be assumed as being identical. Thus, two separate $\text{Al}_2\text{O}_3$ Cauchy layers
were introduced in the SE modelling, as depicted in Figure 2.9c, corresponding to the Al₂O₃ substrate (red) and the Al₂O₃ layer under investigation (green), respectively. To explain the fitting process in more detail, the experimental process and the fitting steps are given in Figure 2.10. In the fitting process the substrate is always characterized at first, followed by fitting of the material on top. To determine the parameters of the substrate layer (B₁ and d₁ in Figure 2.9c), the SE measurement taken prior to the experiment was utilized. Once found, these parameters were kept fixed throughout the rest of the fitting process. Then, the material on top was characterized. For that, the Cauchy parameter of that layer (B₂) should be determined at first, which was enabled by fitting the SE measurement taken after the last ALD cycle. Once found, B₂ was kept fixed throughout the remaining of the fitting process. Lastly, all the measurements taken between the ALD cycles were fitted. This provided the thickness of the material on top as a function of the number of ALD cycles. During the fitting of these measurements, the thickness of the material on top (d₂) was the only parameter allowed to vary.

<table>
<thead>
<tr>
<th>a) Experimental process</th>
<th>Take first SE measurement B₁, d₁</th>
<th>ALD cycle</th>
<th>Take SE measurements in between d₂</th>
<th>Take last SE measurement B₂, d₂(last)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b) Fitting process</td>
<td>Fit first SE measurement B₁, d₁</td>
<td></td>
<td>Fit SE measurements in between d₂</td>
<td>Fit SE measurements in between d₂</td>
</tr>
</tbody>
</table>

Figure 2.10: (a) Experimental process consisting of Al₂O₃ ALD and in-situ SE measurements. The parameters measured with SE during each step of the process are indicated in the corresponding box. B₁ and d₁ correspond to the Cauchy parameter and thickness of the Al₂O₃ substrate layer, while B₂ and d₂ to the Cauchy parameter and thickness of the deposited Al₂O₃ layer. (b) Fitting process employed for the in-situ SE measurements with Al₂O₃ as substrate. The parameters determined in each fitting step are indicated in the corresponding box.

2.5 XPS

X-ray photoelectron spectroscopy (XPS) is based on the photoelectric effect, where electrons are emitted from a surface due to radiation. XPS engages in the study of core electrons, by using incident irradiation with energy in the X-ray region [75] (Figure 2.11). The energy required to extract the core electrons (i.e. the binding energy) is unique for each element, and therefore it corresponds to the element’s characteristic fingerprint in an XPS spectrum. Thus, XPS allows for elemental identification and determination of the sample chemical composition.

![Figure 2.11: Principle of X-ray photoelectron spectroscopy. The X-rays impinging on the surface, result in photo-ejected electrons [76].](image)

A schematic illustration of an XPS setup is given in Figure 2.12. X-rays are generated by pointing an electron gun to a metal anode [77]. From the emitted spectrum, only a narrow band is selected by the monochromator and it is guided to the sample. Then, the kinetic energy of the emitted photoelectrons can be measured by an electron energy analyzer. The kinetic energy can be translated into the binding
energy according to the following formula:

\[ E_B = h\nu - \phi - E_K \]  \hspace{1cm} (2.4)

where \( E_B \) is the electron binding energy, \( h\nu \) the impinging photon energy, \( \phi \) the spectrometer’s work function, and \( E_K \) the measured electron kinetic energy.

Figure 2.12: Schematic of an XPS system. It consists of an X-ray source, monochromator, substrate table, and a hemispherical analyzer [78]. The apparatus is placed under UHV \((10^{-8}\text{mbar})\), to minimize contributions from molecules being present in the atmosphere.

By using equation 2.4, the measured kinetic energy can be accurately assigned to specific binding energies, thereby allowing for the construction of an XPS spectrum. A typical example of an XPS spectrum is given in Figure 2.13. The examined sample was a CoO\(_x\) substrate on which Al\(_2\)O\(_3\) deposition was applied. The binding energy is unique for each element, and therefore electron counts in each region declare the presence of a different element on the sample. In this case, the presence of Co, Al, O and C can be deduced from the corresponding peaks. The last two are commonly detected elements, since the samples are exposed to atmosphere during the transition from the reactor to the XPS setup. XPS also provides the opportunity to perform narrow scans of specific spectra regions, thereby allowing for more accurate analysis and quantification of the elements present on the sample.

Figure 2.13: Example of a typical XPS spectrum. The electron counts/s are plotted as a function of the binding energy, by using equation 2.4. The presence of cobalt, oxygen, carbon and aluminium on the sample can be deduced, from the detection of the corresponding peaks.
3 Inhibitors and precursors: Theory and requirements

During this project, different inhibitors and precursors were explored to identify how selectivity can be affected by the use of alternative compounds and to find the best inhibitor-precursor combination that can further improve the Al₂O₃ area-selective ALD process. In this chapter, the inhibitors and precursors employed are presented, along with the general aspects that these compounds should demonstrate.

3.1 Inhibitors

3.1.1 Inhibitor requirements

As discussed in section 1.5, in this work small organic molecules are utilized as inhibitors to achieve area-selective deposition. The selection of a suitable organic compound is based on some general requirements. These are listed here and discussed below in more detail.

(a) Selective adsorption on the non-growth area

(b) Efficient precursor blocking

(c) Thermal stability within the ALD temperature window

One of the most essential requirements is that the inhibitor should selectively adsorb on the non-growth area. In the SAMs case, this has been achieved by selecting a head group that can readily react with the non-growth area [34, 79]. In some cases, the selective adsorption can be predicted by studying the acidities of the starting surface and the inhibitor. In this project, most of the starting surfaces are metal oxides, where acidity can be predicted by the electronegativity of the M cation in the M-OH surface group [80, 81]. Cations with high electronegativity (e.g. Si) tend to form surface hydroxyl groups that possess a more acidic character, whereas cations with lower electronegativity (e.g. Al) form more basic M-OH groups. Thus, an acidic inhibitor, such as Hacac, would preferably react with an alkaline rather than an acidic surface and the opposite holds for an alkaline inhibitor. This chemoselective behaviour can be investigated with density functional theory (DFT) studies, by which the different energy paths for inhibitor adsorption on various surfaces can be calculated [8]. As will be discussed in section 3.1.2, DFT studies can also provide information on how strongly the inhibitor bonds on the surface, which provides insight into the possible mechanisms affecting an area-selective ALD process.

Apart from selective adsorption, the inhibitor should demonstrate the ability to block precursor adsorption. To achieve this, first and foremost, reactions between the inhibitor and the precursor should not take place. Promising candidates would be molecules that exhibit high stability, such as aromatics [82], and molecules that have functional groups where precursor adsorption does not take place. For instance, earlier studies have shown that TMA does not react with CH₃ groups [11, 34], and therefore formation of a CH₃-terminated surface could possibly result in effective blocking. In case inhibitor-precursor reactions do not occur, the key for effective blocking would be to prevent reactions between the precursor and surface sites on the non-growth area. This could be achieved through various ways, such as selection of an inhibitor that reacts with the same surface groups as the precursor. In such case, the sites facilitating ALD on the non-growth area are consumed by the inhibitor and consequently they are not available for precursor adsorption. For instance, TMA reacts with hydroxyl groups during adsorption [12], hence an inhibitor that reacts with these groups could be a promising candidate. Alternatively, the precursor could adsorb on different surface sites, but block precursor adsorption by steric hindrance. In fact, a combination of these effects could also take place, meaning that some of the groups that facilitate precursor adsorption are consumed by the inhibitor, while the remaining sites are blocked by steric hindrance. Therefore, it is essential to maximize the inhibitor coverage, since more surface sites on the non-growth area would be blocked.

Lastly, the temperature region where the inhibitor is thermally stable should match, at least partially, the ALD temperature window (see section 1.2). If that is not the case, significant inhibitor decomposition and desorption can take place during the process. Therefore, the inhibitor coverage will be significantly reduced, which means that precursor adsorption can readily take place on the non-growth, leading to fast loss of selectivity.

3.1.2 Acetylacetone

The first inhibitor examined in this project is acetylacetone, abbreviated as Hacac, which is an organic compound that can be found in two tautomeric forms, as depicted in Figure 3.1. These are the keto and enol forms, which coexist in gas and condensed phase [83]. The enol form consists of a symmetric structure, in which the C=C and C-C bonds, along with the C-O and C=O bonds become equivalent, with
the hydrogen atom equally shared between the two oxygen atoms [84]. Transition from enol to keto form takes place by shifting the hydrogen from the carbonyl oxygen atom to the carbon atom in between the carbonyl groups, and vice versa. Hacac exhibits good volatility even at lower temperatures [85], and it is capable of forming strong bonds with metal atoms, thereby enabling the preparation of metal-acetonates for catalysis applications [86].

Figure 3.1: Molecular structures of gas-phase Hacac in the keto and enol form respectively [83].

Hacac can bond in two different bonding configurations on the surface, namely, monodentate and chelate, which are shown in Figure 3.2. In the former case, Hacac bonds to the Al site with one of its oxygen atoms. DFT calculations were employed in previous work to study Hacac adsorption on Al$_2$O$_3$, as shown in Figure 3.3 [88]. The energy path for Hacac adsorption in the monodentate configuration (yellow point) is slightly exothermic ($\Delta E=0.07$ eV) with a nearly zero kinetic barrier ($E_a=0.01$ eV), which means that the monodentate is weakly bonded on the surface.

Transition to the chelate configuration (blue point) requires surpassing of the 0.25 eV kinetic barrier. In this case, Hacac donates the hydrogen attached to its O atom to the neighboring OH surface group, while H$_2$O is released. The resulting intermediate complex (green point) is not stable, and therefore the molecule immediately converts to the chelate configuration. The Hacac chemisorption from gas phase to chelate is an irreversible exothermic reaction with an energy gain of 0.49 eV, and therefore results in a stronger Hacac bond with the surface, as compared to the monodentate case. Based on an earlier study from our group [87], Hacac adsorbates can be removed upon TMA doses, and e configuration would be preferable, since it would be harder to remove. Moreover, the chelate configuration provides a CH$_3$-terminated surface, where TMA (and possibly DMAI and TDMAA) does not adsorb [88]. As a result, this configuration is expected to demonstrate better blocking, and is therefore preferred. However, FTIR studies of Hacac adsorption on Al$_2$O$_3$-coated powder suggest that a mixture of chelate and monodentate configuration is obtained, with the monodentate signal becoming more noticeable at higher coverage [88, 55]. These findings are in agreement with other surface functionalization studies, where it was also shown that the binding configuration of bifunctional molecules can be affected by surface coverage [88, 90]. To sum up, maximizing the surface coverage with Hacac adsorbates in chelate configuration could have an impact on precursor blocking. This is discussed in more detail in sections 5.2 and 5.3, where the Hacac coverage is investigated as a function of temperature.

Figure 3.2: Schematic illustration of different Hacac binding configurations on Al$_2$O$_3$ surface: (a) monodentate, (b) chelate.

As mentioned in the previous chapters, CoO$_x$/Co, Al$_2$O$_3$ and HfO$_2$ were employed as non-growth areas in this project. Thus, Hacac should demonstrate selective adsorption on these surfaces relative to SiO$_2$ as the growth area. The selective adsorption of Hacac on Al$_2$O$_3$ and not on SiO$_2$ has been already reported in literature [8, 30], and is discussed in more detail below. Moreover, a successful area-selective ALD process has been reported with Hacac as inhibitor and HfO$_2$ as non-growth area, which suggests that Hacac readily adsorbs on that surface as well [8]. Additionally, Hacac has been employed to fabricate Co complexes [91].
Figure 3.3: DFT calculations for Hacac adsorption on an Al₂O₃ surface. The chemisorption energy path starts with the Hacac adsorption as monodentate (yellow), a process which is slightly exothermic (∆E=−0.07 eV). In case the kinetic barrier of 0.25 eV is surpassed, the monodentate adsorbate reacts with the OH surface group and forms an intermediate complex (green). This complex is energetically unfavorable, and therefore converts into the chelate formation (blue) [30].

thereby suggesting that Hacac and Co form strong and stable bonds. These findings suggest that Hacac can meet the requirement for selective adsorption on the non-growth area. However, they also show that this inhibitor adsorbs on the deposited layer (i.e. Al₂O₃). This does not allow the use of O₂ plasma for co-reactant when Hacac is employed as inhibitor, since earlier studies have shown significant Hacac removal during the O₂ plasma exposure [8, 87]. Removal and reapplication of Hacac would hinder Al₂O₃ deposition on the growth area, as explained in section 2.2.

The chemoselective adsorption behaviour of Hacac can be attributed to the difference in surface acidity between the various starting surfaces. Hacac has a pKa of 9.0 at 25 °C, and therefore it behaves as a weak acid [8, 30]. Thus, reactions between Hacac and hydroxyl groups demonstrating acidic character (e.g. OH on a SiO₂ surface) are in general not favorable, while reactions with basic hydroxyl groups readily proceed. The selective Hacac adsorption is supported by DFT simulations [30], where Hacac reaction on SiO₂ surfaces was calculated to be endothermic, requiring of 0.98 eV, accompanied with a high kinetic energy barrier (Eₐ=2.35 eV). In contrast, Hacac chemisorption on hydroxylated Al₂O₃ was found exothermic ∆E=−0.49 eV, with a very low kinetic barrier, as discussed in Figure 3.3. The chemoselective adsorption has been also confirmed by in-situ FTIR measurements of Hacac adsorption on SiO₂, and Al₂O₃ surfaces, depicted in Figure 3.4. The absorption peaks in the wavenumber range 1300-1650 cm⁻¹ suggest that Hacac adsorption is significantly larger on Al₂O₃, compared to SiO₂ [8].

Figure 3.4: In-situ FTIR spectra measured after a saturated dose of Hacac on Al₂O₃ and SiO₂ surfaces. Hacac adsorption is noticeably larger on Al₂O₃, compared to the SiO₂ surface [8].

Hacac is a promising inhibitor candidate, since it has already demonstrated good blocking ability in SiO₂ area-selective ALD [8]. In Figure 3.5, the thickness evolution as a function of the number of ABC-type cycles is given, on Al₂O₃, HfO₂ and SiO₂ substrates, where A, B, C correspond to Hacac, Si precursor (BDEAS), and O₂ plasma doses respectively. Hacac does not adsorb on SiO₂, and therefore SiO₂ ALD readily starts on that substrate. In contrast, Hacac adsorption on HfO₂ and Al₂O₃ resulted in efficient precursor blocking and a nucleation delay of to 10 and 15 ALD cycles, respectively.
Figure 3.5: *In-situ* ellipsometry measurements for ABC-type ALD of SiO$_2$ on different starting surfaces. Film deposition readily starts on a SiO$_2$ surface, while a nucleation delay of approximately 10 and 15 cycles is demonstrated for HfO$_2$ and Al$_2$O$_3$ substrates, respectively [8].

Lastly, Hacac shows solid thermal stability over a wide temperature region, as depicted in Figure 3.6 [92]. In this experiment, the gaseous products released due to Hacac decomposition and desorption from an Al$_2$O$_3$ sample were detected only for temperatures above 250 °C. Thus, a wide temperature region is available (20-250 °C) for the Al$_2$O$_3$ area-selective ALD process. The overlap of the temperature region where Hacac is thermally stable with the ALD window (explained in section 1.2) corresponding to each Al precursor is further discussed in sections 3.2.2-3.2.4.

Figure 3.6: Identified gaseous products originating from Hacac desorption from Al$_2$O$_3$ sample, as a function of temperature. Desorption initiates around 250 °C, and involves release of various products, such as acetone, methane and acetic acid [92].

3.1.3 Aniline

Aromatic molecules have been utilized as metal precursors for metal oxide ALD [93, 94], suggesting that surface functionalization with similar aromatic compounds could prevent further precursor adsorption. Based on this, aniline (also known as phenylamine or aminobenzene) has also been investigated in this work as an alternative inhibitor candidate. Aniline is an organic compound, corresponding to the formula C$_6$H$_5$NH$_2$. It consists of an amine functional group, attached to a phenyl group, as depicted in Figure 3.7. This ring comprises resonant carbon-carbon bonds, where the "extra" electrons (delocalized electrons) strengthen all the bonds in the ring equally. Molecules that demonstrate this structure are labeled as aromatic compounds and generally exhibit very high stability [95].

According to earlier studies [96, 97], aniline can bond to metal surfaces through the amine group or the aromatic ring. The bonding configurations obtained on a Pt(111) surface are depicted in Figure 3.8. The N atom of the amino group can adsorb by forming a N-Pt bond, as depicted in Figure 3.8a and 3.8d.
Figure 3.7: Schematic representation of an aniline molecule. It consists of a phenyl group, where an amine functional group is attached.

The DFT calculations suggested that the adsorption energy is determined by the orientation of the phenyl group with respect to the surface, with the vertical orientation being less favorable. Moreover, aniline can adsorb by forming C-Pt bonds with all six C atoms of the phenyl group, as shown in Figure 3.8b. The Pt-C bonds are formed by overlapping of the d-band of Pt and the p\_z orbitals of the phenyl group [98]. Lastly, in the configuration depicted in Figure 3.8c, the C atom binding to the amine group was dangling above the surface, while the remaining five C atoms formed Pt-C bonds. Interestingly, the same adsorption energy was found for the configurations in Figure 3.8b and 3.8c.

Figure 3.8: Top and side views of the four aniline bonding configurations on a Pt surface, along with the corresponding adsorption energies [98].

Benzene adsorption on Co at low temperatures (25-70 °C) [99, 100] and formation of stable bonds between Co and other aromatic molecules [101] have been reported in earlier investigations. These findings suggest that aniline might sufficiently cover the Co surface (non-growth area) and prevent precursor adsorption. To get further insight into aniline adsorption on Co, Al\_2O\_3 and SiO\_2, in previous studies of our group (focused on area-selective ALD of TiN) \textit{in-situ} SE measurements were conducted when aniline pulses were applied on the aforementioned surfaces [55]. The measured thickness after several pulses of aniline (i.e. apparent thickness) is depicted for all surfaces in Figure 3.9. Aniline demonstrates considerable adsorption on Co, as indicated by the large increase in apparent thickness. Moreover, no change in apparent thickness was observed during the long purge steps, suggesting the formation of strong and stable bonds with the Co surface. In contrast, adsorption was found nearly zero on SiO\_2 and significantly reduced on the Al\_2O\_3 surface. For the latter surface, the apparent thickness showed a decreasing trend during purging, which indicates that aniline might be weakly bonded on Al\_2O\_3 and therefore can be removed with sufficient purging. These findings suggest that aniline can be applied in every cycle in our area-selective ALD process, since the small adsorption on Al\_2O\_3 might not hinder significantly the Al\_2O\_3 deposition on the growth area. As a result, the ABC type cycles were adopted for all the experiments studying the precursor blocking by using aniline as inhibitor.

Lastly, surface science studies investigating the interactions between aniline and metal surfaces at various temperatures can provide valuable information for aniline thermal stability. Aniline has been reported to undergo hydrogenolysis\(^2\) reactions near 80 °C on Ni and Pt surfaces, even for 1 × 10\(^{-5}\) Torr H\_2 flow [102, 103]. The process involves cleavage of the C-N bond and immediate desorption of the N-containing product, while the resulting benzene desorbed from the Ni surface at 200 °C [102]. Moreover, dehydrogenation\(^3\) reactions have been reported for benzene on Co [101] and aniline on Ni and Pt [102, 103]. In the case of benzene, dehydrogenation takes place in the 70-150 °C temperature range and results in C\(_6\)H\(_5\),

\(^{2}\)Hydrogenolysis is a chemical reaction where a carbon–carbon or carbon–heteroatom single bond undergoes breakdown (cleavage) by hydrogen. The heteroatom could be oxygen, nitrogen, sulfur or others.

\(^{3}\)Dehydrogenation is the chemical process where hydrogen atoms are removed from an organic compound.
which remained adsorbed on the surface for temperatures above 280 °C. For aniline, dehydrogenation can take place in a wider temperature range (70-325 °C) and involves hydrogen removal from either the amino or the phenyl group [102]. Interestingly, hydrogen loss up to 200 °C may force the ring to stand up relative to the surface, with the angle between the ring and the surface estimated to be 75° [102, 103]. In contrast, for temperatures in the range of 200-325 °C, further dehydrogenation may induce ring reorientation toward the Ni surface (i.e. lower angle). Additional substrate heating results in decomposition of the partially dehydrogenated aniline-derived species. Moreover, dehydrogenation of the NH2 group has been associated with polymerization of the adsorbed aniline molecules on the Ni surface [103]. Polyaniline is very stable and does not decompose up to 420 °C [104]. To wrap up the discussion on aniline thermal stability, both hydrogenolysis and dehydrogenation might take place to some extend in our process. Competition between these processes depends markedly on the presence/absence of H2 in the reactor, originating from dehydrogenation reactions and/or from persisting molecules being present in the reactor chamber. For pressures lower than 10⁻⁵, the hydrogenolysis process was not observed [102, 103]. These catalytic surface reactions might contribute to better blocking, but further research into this topic would be essential to estimate the extent and impact of these processes on selectivity.

3.2 Precursors

Similarly to the inhibitors, careful consideration was needed for the selection of Al precursors, since these compounds could also have a large impact on selectivity. In this section, the general precursor requirements for area-selective ALD are first examined, followed by a discussion on properties of the compounds employed in this work.

3.2.1 Precursor requirements for area-selective ALD

First and foremost, the Al precursors should readily react with the surface sites of the growth area and result in immediate growth on that surface. The precursor adsorption reaction should be self-limiting, since this enables accurate thickness control. These requirements are examined for all Al precursor candidates and are discussed in detail in the results section.

Moreover, the precursor should be volatile and demonstrate excellent thermal stability over the temperature region where the area-selective ALD process is applied. If that is not the case, low volatility yields small or zero GPC, and decomposition can lead to loss of the self-limiting growth control. These requirements are often tested with thermogravimetric analysis, where a compound’s mass loss is measured as a function of temperature. An example of thermogravimetric analysis corresponding to an ideal and a non-ideal ALD precursor is depicted in Figure 3.10. Furthermore, the ALD temperature window should be located at relatively low temperatures, since high temperature processes could damage components of the IC.

Finally, efficient precursor blocking is not exclusively an inhibitor requirement, since it also depends on the precursor choice itself. Precursors reacting with the inhibitor functional groups can remove the inhibitor or adsorb on it, resulting in fast loss of selectivity. Moreover, small molecules can more readily reach surface sites that are not covered by the inhibitor and react with them, thereby forming sites that facilitate ALD reactions.
Figure 3.10: Thermogravimetric analysis of an ideal and a non-ideal ALD precursor, illustrated by the blue and red curve, respectively. The descending of curves is an indication of weight loss. An ideal precursor should demonstrate high volatility at low temperatures, which is denoted by the sharp decrease taking place at low temperature. No signs of decomposition can be observed, since no mass residual can be observed in the blue curve. In contrast, in the red curve volatilization takes place slowly over a wide temperature range, and it is accompanied with loss of ligands and the large residual mass, which denote compound decomposition [11].

reactions on the non-growth area. For instance, Hacac is very efficient towards bis(diethylamino)silane (BDEAS) blocking [8, 87], but demonstrated poor blocking abilities towards trimethylaluminum (TMA) [87]. This difference was attributed to the high reactivity and small size of TMA, which allowed TMA to adsorb on defects and/or surfaces sites that were not covered by Hacac.

3.2.2 Trimethylaluminum

TMA, which is depicted in Figure 3.11, is one of the simplest cases of organoaluminium compounds. It consists of an Al center atom bonded to three methyl ligands and it can be found in both monomer and dimer form in gas phase [15]. TMA demonstrates a high vapor pressure even at room temperature [105] (see Table III) and results in high quality Al₂O₃ films with either thermal or plasma processes. Thus, it is one of the most frequently employed precursors for the investigation of ALD surface reactions and for deposition of Al₂O₃ films for various applications [15, 39, 65, 106]. Al₂O₃ ALD with TMA has been demonstrated over a wide temperature range (50 °C to 400 °C [15]), and therefore the temperature window for this precursor overlaps with both inhibitors.

However, this precursor might not be ideal for an Al₂O₃ area-selective ALD process. TMA is very reactive towards hydroxylated surfaces, since it reacts with (almost) all OH groups regardless whether they are acidic, neutral or basic [107]. Moreover, its small size allows for physisorption and reaction with surface sites that are not covered by the inhibitor, thereby making it very challenging to block [82, 34]. Lastly, TMA is pyrophoric, which means that it reacts violently with water, and therefore it is not easy to handle. Its pyrophoricity probably arises from the low mean bond energy of the Al-C bonds [108], compared with Al-X (X=N, O) bonds [108]. Al₂O₃ area-selective ALD with TMA as precursor and Hacac as inhibitor

Monomer is a non-repeating structure, while a dimer consists of two monomers attached to each other.
has been already attempted in previous work [87], where it was reported that the inhibitor was not able to fully block TMA. The goal in this project was to study further Al₂O₃ area-selective ALD with TMA, and also investigate TMA blocking with alternative inhibitors.

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<td>Liquid</td>
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<td>&lt;R.T</td>
<td>82-84 °C</td>
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<tr>
<td>Boiling point</td>
<td>125 °C</td>
<td>172 °C</td>
<td>90 °C</td>
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<td>Pyrophoric</td>
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### 3.2.3 Dimethyl-aluminium isoproxide

An alternative Al precursor investigated in this project is dimethyl-aluminium isoproxide (DMAI), shown in Figure 3.12. The Al center is bonded to two methyl ligands and an additional isopropyl ligand, resulting in the chemical form of \([\text{Al}(\text{CH}_3)_2(\mu-\text{O}^{\text{iPr}})_2]\). Al₂O₃ thermal ALD with this precursor has been already demonstrated for a temperature range from 100 °C to 400 °C [15, 110, 111].

![DMAI molecule](image)

**Figure 3.12:** Schematic illustration of the DMAI molecule. The Al center atom is bonded to two methyl and an isopropyl ligands [15].

DMAI forms dimer structures in gas phase, by forming a bond between the O atom of the O^iPr ligand and the Al center of the other molecule [15]. The DMAI dimer is a more stable form, compared to TMA dimer, since the bond dissociation energy of an Al-O bond present in DMAI is higher compared to an Al-C bonds in TMA [15, 108]. The DMAI dimeric form is expected to dominate at higher temperature, which makes this compound non-pyrohcropic, hence safer to use [15]. Moreover, DMAI bulkier than TMA, which could be beneficial for precursor blocking due to enhanced steric hindrance effects. However, the dimeric structure has been detected intact on the Si(100) surface, and therefore steric hindrace might also affect the GPC on the growth-area. The trade-off between more effective blocking on the non-growth area and lower GPC on the growth area due to steric hindrance is studied in more detail in the results.

### 3.2.4 Tris(dimethylamido)aluminum

The third Al precursor examined for area-selective ALD of Al₂O₃ is tris(dimethylamido)aluminum (TDMAA). As shown in Figure 3.13, the precursor consists of an Al center atom, bonded to three dimethylamine (N(CH₃)₂) ligands. TDMAA exhibits a good vapor pressure and excellent thermal stability (Table III), which enabled ALD of AlN films at a temperature range of 170-290 °C [112] and thermal Al₂O₃ ALD at 200 °C [113] and 250 °C [109]. This precursor differs from TMA and DMAI, since it is the only one who has Al-N bonds.

TDMAA was chosen as an alternative Al precursor candidate since it is 12% bulkier than TMA in terms of molecular volume, it is found in dimeric form in gas phase, and it is non-pyrohcropic [109]. Similarly to DMAI, more effective blocking is expected with this precursor, due to enhanced steric hindrance effects.
Figure 3.13: Schematic illustration of TDMAA. The Al center is bonded to three dimethylamine (N(CH$_3$)$_2$) ligands [109].
4 Process optimization

In order to establish a highly selective process and exploit the key merits of ALD in area-selective ALD, careful process optimization is required. Starting with the experiments performed in the FlexAL reactor, the saturation curves for the separate dosing steps (Hacac, TMA, DMAI, H$_2$O) were investigated, and the effect of purge time on selectivity was studied. Similarly, the recipes employed for the spatial ALD reactor were optimized by investigating the corresponding saturation curves (Hacac, TMA) and studying precursor blocking as a function of the inhibitor/precursor exposure ratio. All the experiments of this chapter were performed on Al$_2$O$_3$ substrates, since the main focus here was optimization, rather than aiming for a specific application of area-selective ALD. The optical model and the fitting process employed for the SE measurements have been explained in Figures 2.9c and 2.10, respectively.

4.1 Temporal ALD

4.1.1 Al$_2$O$_3$ ALD

To investigate qualitatively and quantitatively the Al$_2$O$_3$ ALD process with TMA and DMAI (e.g. thickness trend, nucleation delay, GPC), thermal and plasma BC cycles were applied at 250 °C, while the film growth was measured with in-situ SE.

In Figure 4.1, the thickness is shown as a function of the number of ALD cycles for Al$_2$O$_3$ ALD using TMA and DMAI as precursors. The thickness increases for all cases from the first cycle and grows in a linear trend, indicating that the same amount of material is deposited in every cycle. In thermal ALD, TMA demonstrates a GPC of 1.03 Å/cycle, while the GPC with DMAI corresponds to 0.74 Å/cycle. In the plasma ALD case, TMA and DMAI show a GPC of 0.97 and 0.75 Å/cycle, respectively. These GPC values are consistent with previous studies [15, 66], except from the thermal process with DMAI. In the latter case, the GPC was found approximately 0.3 Å/cycle lower, compared to earlier findings [15].

![Figure 4.1: In-situ ellipsometry measurements for (a) thermal, (b) plasma Al$_2$O$_3$ ALD with TMA and DMAI.](image)

Figure 4.1 shows that the GPC obtained with DMAI is lower than the case of TMA, both for plasma and thermal ALD. This difference can be attributed to the O$i$Pr ligand present in the DMAI molecule. As discussed in section 3.2.3, this ligand physically blocks the access to the neighboring surface sites more easily due to its large size (steric hindrance) and therefore, less DMAI molecules can adsorb on the surface in each cycle [15].

4.1.2 Saturation curves for ALD

Recipe optimization of the Al$_2$O$_3$ ALD process was performed by investigating the precursors and the co-reactant saturation curves. For the different precursors employed, the goal was to identify the minimum precursor dose time, which is sufficient for saturation. This is essential for area-selective ALD, since precursor overdose might result in more physisorbed molecules on the non-growth area [34] and induce larger inhibitor removal, as discussed in more detail in chapter 6. On the other hand, dosing below saturation does not allow for accurate thickness control and can result in less uniform layers.

The TMA saturation curve for thermal Al$_2$O$_3$ ALD is given in Figure 4.2. The GPC remains stable for doses larger than 40 ms, indicating that TMA adsorption takes place in a self-limiting way. Saturation
is very fast, since TMA is very reactive and has a high vapor pressure, even at room temperature (12.2 Torr [51]). This is in line with previous studies, where fast TMA saturation was also observed [15].

Figure 4.2: TMA saturation curve for Al₂O₃ ALD, where the water dose was kept fixed at 0.3 s. The error bars are in the order of 0.02 Å/cycle and therefore not visible in this graph.

In contrast, larger doses are generally required for saturation in the case of DMAI, as depicted in Figure 4.3a. Above 0.3 s of DMAI dosing, the GPC slightly increases in a linear trend, suggesting that the surface is not completely saturated, even for large doses (soft saturation). Interestingly, soft saturation behaviour for DMAI has not been reported in earlier studies, where saturation was observed for doses varying from 0.1 s to 0.5 s, depending on the DMAI bubbler temperature [15, 114]. In this work, a dose of 0.4 s was employed in the following experiments, since the GPC obtained with this dose is relatively close to the saturated value.

Lastly, the water saturation curve for Al₂O₃ ALD with DMAI is given in Figure 4.3b. The GPC does not increase for doses larger than 0.2 s, suggesting that ligand removal is saturated. Saturation below 0.3 s of H₂O has been also reported with TMA as precursor, which indicates that the O’Pr ligand on the DMAI molecule can be easily removed during the H₂O step [15, 66]. To ensure that the majority of ligands is consistently removed, a water dose of 0.3 s was employed in the following experiments of this project for both precursors.

Figure 4.3: Saturation curves for (a) DMAI with the water dose fixed at 0.3 s. (b) Water with the DMAI dose fixed at 0.4 s. The error bars are in the order of 0.02 Å/cycle and therefore not visible in this graph.

4.1.3 Saturation curves for area-selective ALD

In this section, further optimization was performed by investigating Al₂O₃ area-selective ALD processes. First of all, the Hacac saturation curve was studied to make sure that the non-growth area is sufficiently covered by the inhibitor. Moreover, the effect of purge time on selectivity was explored, since physisorbed precursor and/or co-reactant molecules are often associated with loss of selectivity [34, 36]. Extended
purge steps might remove these physisorbed molecules, thereby improving selectivity. On the other hand, unnecessary long purge steps result in time-inefficient recipes.

The Hacac saturation curve was measured by applying ABC type cycles (see section 2.2) with TMA as precursor and O\textsubscript{2} plasma as co-reactant. This dosing strategy was chosen over the A+BC type, since in ABC cycles Hacac is reapplied in every cycle. This makes measuring the effects of the Hacac dose on precursor blocking less difficult. In this experiment, a lower GPC would indicate more efficient precursor blocking.

As shown in Figure 4.4, the GPC quickly drops below 0.3 Å/cycle, even for short Hacac exposure time (2 s). For larger doses, a marginal decrease can be observed, and finally the GPC saturates at 0.23±0.02 Å/cycle for a 10 s Hacac dose. To make sure that the non-growth area is consistently covered by Hacac, in all the following experiments a 15 s Hacac dose was adopted. This dose was split into three consecutive Hacac doses of 5 s each with a reaction step in between, as explained in section 2.1.1. Lastly, a comparison with the case without inhibitor reveals that a saturated Hacac dose results in an 79% decrease in GPC, which is larger than a previous study with Hacac and TMA (57%) [39]. However, it should be noted that in [39] different co-reactant was used (O\textsubscript{3}), and the process was performed at lower substrate temperature (200 °C).

To investigate the effect of purge time applied after the Hacac dose on GPC, ABC type cycles were applied with TMA and O\textsubscript{2} plasma as Al precursor and co-reactant, respectively. Similarly to the Hacac saturation experiments, the ABC type cycles were preferred to make the effect of longer purges after Hacac easier to detect. However, no difference in GPC was found even for large purge times, as depicted in Figure 4.5. This finding suggests that the duration of this purge step is not a key parameter in this process. The exact same values were found when the purging time in between the consecutive Hacac doses was altered. This again indicates that the removal of reaction products, such as H\textsubscript{2}O, is saturated after a 3 s purge step.

The effect of the purge step duration applied after the precursor dose was investigated with the A+BC type cycles (see section 2.2), since reapplication of Hacac should not affect the outcome of this experiment. The A+BC type cycles consisted of Hacac (step A), TMA (step B) and H\textsubscript{2}O (step C), respectively. The thickness was measured with in-situ SE and it is plotted as a function of the number of cycles in Figure 4.6. A slower increase in thickness (or longer nucleation delay) would indicate less physisorbed precursor. However, no difference was observed for the first 20 cycles in any of the cases, which suggests that no additional physisorbed TMA can be removed with longer purges. The case of 20 s purging (green dataset) was extended up to 70 cycles to check whether the GPC returns back to the growth rate measured without the inhibitor. The GPC for this case was found 0.99 Å/cycle, while the BC cycles in Figure 4.1.1 showed 1.03 Å/cycle . Taking into account the error introduced by the SE fitting in these measurements (±0.02 Å/cycle), it can be concluded that the GPC was not completely restored to the value without inhibitor. This discrepancy could be attributed to changes in the substrate surface due to functionalization with Hacac and/or persisting Hacac molecules being present in the chamber (e.g. on the walls) that hinder the ALD process.

The A+BC type cycles with Hacac, TMA and H\textsubscript{2}O was also employed to study the effect of purge time after the H\textsubscript{2}O dose. As shown in Figure 4.7a, material deposition is hindered for all cases during the first 20 cycles, while for larger number of cycles the thickness follows again a linear trend. The GPC in the linear region was found marginally different in each case (1.0 Å/cycle, 0.99 Å/cycle, and 0.98 Å/cycle),
Figure 4.5: GPC as a function of the purge time applied after the Hacac dose, for ABC type cycles (A=Hacac; B=TMA (0.04 s); C=O₂ plasma (5 s)).

Figure 4.6: (a) In-situ SE measurements for A+BC type cycles with Hacac, TMA and H₂O. The thickness is given as a function of the number of cycles for different purge times applied after the TMA dose. The GPC noted in the text corresponds to the linear region, thus after 20 cycles. (b) Zoomed version, including only the first 20 cycles.

Figure 4.7: (a) In-situ SE measurements for A+BC type cycles with Hacac, TMA and H₂O. The thickness is given as a function of the number of cycles for different purge times applied after the H₂O dose. The GPC noted in the text corresponds to the linear region, thus after 20 cycles. (b) Zoomed version, including only the first 20 cycles.

but this difference is equal or smaller than the error introduced by the SE fitting (±0.02 Å/cycle). Thus,
it could be assumed that the GPC returns to $\sim 0.99$ Å/cycle for all cases. However, this value is again slightly lower compared to the GPC of the BC cycles in Figure 4.1a (1.03 Å/cycle). Therefore, changes in the substrate surface and/or persisting Hacac molecules in the chamber could have an impact on this experiment, as well. Moreover, a closer observation of the first 20 cycles, depicted in Figure 4.7b, shows some interesting results. The case of 3 s shows a slightly sharper increase, when compared to the other two cases. This behaviour indicates that water molecules still remained on the Hacac-functionalized substrate after the H$_2$O dose, and functioned as additional surface sites for precursor adsorption. A small difference can be also observed between the cases of 10 s and 30 s, with the latter case showing a slightly sharper increase during the first 20 cycles and a slightly slower GPC in the linear region. However, the difference in thickness is very small throughout the experiment and could be attributed to an error in SE measurements. Since there was no significant difference between the 10 s and 30 s of purging, in the following experiments a 10 s step was employed to make the process more time efficient.

4.2 Spatial ALD

Recipe optimization was also performed for the area-selective ALD process in spatial ALD, by investigating the TMA and Hacac saturation curves, and studying the GPC as a function of the Hacac/TMA ratio. The experiments discussed in this section were performed at 100 °C, unless stated otherwise.

The TMA saturation curve was studied by applying BC type cycles with TMA and O$_2$ plasma on c-Si substrates at 30 rpm, while the thickness was measured with ex-situ SE. As shown in Figure 4.8, the surface is saturated after 0.017 Torr·s of TMA exposure and the resulting GPC corresponds to 1.2 Å/cycle. The GPC in this case was found to be higher compared to the plasma process in temporal ALD (1.09 Å/cycle, shown in Figure 4.1b). This discrepancy can be attributed to the lower substrate temperature employed for the saturation curves in the spatial ALD (100 °C with spatial and 250 °C with temporal ALD). Typically, plasma-assisted Al$_2$O$_3$ ALD with TMA shows a decreasing GPC with increasing temperature due to surface dehydroxylation [15, 11], which is in agreement with the measurements discussed here. Moreover, the growth rate can be affected by the operating pressure in an ALD reactor. Earlier studies reported that higher reactor pressures result in faster growth, since desorption of physisorbed growth species is slower under these conditions [115, 116]. For instance, additional physisorbed H$_2$O molecules may cause an excess of TMA adsorption, thereby adding a chemical vapor deposition component on film growth [116]. As a result, the higher GPC measured in the spatial ALD process could also be attributed to higher reactor pressure, since the spatial ALD reactor operates at atmospheric pressures.

![Figure 4.8: TMA saturation curve for plasma ALD of Al$_2$O$_3$, where the O$_2$ flow was kept fixed at 100 sccm. The error bars are not visible in this graph.](image)

The Hacac saturation curve was investigated by using ABC type cycles with TMA and O$_2$ plasma and ex-situ SE for thickness measurements. Similarly to the Hacac saturation in temporal ALD, a lower GPC would indicate more efficient TMA blocking. As shown in Figure 4.9, the GPC saturates after an Hacac dose of 0.4 Torr·s at 0.61 Å/cycle, which is significantly higher compared to the temporal ALD case ($\sim 0.23$ Å/cycle, shown in Figure 4.4). As shown later in the beginning of chapter 5, this difference can be attributed to the lower substrate temperature used in the spatial ALD reactor.

The GPC was also investigated as a function of the Hacac/TMA exposure ratio, as depicted in Figure 4.10. The data points in the same color group have been exposed to the same TMA dose, which is given in the graph legend. Moreover, the number next to each data point shows the corresponding Hacac exposure in Torr·s. In general, the GPC drops as the Hacac/TMA ratio increases, indicating that a higher
Figure 4.9: Hacac saturation curve for ABC type cycles, with A corresponding to Hacac, B to TMA and C to \( \text{O}_2 \) plasma respectively. TMA exposure and the \( \text{O}_2 \) flow were fixed at 0.017 Torr·s and 100 sccm respectively. The error bars are not visible in this graph.

Relative amount of Hacac results in better blocking. Moreover, the group corresponding to the lowest TMA exposure (red group) shows the lowest GPC. A closer look at the graph also reveals that points within the same color group demonstrate approximately the same GPC, despite having different ratio (e.g. the red group). These findings suggest that above Hacac saturation, the TMA dose is the dominant factor in blocking. This can be mainly attributed to significant Hacac removal by TMA, which does not saturate as fast as the Hacac adsorption. The Hacac removal by TMA has been reported in earlier work [87], and was also confirmed here (Chapters 5 and 6). A TMA overdose results in larger Hacac removal, which might not be replaced during the next Hacac dose. As a result, additional surface sites might be available during the next TMA exposure, where TMA can readily adsorb due to its high reactivity, as discussed in section 3.2.2.

Figure 4.10: GPC as a function of the Hacac/TMA ratio. The data points in the same color group were exposed to the same TMA dose, which is given in the graph legend. The number next to each data point shows the Hacac exposure in Torr·s.

Finally, the GPC was studied as a function of the substrate rotational speed at 100 and 200 °C. As discussed in section 2.1.3, the rotational speed determines the exposure time in a spatial ALD reactor, and it is coupled for all the recipe compounds. Nevertheless, the exposure (pressure x time) can be accurately controlled by varying the partial pressure of each compound independently. In this experiment, the Hacac and TMA exposures were kept fixed to 0.96 Torr·s and 0.058 Torr·s respectively in all runs, which are exposures above saturation according to Figures 4.8 and 4.9. To achieve fixed exposure in all runs despite the difference in the rotational speed, the Hacac and TMA flows had to be changed accordingly. For instance, higher Hacac/TMA flows were applied at higher rotational speed, to compensate for the shorter exposure time. Lastly, the oxygen flow employed for \( \text{O}_2 \) plasma was kept fixed, since it was above saturation
for all cases. The experimental details are given in Table IV.

Table IV: Experimental details for investigation of the rotational speed effect on GPC. (RT = room temperature).

<table>
<thead>
<tr>
<th>Rotational speed (rotations per min)</th>
<th>Hacac bubbler temperature (°C)</th>
<th>Hacac flow (flow+ N₂ dilution) (sccm)</th>
<th>TMA bubbler temperature (°C)</th>
<th>TMA flow (sccm)</th>
<th>O₂ flow (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>20</td>
<td>200+200</td>
<td>RT</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>20</td>
<td>38</td>
<td>140+200</td>
<td>RT</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>30</td>
<td>38</td>
<td>320+200</td>
<td>RT</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>60</td>
<td>55</td>
<td>220+200</td>
<td>RT</td>
<td>120</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 4.11 depicts the GPC as a function of the rotations per minute (rpm) for two different temperatures. At 100 °C, a clear increase in GPC can be observed for faster rotations, which indicates that blocking is less effective in that region. A possible explanation for this trend could be the increased precursor pressure applied at faster rotations. It has been reported that high-pressure with short duration TMA doses result in larger TMA physisorption on SAM-functionalized substrates, compared to low-pressure with long-duration doses [34]. In fact, in the same study it has been reported that TMA physisorption is affected dominantly by pressure, and not by the exposure time. This effect could be enhanced in our case, since at high rotational speed the time interval between the precursor and the co-reactant step is smaller. As a result, there is less time available for desorption of physisorbed species.

Furthermore, a comparison between the datasets at 100 °C and 200 °C, show a significantly reduced GPC in the latter case. This indicates that blocking is favored by increased temperatures. The effect of temperature on our area-selective ALD processes is studied in detail in the next chapter. Interestingly, the effect of rotational speed was not very distinct at 200 °C, since only a marginal increase in GPC can be observed at faster rotations. These findings suggest that desorption of physisorbed species is predominantly affected by the substrate temperature, rather than the time interval available for desorption at different rotational speeds.

Figure 4.11: GPC as a function of the rotation speed for ABC type process with Hacac, TMA, and O₂ plasma. The error bars are not visible in this graph.
The effect of temperature on Al₂O₃ area-selective ALD

The substrate temperature can heavily influence an area-selective ALD process, as shown by earlier studies of TiO₂ and SiO₂ area-selective ALD [26, 30]. To investigate that parameter, the GPC for ABC type cycles with Hacac (step A), TMA (step B), and O₂ plasma (step C) was investigated as a function of temperature. The experiments took place in the spatial ALD reactor, with the Hacac and TMA exposures being above saturation (2.06 Torr·s and 0.017 Torr·s, respectively).

Figure 5.1: GPC as a function of the substrate temperature for plasma ABC type process with Hacac (A), TMA (B) and O₂ plasma (C).

As shown in Figure 5.1, the GPC drops as the temperature increases. This trend suggests that precursor blocking is more effective with increasing temperature, since reduced precursor adsorption results in lower GPC [11]. In this work, three hypotheses were formulated and investigated to explain the findings of Figure 5.1:

1. Reduced TMA adsorption due to surface dehydroxylation. The OH surface concentration reduces as temperature increases, and therefore, less reactive sites are available for TMA adsorption at higher temperatures [106, 117].

2. Increasing Hacac coverage with increasing temperature. Assuming that Hacac blocks precursor adsorption by acting as a physical barrier, formation of a more dense Hacac layer at higher temperatures could enhance precursor blocking.

3. Temperature-dependent Hacac removal. Hacac removal upon TMA dose has been already reported in earlier work [57], at 150 °C. However, the removal mechanism could be temperature-dependent, and therefore, decreased removal might take place at higher temperatures. This effect would result in increasing remainder of Hacac adsorbates at higher temperatures, and therefore enhanced blocking.

In the following sections, these hypotheses are discussed in detail

5.1 Hypothesis 1: Surface dehydroxylation

To study the effect of surface dehydroxylation, the TMA adsorption on an Al₂O₃-coated powder was examined as a function of temperature using in-situ FTIR. The experiment was performed in ALD-I (temporal ALD) and the measurement process is explained in Figure 5.2.

Figure 5.3a depicts the FTIR spectra for the region of 3200-2700 cm⁻¹, for different temperatures. The positive peaks correspond to symmetric and asymmetric C-H stretch [59, 60, 61], and therefore denote the presence of TMA ligands (CH₃) on the surface. The area below the peaks for the region 3000-2750 cm⁻¹ was calculated to quantify the amount of adsorbed TMA on the powder. As shown in Figure 5.3b, the integrated signal drops in a linear trend, with increasing temperature. For instance, from 100 °C to 200 °C the integrated TMA signal decreased by 13.0±2 %.

Moreover, Figure 5.4a shows the region between 4000 cm⁻¹ and 3200 cm⁻¹, where signal from surface OH groups can be measured. The OH absorption frequency and acidity depend on the number of bonds formed between the hydroxyl O atom and the neighboring Al sites, [107, 118, 119]. Hydroxyl groups bonded to one, two, or three Al atoms show increasingly acidic character (from basic to acid) and they can be observed at 3790 cm⁻¹ [107], 3726 cm⁻¹ [107], and 3700-3600 cm⁻¹ [107], respectively. Additionally,
Saturation: \( \log\left(\frac{l_{B1(N-1)}}{l_{B1}}\right) = \log\left(\frac{l_{BN}}{l_{BN}^{\text{init}}}\right) \)

FTIR spectra: \( A = -\log\left(\frac{l_{A2}}{l_{A1}}\right) \)

Figure 5.2: Schematic illustration of the FTIR measurement procedure for a run at \( T_1 \) °C. A background measurement was taken prior to the start of each run, always at 100 °C. Then, the temperature was set at \( T_1 \) °C, where an FTIR measurement was taken. Then, a two-step process consisting of a TMA pulse followed by an FTIR measurement was repeated until saturation was reached. The surface was considered saturated when the pulse had (almost) no impact on the surface, as discussed in section 2.3. Lastly, the temperature was restored to 100 °C for the final measurement. The resulting FTIR spectra were shown by plotting the final measurement with respect to the background. After the run completion, the TMA ligands were removed by applying a saturated H\( _2 \)O dose to prepare the Al\( _2 \)O\( _3 \) surface for the next run at \( T_2 \) °C. The runs were performed in random order.

Figure 5.3: (a) In-situ FTIR adsorption spectra after saturated TMA doses on Al\( _2 \)O\( _3 \)-coated powder at different temperatures. (b) Integrated absorbance of the CH stretch, as a function of temperature. The amount of adsorbed TMA shows a linear decrease.

In Figure 5.4a, a broad negative region from 3790 cm\(^{-1}\) to 3200 cm\(^{-1}\) can be observed, indicating that TMA reacts with the OH groups according to equation 1.1, regardless of their acidic character, which is in agreement to previous studies [107]. Lastly, an integration of the OH negative features from 3790 cm\(^{-1}\) to 3200 cm\(^{-1}\) in Figure 5.4a results in a decreasing OH consumption with increasing temperature, as depicted in Figure 5.4b. For instance, from 100 °C to 200 °C the OH signal decreased by 11.3±2 %. The Figures 5.3b and 5.4b suggest lower TMA adsorption at higher temperatures, which can be associated to lower GPC, as shown previously in Figure 5.1.

According to an earlier study by Elliot et al. [121], TMA adsorption can also take place without OH consumption. The adsorption mechanism has been studied with DFT simulations, by investigating the interaction between TMA and fully dehydroxylated surfaces. During dehydroxylation, two neighboring Al-OH sites react and form Al-O-Al bridges, while H\( _2 \)O is released. TMA can directly adsorb on Al-O-Al sites, as illustrated in Figure 5.5. Since there is no H to form the volatile CH\(_4\) product in this case,
Figure 5.4: (a) In-situ FTIR adsorption spectra indicating consumption of OH groups during saturated TMA doses at different temperatures. (b) Integrated OH consumption as a function of temperature. The consumption shows a linear decrease as the sample temperature increases.

the methyl groups diffuse until the surface becomes methyl terminated. Based on this mechanism, the decrease in the TMA integrated signal should be slower, compared to the integrated OH signal, since TMA adsorption takes place without OH consumption. However, our findings show that the decrease in TMA adsorption and OH consumption is similar (decrease of 13.0±2 % and 11.3±2 % from 100 °C to 200 °C respectively). This indicates that this mechanism probably does not occur to a large extend within the temperature range of our experiments.

Figure 5.5: Schematic illustration of the TMA adsorption mechanism on dehydroxylated A2O3 surface.

Summarizing, in this section, it has been shown that the amount of TMA absorbed on the Al2O3 surface decreases in a linear trend, as the substrate temperature increases. Since less TMA adsorption can be related to lower GPC [11, 106], the first hypothesis is confirmed. Interestingly, decreasing GPC with increasing temperature has been also reported for Al2O3 plasma ALD with TMA (i.e. BC cycles) [11, 15] and had been attributed to surface dehydroxylation. However, the decrease in GPC shown in Figure 5.1 (ABC cycles) was found to be more significant as compared to the aforementioned studies (BC cycles). For instance, 63% decrease in GPC in the area-selective ALD process was observed when the substrate temperature was increased from 100 °C to 200 °C, while the decrease in GPC was only 14% for the ALD process itself. This disparity indicates that apart from dehydroxylation, hypotheses 2 and 3 might also contribute to the reduced TMA adsorption at higher temperatures for the area-selective ALD process.

5.2 Hypothesis 2: Increasing Hacac coverage with increasing temperature

To investigate the second hypothesis, the Hacac adsorption on an Al2O3-coated powder was examined as a function of temperature by using ALD-I and in-situ FTIR. In this experiment, the powder had to be re-coated with an Al2O3 layer before using it for the next run. However, coating significantly reduces the effective area of the powder, since surface sites can become inaccessible [8]. This can heavily influence the amount of adsorbed molecules on the surface. To correct for that, the experimental process illustrated in Figure 5.6 was adopted.

In Figure 5.7a the FTIR adsorption spectra after a saturated Hacac doses at various temperatures is depicted, for the 1800-1200 cm⁻¹ region. The peak assignment is summarized in Table V, but also discussed here. The shoulder appearing at 1700 cm⁻¹ for the experiments done at 163 °C, 227 °C, 290 °C is attributed
Figure 5.6: Illustration of the experimental process employed to study the Hacac adsorption at different temperatures. First, a saturated TMA dose was applied on the Al₂O₃-coated powder at 250 °C and the adsorption signal was measured with FTIR. The integrated TMA signal from this measurement was utilized as a benchmark for the effective powder surface available in each run of the experiment. The TMA ligands were subsequently removed with a saturated H₂O dose, resulting in again an Al₂O₃-coated powder. Then, the Hacac adsorption signal was investigated at different temperatures with the FTIR measurement process presented earlier in Figure 5.2. The only difference is that in the current experiment, Hacac pulses were applied instead of TMA pulses, until saturation was reached. Lastly, the powder was cleaned with a 10 min O₂ plasma step to remove the Hacac molecules from the surface and finally the powder was coated again to prepare for the next run.

to C=O [42, 123]. As discussed in section 3.1.2, this type of bond can be seen only in the monodentate configuration, and therefore suggests increased monodentate signal at these temperatures. The peak at 1607 cm⁻¹ consists of two distinct C-O stretch peaks, located at 1625 cm⁻¹ and 1595 cm⁻¹, rising from Hacac in monodentate and chelate configuration respectively [123]. The distinction between monodentate and chelate contributions is more pronounced at 350 °C, since this temperature is well above the Hacac desorption/dissociation temperature (250 °C, Figure 3.6). The monodentate peaks at 1700 cm⁻¹ and 1625 cm⁻¹ are not observed in this case, leaving only the chelate contribution at 1595 cm⁻¹. This indicates that thermal desorption of Hacac molecules in monodentate configuration occurs first, which can be explained by the weak Hacac binding in this configuration (section 3.1.2). Moreover, a peak at 1530 cm⁻¹ can be observed in Figure 5.7a, consisting of contributions from C-O and C-CH stretch [123, 124]. The dip at 1490 cm⁻¹ could be assigned to decomposition signal of Hacac adsorbates [92, 125]. The shoulder at 1459 cm⁻¹ and the sharp peak at 1398 cm⁻¹ can be attributed to C-O stretch [123, 121], C-CH₃ stretch [123, 121], and CH₃ deformation [126]. The rest of the signal from 1362 cm⁻¹ to 1250 cm⁻¹ can be similarly assigned to C-C stretch, CH₃ stretch and C-C-O vibrations, all originating from (H)acac adsorbates [92, 123, 127].
Table V: Band assignment for the IR spectrum of Hacac adsorbates

<table>
<thead>
<tr>
<th>Peak (cm(^{-1}))</th>
<th>Modes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1700</td>
<td>C=O</td>
<td>[62, 122]</td>
</tr>
<tr>
<td>1625</td>
<td>C-O (monodentate)</td>
<td>[55]</td>
</tr>
<tr>
<td>1595</td>
<td>C-O (chelate)</td>
<td>[124]</td>
</tr>
<tr>
<td>1530</td>
<td>C-O, C-CH</td>
<td>[122, 124]</td>
</tr>
<tr>
<td>1459</td>
<td>C-O, C-CH(_3), CH(_3)</td>
<td>[123, 124, 126]</td>
</tr>
<tr>
<td>1398</td>
<td>C-O, C-CH(_3), CH(_3)</td>
<td>[123, 124, 126]</td>
</tr>
<tr>
<td>1362-1250</td>
<td>C-CO, CH(_3) (chelate)</td>
<td>[92, 123, 127]</td>
</tr>
</tbody>
</table>

In order to quantify the adsorption signal in Figure 5.7a, the area below the features in the region 1750-1250 cm\(^{-1}\) was calculated and plotted against temperature in Figure 5.7b. Focusing on the 100-290 °C region at first, it can be seen that the integrated signal rises with increasing temperature, suggesting that Hacac coverage increases with temperature. Interestingly, this trend extends up to 290 °C, indicating that desorption might not initiate at 250 °C, as suggested in Ref. [92] (see Figure 3.6). In contrast, the integrated signal is significantly decreased at 350 °C.

The findings discussed so far seem to be in line with the enhanced blocking shown earlier in Figure 5.1. To gain more insight in the configuration of the additional Hacac adsorbates, the OH absorption spectra was also studied for the same experiment. According to the DFT calculations discussed in section 3.1.2, consumption of an OH group during Hacac adsorption results in solely acac in chelate configuration [8]. Thus, higher OH consumption would indicate more chelate acac adsorbates.

The OH absorption spectra are given in Figure 5.8a. The negative features are limited in the 3800-3650 cm\(^{-1}\) region, which indicates that Hacac tends to react with the more basic OH sites and does not react with the hydrogen-bonded OH groups found below 3600 cm\(^{-1}\). Integration of these features was performed between 3800 cm\(^{-1}\) and 3650 cm\(^{-1}\), and it is given in Figure 5.8b. Surprisingly, the OH consumption remains approximately the same, suggesting that most of the additional Hacac adsorbates found at higher temperatures are in monodentate form. These results contradict the enhanced blocking in Figure 5.1, since Hacac in monodentate configuration is weakly bonded on the surface and therefore it is not expected to show good blocking ability, as discussed in section 3.1.2. Thus, there might be an alternative mechanism for Hacac adsorption on Al\(_2\)O\(_3\) surface in a stable form, without consumption of an OH surface group.

![Graphs](image)

Figure 5.8: (a) In-situ FTIR adsorption spectra indicating consumption of OH groups during saturated Hacac doses on Al\(_2\)O\(_3\)-coated powder, as a function of temperature. (b) Integrated absorbance suggesting the consumption of OH groups during saturated Hacac doses, as a function of temperature.

A possible explanation is the Hacac interaction with the Al-O-Al bridges (or coordinatively unsaturated bonds, CUS). The Hacac reaction mechanism with Al-O-Al sites has been previously reported in literature [92, 128] and it is schematically shown in Figure 5.9. The acac molecule bonds to one of the Al sites, while the proton transfers to the neighboring O, forming a new Al-OH site. This mechanism allows for Hacac adsorption as an enolate (i.e. chelate) without OH consumption and might become more significant at higher temperatures, when Al-O-Al bridges are formed during dehydroxylation [129, 130]. Furthermore, the new Al-OH sites formed due to this reaction (see Figure 5.9) can partially compensate for the additional OH consumption that was expected at higher temperatures. Based on this mechanism, the additional Hacac
signal at higher temperatures could be attributed to a mixture of monodentate and chelate adsorbates.

The question is, what happens to the Al-OH site formed with the above mechanism, since it is an additional surface site available for either Hacac or TMA adsorption. According to theoretical studies the distance between an Al and its neighboring O atom is approximately 1.8 Å [131, 132]. Moreover, the Van der Waals radius of a CH$_3$ [133] group, which can be found on the Hacac molecule, has been reported to be 2.0 Å. This means that an acac molecule adsorbed on the Al site by the aforementioned mechanism can probably cover the neighboring Al-OH site. Therefore, access to this Al-OH site is could blocked by steric hindrance.

Figure 5.9: Schematic illustration of the Hacac adsorption mechanism on dehydroxylated Al$_2$O$_3$ surface.

To sum up, the Hacac coverage increased with increasing substrate temperature, which can result in enhanced TMA blocking at higher temperatures. Based on the above discussion, the additional Hacac signal could be assigned to a mixture of monodentate and chelate adsorbates. Additional evidence supporting that concept is provided in the following section, where the TMA adsorption on Hacac-functionalized Al$_2$O$_3$ powders is examined.

5.3 Hypothesis 3: Temperature-dependent Hacac removal

Investigation of the third hypothesis was performed by studying the TMA adsorption on Hacac-functionalized powders at various temperatures by using in-situ FTIR on ALD-I. The experimental procedure followed in this case is explained in Figure 5.10.

Figure 5.10: Illustration of the experimental procedure employed to study the interaction between Hacac-functionalized powder and TMA at temperature T$_1$ °C. The background measurement ($I_A$) was first taken at T$_1$ °C. Then, Hacac pulses were applied at the same temperature, until saturation was reached (as explained in section 2.3). The saturated Hacac signal was calculated by subtracting the FTIR measurement taken after the last Hacac pulse ($I_{BN}$), which was taken having $I_A$ as background. Next, TMA pulses were applied, which resulted in (H)acac removal from the substrate. The removal was shown by taking an FTIR measurement after each TMA pulse ($I_{C1}$), which was plotted having the measurement taken after the last Hacac dose ($I_{BN}$) as background. Lastly, the (H)acac remainder was calculated by using the FTIR measurement taken after the last TMA pulse ($I_{CM}$), and the background measurement ($I_A$).

The FTIR spectra of this experiment are depicted in Figure 5.11 for 100 °C, 150 °C, 200 °C, and 250 °C. The black curve corresponds to the absorbance signal after the saturated Hacac dose, as explained...
in Figure 5.10 \( (A = -\log(\frac{\text{Hacac}}{\text{AlBN}})) \). The red curve shows the displacement of Hacac adsorbates from the surface, as TMA was dosed on the Hacac-functionalized powder \( (A' = -\log(\frac{\text{Hacac}}{\text{CM}})) \), and finally the blue curve depicts the remaining (H)acac signal \( (A'' = -\log(\frac{\text{Hacac}}{\text{CM}})) \). It is important to mention here that the effective powder surface area was not the same in any of these runs. To correct for that, the data in Figure 5.7b were used, while the integrated area of the black curve in Figure 5.11a was utilized as benchmark. For example, in Figure 5.7b, the Hacac integrated area at 150 °C is 25% larger compared to 100 °C. The integrated areas of the black curves in Figures 5.11a and 5.11b should have the same ratio, since they also concern Hacac adsorption on \( \text{Al}_2\text{O}_3 \) powder. For the sake of this example, the integrated area of black curve in Figure 5.11a is assumed to be 1.0, while the integrated area in Figure 5.11b is assumed only 10% larger, hence 1.1. This means that the dataset in Figure 5.11b should be corrected by a factor of 1.136, to result in an integrated (H)acac signal of 1.1\cdot1.136\approx1.25, which is 25% higher compared to Figure 5.11a (100 °C). This multiplication was applied in all curves of the 150 °C dataset (black, red and blue). All data given in Figure 5.11 correspond to the corrected datasets.

![Figure 5.11: In-situ FTIR adsorption spectra at (a) 100 °C, (b) 150 °C, (c) 200 °C, and (d) 250 °C. The black curve shows the absorption spectra after powder coating with Hacac was finished. The red curve depicts the inhibitor removal, after saturated TMA doses on the powder covered with the inhibitor. The blue curve corresponds to the inhibitor remainder on the surface. The colors are matched with the colors of Figure 5.10.](image)

As depicted in Figure 5.11, the shoulder at 1700 cm\(^{-1}\) (C=O) completely disappears upon TMA dosing at all temperatures, indicating that the monodentate species are easily removed. This is further supported by the shift in the 1607 cm\(^{-1}\) peak. The monodentate C-O contribution at 1625 cm\(^{-1}\) is removed, leaving only the chelate C-O contribution at 1586 cm\(^{-1}\). Moreover, comparison between the Hacac adsorption signal (black curve) and the remainder signal (blue curve) reveals shifts also for the other two main peaks at 1530 cm\(^{-1}\) and 1398 cm\(^{-1}\). Particularly, there is a consistent shift towards higher wavenumbers for the peak at 1530 cm\(^{-1}\) and towards lower wavenumbers for the peak at 1398 cm\(^{-1}\), for all temperatures. This indicates that the removal mechanism could be the same for all temperatures examined. However, it is challenging to extract more information from the changes in these two peaks, since they consist of
contributions from many different bonds, as discussed earlier in section 5.2.

Moreover, the feature at 1490 cm\(^{-1}\), assigned to the (H)acac decomposition [92, 125], again shows an increasing trend with increasing temperature (black curves). The decomposed molecules were not fully removed upon TMA dosing, since the remaining signal is non-zero in this region. In fact, the amount of remaining decomposed molecules increases at higher temperatures. This suggests that the decomposition products are strongly bonded on the surface and can also demonstrate good TMA blocking.

To quantify the spectral signal in Figure 5.11, integration was performed over region of 1800-1200 cm\(^{-1}\). The integrated area corresponding to the Hacac coverage, removal and remainder is given in Figure 5.12 in black, red and blue, respectively. Interestingly, the inhibitor removal is approximately constant up to 200 °C, while only a small increase appears at 250 °C. The Hacac coverage increases faster than the removal, which results in an increasing remainder with increasing temperature. This behaviour indicates that most of the additional Hacac adsorbates at high temperatures were strongly bonded on the surface, and therefore contribute to precursor blocking. These findings also provide further support on the Hacac adsorption mechanism discussed in Figure 5.9.

![Figure 5.12: Quantification of the 1800-1200 cm\(^{-1}\) region in Figure 5.11, showing the Hacac initial coverage, removal during the TMA dose, and remainder. The inhibitor coverage, depicted in black, shows a sharp increase as temperature rises. In contrast, the inhibitor removal (red) remains relatively constant from 100 °C to 200 °C, and shows a small increase at 250 °C. Coverage rises faster than removal as temperature increases, resulting in increasing (H)acac remainder. The last point at 250 °C deviates from this behaviour.](image)

Lastly, the TMA adsorption on the Hacac-functionalized Al\(_2\)O\(_3\) powders was also quantified. The spectra were calculated by plotting the FTIR measurement taken after the last TMA pulse (\(l_{CM}\)), while having the FTIR measurement taken after the last Hacac pulse (\(l_{BN}\)) as background (\(A' = -\log(l_{BN}/l_{CM})\)), as explained in Figure 5.10. Peak integration was performed in the region of 2800-3000 cm\(^{-1}\), in the same way discussed in section 5.1. The integrated signal is given in Figure 5.13a, while in Figure 5.13b the integrated TMA signal on Al\(_2\)O\(_3\) powder is provided again (data similar to Figure 5.3b). A comparison between graphs 5.13a and 5.13b reveals a sharper decrease in TMA signal in the former case. For instance, a temperature increase from 100 °C to 200 °C results in 36% lower TMA signalon the Hacac-functionalized powder (Figure 5.13a), whereas a 14% decrease on the Al\(_2\)O\(_3\) powder (Figure 5.13b).

In this chapter it was shown that more effective blocking takes place at higher temperatures. A comparison between BC and ABC type cycles revealed a sharper decrease in GPC with increasing temperature for the latter case. A similar difference was found in the FTIR measurements, where a temperature increase from 100 °C to 200 °C resulted in a 16% decrease in TMA adsorption signal on Al\(_2\)O\(_3\)-coated powder, and a 36% decrease on Hacac-functionalized powder (Figures 5.13a and 5.13). These findings suggest that the enhanced blocking at higher temperatures should not be attributed exclusively to surface dehydroxylation. Indeed, 37% higher (H)acac absorbance signal was measured at 200 °C, compared to 100 °C. Although the OH consumption during the Hacac doses remained approximately the same for all temperatures, Hacac adsorption in chelate configuration could take place without consumption of an OH group on the Al-O-Al bridges. During this reaction an additional Al-OH site is also formed, which would result in opposite contribution to the OH peak in the FTIR spectrum. Strong Hacac binding with this mechanism was further supported by the FTIR measurements of TMA on Hacac-functionalized powders. In this experiment, the additional Hacac adsorbates were not easily removed upon TMA dosing and demonstrated good blocking, suggesting the formation of strong Hacac-surface bonds. To sum up this chapter, the temperature effect and all the aforementioned surface interactions are summed in Figure 5.14, where the case of 100 °C and
Figure 5.13: Integrated absorbance signal as a function of temperature for saturated TMA doses on (a) Al₂O₃-coated powder covered with Hacac (b) Al₂O₃-coated powder. 200 °C are depicted for comparison. The latter case shows 30% less OH sites [118], 37% higher Hacac adsorption signal and 36% reduced CH-stretch signal.

Figure 5.14: Schematic illustration of the temperature impact on the surface interactions. The cases of 100 °C (left) and 200 °C (right) substrate temperature are shown for comparison. (a,b) show the hydroxylated surfaces, (c,d) the surface after the saturated Hacac dose, and (e,f) the surface after the saturated TMA dose. At 200 °C, the OH density drops by 30% [118], due to surface dehydroxylation. Moreover, the Hacac absorbance signal increases by 37%, while the TMA absorbance signal on the Hacac-functionalized powder was found 36% smaller. The interaction of Hacac and TMA with Al-O-Al sites are also illustrated at the case of 200 °C.
6 Area-selective ALD of Al₂O₃ with alternative precursors and inhibitors

To further improve area-selective ALD of Al₂O₃, the studies on alternative precursors and inhibitors are discussed in this chapter. The precursors were employed in both ALD and area-selective ALD processes and they are compared here in terms of their ALD behaviour and their aptness for Al₂O₃ area-selective ALD. Moreover, the Hacac and aniline performance towards TMA and DMAI is examined, which provides further insights into the importance of the inhibitor-precursor combination.

6.1 ALD processes using TMA, DMAI and TDMAA

Firstly, the BC type cycle was investigated for all precursors, with the experimental procedure explained in Figure 6.1. The goal in these experiments was to (a) study the surface interactions between the Al₂O₃ powder and the precursors, (b) check whether precursor adsorption takes place in a self-limiting way, and (c) investigate the removal of precursor ligands and surface rehydroxylation by H₂O. The latter can provide valuable information regarding the feasibility of an ALD process with the corresponding precursor.

![Figure 6.1: Illustration of the experimental procedure employed to study the surface interactions during a BC type cycle, with different precursors. At first, a background FTIR measurement was taken ($l_A$). Then, a two-step process consisting of a precursor pulse and an FTIR measurement was repeated, until the surface was saturated. The precursor absorbance signal was shown by plotting the FTIR measurement taken after the last precursor pulse, with respect to the background. Lastly, consecutive H₂O pulses were applied with FTIR measurements in between, until removal of precursor ligands was saturated. The final FTIR measurement ($l_{CM}$) was plotted with the FTIR measurement taken after the last precursor pulse ($l_{BN}$) as background, to investigate the ligand removal and surface hydroxylation during the H₂O dose.](image)

Figure 6.2a depicts the FTIR absorbance spectra measured after a saturated TMA (red) and H₂O dose (blue) on Al₂O₃ powder. During the TMA dose, positive features around 2800-3000 cm⁻¹ can be observed, which correspond to asymmetric and symmetric C–H stretches [59, 60, 61]. The negative features in the OH region extend from 3800 cm⁻¹ to 3100 cm⁻¹, since TMA reacts with (almost) all OH groups [107], as discussed in section 5.1. During the H₂O dose, positive features can be observed in the region 3800-3100 cm⁻¹, suggesting that the powder surface is rehydroxylated. At the same time, the negative features around 2800-3000 cm⁻¹ show the removal of TMA ligands by H₂O. The spectra during the TMA and H₂O doses are mirrored, which suggests that the half-cycle reactions are consistent with equations 1.1 and 1.2.

In Figure 6.2b the FTIR absorbance spectra for the BC type cycle with DMAI are given. Similarly to TMA, positive features show up in the region 2800-3000 cm⁻¹, originating from the CH₃ groups present in the DMAI ligands (see section 3.2.3 for the DMAI molecule). Interestingly, the OH absorbance signal (3800-3100 cm⁻¹) deviates from the previous case. Negative features are mostly observed between 3800 cm⁻¹ and 3650 cm⁻¹, while OH consumption is nearly zero in the region of 3650-3100 cm⁻¹. This behaviour suggests that DMAI preferably reacts with the more basic OH groups, measured at high wavenumbers (see section 5.1), rather than the more acidic or hydrogen-bonded OH sites. This can be also observed during surface hydroxylation in the H₂O dose. Positive features are mainly accumulated in the region of 3800-3650 cm⁻¹, while only a marginal increase is observed from 3650 cm⁻¹ to 3100 cm⁻¹.
Lastly, the FTIR spectra for a BC type cycle with TDMAA are shown in Figure 6.2c. Apart from the CH stretch signal from 3000 cm\(^{-1}\) to 2800 cm\(^{-1}\), an additional peak arises at 2773 cm\(^{-1}\). This peak is assigned to a CH stretch mode and results from the interaction between the N lone pair orbital and the CH\(_3\) group in N(CH\(_3\))\(_2\) [134, 135, 136] (see section 3.2.4 for the TDMAA molecule). Similarly to DMAI, TDMAA does not react with the hydrogen-bonded OH surface sites, since negative features are observed almost exclusively within the region of 3800-3600 cm\(^{-1}\). A striking difference in the OH stretch region can be seen during the H\(_2\)O dose. The positive features in the region of 3800-3600 cm\(^{-1}\) were significantly larger than the corresponding negative features in the red curve. Moreover, the positive features were extended down to 3100 cm\(^{-1}\), even though the hydrogen-bonded OH groups were not consumed during the TDMAA dose. Differences can be also observed in the CH stretch region (3000-2800 cm\(^{-1}\)). The positive and negative features did not match in terms of shape in this part of the spectrum, indicating incomplete removal of precursor TDMAA ligands from the surface. These findings in combination with the large increase in OH signal after the H\(_2\)O dose suggest significant change in the powder surface after a BC cycle with TDMAA+H\(_2\)O. This behaviour deviates from the ideal ALD behaviour discussed in section 1.2 and demonstrated by TMA and DMAI.

Moreover, investigation of the 1800-1300 cm\(^{-1}\) region during the TDMAA dose provided further insight into the TDMAA surface decomposition. The spectra shown in Figure 6.3 were calculated by plotting the FTIR measurement taken after each TDMAA pulse (\(l_B\)), while having the initial FTIR measurement (\(l_A\)) as background (i.e. \(A = -\log(l_A/l_B)\), see Figure 6.1). The peak at 1671 cm\(^{-1}\) is attributed to N=CH\(_2\) bonds [62, 134, 135] and could originate from reaction between neighboring CH\(_3\) groups, according to the mechanism depicted in Figure 6.4 [134, 135]. Although this mechanism has been reported for temperatures above 200 °C, it is shown here that it can also take place at lower temperatures (150 °C). The peak at 1614 cm\(^{-1}\) has been identified as C=C stretch [135], but the decomposition path leading to this mode was
reported unknown by the authors of the latter study. Moreover, the small peaks at 1473 cm\(^{-1}\) and 1441 cm\(^{-1}\) correspond to CH\(_3\) deformation [92, 135, 137]. A closer look at these peaks reveals that after the dose of 45 s the peak intensity drops, thereby suggesting that the decomposition mechanism in Figure 6.4 takes place for longer doses. Furthermore, the features observed around 1405-1350 cm\(^{-1}\) are assigned to C-N and CH\(_3\) modes [122, 138]. The decomposition of TDMAA on the Al\(_2\)O\(_3\) surface might be associated with the non-ideal behaviour observed in Figure 6.2c, but more research needs to be undertaken to clearly understand the surface reactions that take place during TDMAA adsorption.

Figure 6.3: *In-situ* FTIR adsorption spectra after an extended TDMAA dose on Al\(_2\)O\(_3\)-coated powder. The spectra are plotted by using the FTIR measurements taken after each TDMAA pulse (\(l_{Bi}\)) and the initial FTIR measurement (\(l_A\)) as background (i.e. \(A = -\log(\frac{l_A}{l_{Bi}})\)).

Figure 6.4: Schematic illustration of TDMAA decomposition mechanism. The reaction between the methyl ligands results in an N=CH\(_2\) fragment, which stays on the surface, and the release of CH\(_4\).

Further insight into the saturation behaviour of the Al precursors was enabled by investigation of the corresponding saturation curves. For that, the FTIR measurements taken after each precursor pulse (\(l_{Bi}\)) were plotted with the initial FTIR measurement (\(l_A\)) as background (spectra shown in Appendix in Figure A.1). Integration of the spectra was performed in the region of 3000-2750 cm\(^{-1}\) for the TMA and DMAI cases and from 3000 cm\(^{-1}\) to 2700 cm\(^{-1}\) for TDMAA, since in the latter case additional features were observed due to the N(CH\(_3\))\(_2\) ligands. The normalized integrated absorbance is given as a function of the corresponding precursor dose in Figure 6.5. From these graphs, it can be seen that saturation was achieved in all three cases. Interestingly, the dose time required for saturation differ significantly in each case. This discrepancy could be attributed to difference in the effective powder surface available during the TMA, DMAI and TDMAA experiments. A sample containing a larger amount of powder provides more surface sites for precursor adsorption, and consequently requires a larger dose for saturation. Unfortunately, there was no benchmark for the amount of powder employed in each case, and therefore it was difficult to determine the exact effect of this parameter. Additionally, the dose time required for saturation can possibly be affected by difference in precursor reactivity towards the surface groups, and enhanced steric hindrance effects. A comparison of earlier studies shows that on planar wafers, saturation for TMA typically take places within 40 ms [15], for DMAI from 0.1 s to 0.5 s [15, 114], while for TDMAA at 4 s [109].
Therefore, it seems reasonable to observe such variation in the dose time required for saturation. Lastly, it should be noted specifically for TDMAA that saturation occurred at 45 s, while the features discussed in Figure 6.3 kept increasing for doses up to 125 s. This further supports that TDMAA decomposition takes place on the $\text{Al}_2\text{O}_3$ powder.

![Graphs](a) (b) (c)

Figure 6.5: Integrated absorbance of the peaks associated with the ligands of (a) TMA, (b) DMAI and (c) TDMAA, as a function of their corresponding dose time. The error bars are not visible in these graphs.

Lastly, the $\text{H}_2\text{O}$ saturation curve was studied to investigate the precursor ligand removal by $\text{H}_2\text{O}$ for all precursors. The FTIR measurements taken after each $\text{H}_2\text{O}$ pulse were plotted using as background the FTIR measurement taken after the last TMA pulse (i.e. $A'_i = -\log\left(\frac{I_{BNi}}{I_{Ci}}\right)$ in Figure 6.1). The FTIR spectra (given in Appendix in Figure A.2) were integrated in the region 3000-2750 cm$^{-1}$ for TMA and DMAI, and at 3000-2700 cm$^{-1}$ for TDMAA. The area of the negative features for each precursor was normalized by using the corresponding saturated integrated areas from Figures 6.5a, 6.5b and 6.5c, respectively. The results are given for all precursors in Figure 6.6, where it can be seen that saturation in ligand removal was achieved in all three cases. The percentage of removed ligands concerns the precursor ligands from the last precursor dose and not the persisting ligands resulting from previous processes (e.g. powder coating). For TMA, the $\text{H}_2\text{O}$ dose required was found 80% smaller compared to the DMAI case, and 87% smaller compared to TDMAA, suggesting that the reaction between $\text{H}_2\text{O}$ and the TMA ligands proceeds more easily. Lastly, although the removal of TMA ligands seems to saturate at higher percentage, a comparison with the DMAI and TDMAA cases should be interpreted with caution, considering the error involved in the measurements.
6.2 Precursor adsorption on Hacac-functionalized powders

To determine which precursor is more suitable for an Al₂O₃ area-selective ALD process, the TMA, DMAI and TDMAA adsorption on Hacac-functionalized powders was investigated. The precursors were compared in terms of how effectively they can be blocked by Hacac and in terms of Hacac removal. The experimental procedure employed here was the same as in section 5.3 (see Figure 5.10) and it was performed for all Al precursors at 150 °C. The precursor dose times applied in each case were determined by the saturation curves in Figure 6.5 (i.e. 1 s for TMA, 35 s for DMAI and 45 s for TDMAA). This allows for comparison of precursor adsorption and Hacac removal for a dose sufficient for saturation for all precursors.

In Figure 6.7, the red curves show the FTIR absorbance spectra after a saturated precursor dose on Hacac-functionalized powders, while in green the precursor adsorption on Al₂O₃-coated powders is again provided for comparison (taken from Figure 6.2). In the case of TMA depicted in Figure 6.7a, the CH stretch signal can be clearly seen in both the green and the red curves. The integrated signal for both curves was calculated in the region of 3000-2750 cm⁻¹, and it was found reduced by only 22% on the Hacac-functionalized powder. Moreover, differences in the OH signal were found in these two curves. Interestingly, the negative features between 3800 and 3700 cm⁻¹ indicating isolated OH groups were not observed in the red curve. As discussed in Figure 5.8a, these features originate from more basic OH groups and therefore were consumed during the Hacac dose. As a result, these OH sites were not available during the TMA dose. In contrast, negative features were observed in both curves from 3600 to 3100 cm⁻¹, suggesting that these OH sites were not consumed by Hacac and that TMA was able to react with them. The small size and high reactivity of TMA towards all OH groups allowed TMA to fit in between neighboring Hacac adsorbates, reach these available OH sites and react with them, thereby making blocking very challenging. Lastly, two small negative features can be observed at 3002 cm⁻¹ and 3099 cm⁻¹, in the red curve. These are attributed to CH and CH₃ vibrations of the acac ring attached to the surface [92], and therefore indicate removal of Hacac adsorbates during the TMA dose. The inhibitor removal during the precursor doses will...
be also discussed in detail later in this section.

![Figure 6.7: (a) In-situ FTIR adsorption spectra after a saturated dose of (a) TMA, (b) DMAI, (c) TDMAA on Al₂O₃-coated powder with and without inhibitor.](image)

The experiment was repeated by dosing DMAI instead of TMA, and the results are depicted in Figure 6.7b. DMAI adsorption on Al₂O₃-coated powder is denoted by the rise of CH stretch modes from 3000 to 2800 cm⁻¹, and the consumption of OH sites in the region of 3800-3650 cm⁻¹, as depicted by the green curve. Striking differences in the absorbance signal can be seen when DMAI was dosed on Hacac-functionalized powder (red curve). The CH stretch modes and the OH signal are absent in this case, indicating that DMAI adsorption was below the detection limit. This highly effective blocking could be attributed to multiple factors, such as the DMAI and Hacac preference towards the same OH groups. As shown in Figures 6.7b (green curve) and 5.8a, both molecules react with the OH sites giving signal in the region of 3800-3650 cm⁻¹, but they do not adsorb on the hydrogen-bonded OH groups (3600-3100 cm⁻¹). This overlap blocks DMAI adsorption on the Hacac-functionalized powder, since the OH groups reacting with DMAI have been already consumed during the Hacac dose. Additionally, DMAI blocking could be also enhanced by steric hindrance effects. The large DMAI molecular size could prevent this precursor from reaching OH groups that are not consumed by Hacac. Lastly, the negative features at 3002 cm⁻¹ and 3099 cm⁻¹ were not observed, suggesting that removal of Hacac adsorbates was significantly reduced for this precursor.

Finally, the case of TDMAA is shown in Figure 6.7c. Similarly to DMAI, TDMAA does not react with the hydrogen-bonded OH groups and it s 12% larger than TMA in terms of molecular volume [109], as discussed in section 3.2.4. As a result, TDMAA adsorption on the Hacac-functionalized powder was also below the detection limit. Moreover, the negative features resulting from vibrations of the acac ring on the surface (at 3002 cm⁻¹ and 3099 cm⁻¹) were absent, again suggesting significantly reduced removal of Hacac adsorbates. These findings suggest that DMAI and TDMAA are more suitable for an Al₂O₃ area-selective ALD process when Hacac is employed as inhibitor.

Moreover, the wavenumber region of 1800-1200 cm⁻¹ for the same experiment was studied in detail, to quantify the removal of Hacac adsorbates upon saturated precursor doses. The saturated Hacac signal,
depicted by the black curves in Figure 6.8, were calculated by utilizing the FTIR measurement taken after the last Hacac pulse ($l_{BN}$) and the background ($l_A$) (i.e. $A = -\log \left( \frac{l_{BN}}{l_A} \right)$ in Figure 5.10). The Hacac removal signal was calculated by using the FTIR measurement taken after the last precursor pulse ($l_{CM}$) and $l_{BN}$ as background (i.e. $A = -\log \left( \frac{l_{BN}}{l_{CM}} \right)$ in Figure 5.10). This is shown by red the curves in Figure 6.8. By calculating the integrated absorbance as shown by the the black and red curves in the region of 1750-1250 cm$^{-1}$, the percentage of removed Hacac adsorbates can be extracted. In the case of TMA, approximately 24% of Hacac adsorbates were displaced with a single saturated TMA dose. Taking into account a previous FTIR study reporting 20%±5% of the adsorbed Hacac molecules being in monodentate configuration [55], it could be assumed that most of monodentates are displaced upon the TMA dose. In contrast, significantly less displacement of Hacac adsorbates was observed in the other two cases. Approximately 3.0±0.2 % was removed after a saturated DMAI dose, while this percentage dropped to 1.71±0.03 % when TDMAA was employed. These findings indicate that the Hacac-TMA combination does not result in any nucleation delay, due to significant removal of the Hacac adsorbates even from the first cycle. The removal observed in the cases of DMAI and TDMAA might also cause loss of selectivity, which is a scenario further investigated in sections 6.3 and 6.4.

![Figure 6.8](image)

Figure 6.8: (a) In-situ FTIR adsorption spectra before (blue) and after (red) a saturated dose of (a) TMA, (b) DMAI, (c) TDMAA on Al$_2$O$_3$-coated powder covered with Hacac.

Lastly, Figure 6.9 shows the percentage of removed of Hacac adsorbates as a function of the precursor dose times. The TMA and DMAI dose times were extended up to 45 s, to investigate the removal for the same dose time as TDMAA. In the case of TMA, the removal percentage shows a rapid increase within the first second, and subsequently follows a linear trend. This suggests that the weakly bonded Hacac adsorbates were easily removed even for short dose times, while the strongly bonded acac molecules were more persistent. Interestingly, the inhibitor removal did not show any signs of saturation up to 45 s of exposure time. In contrast, removal was found very small for both DMAI and TDMAA. In the case of DMAI, removal did not increase after 30.5 s, but it might be difficult to identify the saturation point (if any), due to the error in these measurements. For TDMAA, the percentage kept increasing by ∼ 0.2% for every 10 s of TDMAA exposure in the last three measurements. These results suggest that the removal of
Hacac adsorbates does not saturate after a single saturated dose for any of these precursors. Therefore, the removal could pile up when consecutive BC cycles are applied on an Hacac-functionalized surface (e.g. in the A+BC type cycles).

Figure 6.9: Normalized removal of Hacac adsorbates as a function of (a) TMA, (b) DMAI and TDMAA doses.

The findings in this section indicate that DMAI and TDMAA are more suitable Al precursors for area-selective ALD of Al₂O₃, since they are much more efficiently blocked and they removed only a small percentage of the inhibitor. Nevertheless, inhibitor removal might result in loss of selectivity, especially when A+BC type cycles are employed. As explained in section 2.2, in A+BC type cycles the inhibitor is applied only once in the beginning, and therefore the removed inhibitor is not replaced in the next cycle. The surface sites previously covered by the inhibitor are re-hydroxylated during the H₂O step, and therefore they are available for precursor adsorption. This could pile up since inhibitor removal continues, thereby resulting in fast loss of selectivity after some cycles. This scenario is examined in the following sections, where the of nucleation delay on CoOₓ and HfO₂ substrates is investigated.

6.3 Al precursor comparison: Nucleation delay on CoOₓ

The Al₂O₃ nucleation was investigated by applying A+BC type cycles (see section 2.2) with Hacac, TMA or DMAI and H₂O on CoOₓ samples, at 250 °C. The experiments were carried out in a temporal ALD reactor (FlexAL) and the samples were characterized by XPS, by specifically looking at the Al2p peak (i.e. energy range of 71-77 eV). Small or absent Al2p signal in these experiments would indicate efficient precursor blocking.

The Al2p peak is given in Appendix in Figures B.1a and B.1b as a function of ALD cycles for TMA and DMAI, respectively. To quantify the data in Figure B.1, the area below the peaks was calculated and it is given for both precursors in Figure 6.10. Valuable insights can be provided by studying the horizontal lines in Figure 6.10. The solid black line shows the integrated signal after a BC cycle (i.e. without Hacac) with TMA on SiO₂ sample. Approximately the same integrated area was found after an A+BC type cycle with TMA on SiO₂ (not shown here), indicating that Al₂O₃ deposition on SiO₂ is not affected by the addition of the Hacac step. Moreover, the black dashed line in the same Figure shows the integrated area for the single BC cycle with TMA on the CoOₓ. Interestingly, a comparison between the dashed and solid black lines suggests that TMA adsorption is significantly larger on CoOₓ, compared to SiO₂. This observation could be attributed to the increased CoOₓ surface roughness [139], which can provide additional surface sites for precursor adsorption. Furthermore, the red dashed line shows the integrated area for the single BC cycle with DMAI on the CoOₓ. Comparing the red and black dashed lines reveals that a single BC cycle with TMA results in ~2.6 times larger Al signal, as compared to DMAI. This difference can be explained by the high TMA reactivity towards the OH surface groups. As discussed in Figures 6.7a and 6.7b, TMA reacts with (almost) all OH groups, while DMAI only reacts with a fraction of them. Thus, additional surface sites for precursor adsorption are available for the TMA case, resulting in a notably larger Al signal. The smaller Al2p peak in the case of DMAI can be also attributed to enhanced steric hindrance effects, due to the large DMAI molecular size.

Moreover, the data points of TMA and DMAI in Figure 6.10 showed significantly different trends. The presence of Al on the samples was identified right from the first cycle in the case of TMA, with the signal...
growing in the next BC cycles. This trend suggests poor precursor blocking, in agreement with the FTIR measurements discussed in the previous chapter. A comparison between a single BC and A+BC type cycle on CoOx (i.e. the black dashed line and the black dot, respectively) shows that addition of the Hacac step can partly hinder TMA adsorption, since the integrated area drops from 6200 to ~1600. Nevertheless, this decrease is not sufficient, since an A+BC cycle on CoOx (black dot) and on SiO₂ (black solid line) were found to have approximately the same amount of Al. These findings suggest that selectivity is low and therefore it is very challenging to obtain area-selective deposition by using the Hacac-TMA combination.

In contrast, a nucleation delay of 3-4 cycles was measured with DMAI, since (almost) no Al signal was detected in the corresponding measurements. For a larger number of cycles selectivity was, however, quickly lost. The measured integrated area was already 33% of the signal measured without inhibitor (red dashed line), thereby indicating that DMAI blocking degrades after the first cycles. These findings can be explained by the removal of Hacac adsorbates, as discussed in Figure 6.8. Approximately 3% of Hacac adsorbates were removed by a single saturated DMAI dose on the Hacac-functionalized powder. Taking into account that in the A+BC type cycles employed here the Hacac step is applied only once in the beginning, removal of Hacac adsorbates could pile up within the next 3-4 cycles. The surface sites previously covered by the inhibitor facilitate DMAI adsorption, thereby resulting in nucleation on the non-growth area and quick loss of selectivity. Lastly, it should be noted that an A+BC cycle with DMAI on SiO₂ was not performed in this work, and therefore it is not possible to estimate the level of selectivity for this case.

![Figure 6.10: Integrated Al signal for BC cycles with TMA (black) and DMAI (red). The black solid line depicts the integrated Al signal after a BC cycle (i.e. without inhibitor) with TMA on SiO₂ substrate. The black and red horizontal dashed lines indicate the Al signal resulting from a single BC cycle on CoOₓ, with TMA and DMAI, respectively.](image)

In summary, in this section the precursors were compared in terms of nucleation delay measured on Hacac-functionalized CoOₓ samples. Significant differences in the Al signal were found for TMA and DMAI, with the latter demonstrating a nucleation delay of 3-4 cycles. For large number of cycles DMAI was not efficiently blocked, probably due to removal of Hacac adsorbates from the CoOₓ surface. Based on the discussion in section 3.1.2, we could assume that Hacac does not adsorb on SiO₂, and therefore, the deposition with A+BC type cycles with DMAI on SiO₂ would proceed in the same manner as the BC cycles. Based on that hypothesis, the nucleation delay on CoOₓ enables a 4-cycle selective deposition on SiO₂, with CoOₓ as non-growth area, which translates into a 3 Å Al₂O₃ film.

### 6.4 Al precursor comparison: Nucleation delay on HfO₂

The difference in nucleation between TMA and DMAI was further investigated by testing the Al₂O₃ area-selective ALD process while having HfO₂ substrates as non-growth area. These experiments were also carried out in the temporal ALD reactor (FlexAL), where BC and A+BC type thermal cycles with either TMA or DMAI were applied on HfO₂ samples, at 250 °C. The thickness was measured with in-situ SE, and the details of the optical employed to fit the data given in Figure 2.9b.

Figure 6.11 depicts the thickness as a function of the number of BC and A+BC cycles with either TMA or DMAI. For the case of TMA, the BC cycles resulted in thickness increase from the first cycle, with a GPC corresponding to 1.06 Å/cycle. Thickness increase was also measured from the first cycle in the A+BC type cycles (with TMA), thereby suggesting fast nucleation on the Hacac-functionalized HfO₂ sample. After 30 cycles, the GPC saturates to 1.06 Å/cycle indicating that inhibitor is either completely
removed or covered by a thin Al$_2$O$_3$ layer. For the case of DMAI, the GPC measured for the BC cycles corresponds to 0.73 Å/cycle. However, the thickness follows a different trend in the A+BC type cycles. No increase was detected for approximately 10 cycles, suggesting that the Hacac adsorbates were able to efficiently block DMAI adsorption. For larger number of cycles the thickness slowly starts increasing, but no linear trend was observed up to 60 cycles. This finding indicates that Hacac adsorbates and/or Hacac fragments were still present on the surface, thereby hindering DMAI adsorption. Lastly, it should be noted that the 10 cycle nucleation delay observed here with DMAI was larger, compared to the 3-4 cycle delay observed with DMAI on CoO$_x$ in the previous section. This difference should be interpreted with caution, since it should not be attributed only to the different substrate, but also to the different sensitivity of the SE and XPS measurements. XPS measures the emitted substrate electrons, and therefore it is more sensitive to the presence of Al$_2$O$_3$ on the CoO$_x$ surface. Further examination of the HfO$_2$ samples with XPS could provide a more straightforward comparison for DMAI blocking Co and HfO$_2$ substrates.

Figure 6.11: In-situ ellipsometry measurements for BC and A+BC type thermal cycles with TMA or DMAI on HfO$_2$ samples.

In summary, BC and A+BC type cycles were applied on HfO$_2$ samples, to compare TMA and DMAI in terms of the nucleation delay measured with in-situ SE. For the A+BC type cycles, thickness increase even from the first cycle was measured with TMA, whereas a 10-cycle nucleation delay was observed with DMAI. This delay allows for a selective deposition of 7.4 Å Al$_2$O$_3$ on SiO$_2$, while having HfO$_2$ as non-growth area.

6.5 Precursor blocking with aniline

In this section, precursor blocking is studied by using aniline as inhibitor. The goal of these experiments was to compare the inhibitors in terms of precursor blocking and investigate whether the conclusions drawn from the precursor comparison studies can be extrapolated to aniline as well.

Based on the findings discussed in Figure 3.9, aniline enables the use of ABC type cycles, with aniline (step A), Al precursor (i.e. TMA/DMAI) (step B) and H$_2$O (step C). Thus, BC and ABC type cycles were applied on SiO$_2$ (growth area) and Co (non-growth area) in the FlexAL reactor, at 250 °C. Sample analysis was performed with in-situ SE for SiO$_2$ (see section 2.4.2 for the model and fitting process) and with XPS for Co.

In Figure 6.12 the thickness is depicted for the BC and ABC type cycles with TMA and DMAI on SiO$_2$. Ideally, the BC and ABC cycles with the same precursor should demonstrate the same nucleation and GPC on SiO$_2$, since addition of the inhibitor step should not hinder the Al$_2$O$_3$ deposition on the growth area. In the case of TMA (black and green curves), the GPC was found ∼14% lower during the ABC cycles, compared to the BC cycles. This discrepancy indicates that some aniline adsorption takes place in every cycle on the deposited Al$_2$O$_3$ film, which reduces the GPC. That finding is in agreement with the data discussed in Figure 3.9. Nevertheless, Al$_2$O$_3$ nucleates from the first cycle and the decrease in GPC is relatively small. Thus, the addition of step A in the process (ABC type cycles) does not affect the Al$_2$O$_3$ deposition significantly for TMA.

In contrast, there is a considerable difference between BC and ABC type cycles in the case of DMAI. For the BC cycles, Al$_2$O$_3$ nucleates from the first cycle and the slope shows a GPC of 0.74 Å/cycle. Addition of the aniline dose results in a 5 cycle nucleation delay, and a noticeably smaller GPC for the larger number of cycles. Between 5 and 15 cycles the GPC corresponds to 0.22 Å/cycle and subsequently increases to 0.43 Å/cycle. The nucleation delay observed in the ABC type cycles suggests that aniline adsorbs also on
SiO\(_2\) and prevents DMAI adsorption. A similar nucleation delay was not observed with TMA, probably due to the high reactivity of this precursor, as shown in the FTIR measurements. Interestingly, aniline adsorption on both SiO\(_2\) and Al\(_2\)O\(_3\) substrates contradicts the findings discussed in Figure 3.9, since no adsorption was detected on SiO\(_2\) in that experiment. Lastly, similar results were extracted when long purges after the aniline dose were applied (up to 2 minutes).

![Figure 6.12: In-situ ellipsometry measurements, showing the Al\(_2\)O\(_3\) thickness as a function of BC and ABC type cycles with TMA, DMAI and aniline as inhibitor. The GPC given in the graph was calculated from the curve slope in the linear regions.](image)

As mentioned earlier, sample analysis was performed with XPS for the Co samples. The presence of Al was quantified by integrating the Al\(_{2p}\) peaks, given in Appendix in Figure C.1, while the integrated area is plotted as a function of the number of ABC cycles for both precursors in Figure 6.13. The dashed black and red lines again indicate the Al signal for a single BC cycle on Co, for TMA and DMAI respectively. For TMA, a nucleation delay of 10 cycles can be observed, since no Al signal was detected up to that point. This delay in nucleation on Co allows for a 10-cycle selective deposition on SiO\(_2\), since no delay was observed on SiO\(_2\) in Figure 6.12 for TMA. Based on the GPC measured for ABC type cycles on SiO\(_2\) (0.89 Å/cycle), it is expected that approximately a 9 Å Al\(_2\)O\(_3\) film can be selectively deposited on SiO\(_2\), while having Co as non-growth area.

In the case of DMAI, the nucleation delay is roughly extended to 25 cycles, as depicted in Figure 6.13. However, a 5-cycle nucleation delay was also observed in Figure 6.12 on SiO\(_2\) which means that the selectivity window is approximately 20 cycles. During the first 10 cycles of that window, the GPC on SiO\(_2\) was found 0.22 Å/cycle, while for the rest 0.43 Å/cycle. As a result, 6.5 Å can be selectively deposited by using ABC type cycles with aniline and DMAI.

![Figure 6.13: Integrated Al signal for BC cycles with TMA (black) and DMAI (red). The black and red horizontal dashed lines indicate the integrated Al signal resulting from a single BC cycle on Co without inhibitor, with TMA and DMAI respectively.](image)

The above findings suggest that aniline does not perfectly meet the inhibitor requirements, since it partially adsorbs on the growth area (SiO\(_2\)) and the deposited film (Al\(_2\)O\(_3\)). Nevertheless, the nucleation
windows observed with this inhibitor were longer as compared to Hacac, which enabled selective deposition of thicker Al₂O₃ films for both Al precursors. Particularly, nucleation delay with Hacac as inhibitor was achieved only when DMAI was used, which allowed for selective deposition of only 3 Å Al₂O₃ film (assuming no Hacac adsorption on SiO₂). On the other hand, nucleation windows were observed with both Al precursors when aniline was employed. Approximately 9 Å of Al₂O₃ was selectively deposited with TMA and ~6.5 Å with DMAI. This comparative study also shows that different Al precursors can match better with different inhibitors. DMAI is more suitable when Hacac is employed, while TMA demonstrated the best results reported in this project when used in combination with aniline.
7 Conclusions

This work is focused on gaining further insight into the underlying mechanisms of area-selective $\text{Al}_2\text{O}_3$ ALD. To achieve that goal, three main questions were formulated and researched:

1. Which parameters can influence the selectivity of $\text{Al}_2\text{O}_3$ area-selective ALD?

   The *in-situ* ellipsometry (SE) measurements performed for ABC and A+BC type cycles (A: Hacac, B: TMA, C: $\text{H}_2\text{O}$ or $\text{O}_2$ plasma) suggested that the dose time and partial pressure of TMA are the dominant factors that affect precursor blocking. Based on these findings, the precursor dose should always be optimized first, and set to the minimum dose that is sufficient for saturation on the growth area. Moreover, effective precursor blocking was found to require extended Hacac doses, to ensure maximum inhibitor coverage of the non-growth area. Lastly, precursor blocking was not improved by extending the purge steps, thereby indicating that removal of gas-phase molecules and physisorbed species from the substrate surface was completed after a 3 s purge step.

2. How does the substrate temperature affect the area-selective $\text{Al}_2\text{O}_3$ ALD process?

   *Ex-situ* SE measurements for ABC type cycles with Hacac, TMA and $\text{O}_2$ plasma showed that up to a temperature of 250 $^\circ\text{C}$, precursor blocking is significantly improved with increasing temperatures. Multiple factors can contribute to this observation, and therefore the effect of temperature was further investigated by studying the following three hypotheses with *in-situ* Fourier Transform Infrared Spectroscopy (FTIR):

   (I) Reduced TMA adsorption, due to surface dehydroxylation. Increased temperatures can result in loss of hydroxyl groups (OH), which could lower the TMA adsorption and lead to lower GPC. The FTIR measurements confirmed this hypothesis, since the TMA adsorption signal on $\text{Al}_2\text{O}_3$ powders decreased by 13.0±2 % with a temperature increase from 100 $^\circ\text{C}$ to 200 $^\circ\text{C}$. The OH consumption was found decreasing by a similar percentage (11.3±2 %), thereby indicating that TMA adsorption on the Al-O-Al bridges does not take place to a large extent within the temperature range of our experiments.

   (II) Increased Hacac coverage with increasing temperature. Adsorption of additional Hacac molecules at higher temperatures means that more OH surface groups are consumed, and therefore they will not be available for TMA adsorption. Moreover, a higher Hacac coverage can hinder reactions between the precursor and the remaining OH sites more effectively by steric hindrance. This hypothesis was also confirmed by the FTIR measurements, since a temperature increase from 100 $^\circ\text{C}$ to 200 $^\circ\text{C}$ resulted in a 37% higher Hacac signal on the $\text{Al}_2\text{O}_3$ powder. Interestingly, the OH consumption did not follow the Hacac trend, which was explained by direct Hacac adsorption on the Al-O-Al bridges.

   (III) Temperature-dependent Hacac removal by TMA. Intuitively, removal of Hacac adsorbates should be kept at minimum in order to enhance precursor blocking. To investigate the effect of substrate temperature on the Hacac removal, saturated TMA doses were applied on Hacac-functionalized powders at various temperatures. The FTIR investigations for this hypothesis showed that the Hacac removal was only marginally increasing within the temperature range of 100-200 $^\circ\text{C}$. Since the increase in Hacac coverage was found sharper than the increase in Hacac removal within the same temperature range, the Hacac remainder was found larger at high temperatures (up to 200 $^\circ\text{C}$). This finding suggests that the Hacac adsorbates are strongly bonded on the surface in chelate configuration even at higher temperatures, and therefore contribute to precursor blocking. Lastly, the TMA adsorption signal on Hacac-functionalized powder decreased by 36% from 100 $^\circ\text{C}$ to 200 $^\circ\text{C}$, which is noticeably larger compared to the decrease of 13% observed as a result of dehydroxylation of the $\text{Al}_2\text{O}_3$ powder (hypothesis I). This again shows that enhanced precursor blocking at higher temperatures should be assigned to a combination of the aforementioned effects, rather than a single factor.

3. How is the selectivity affected by the inhibitor/precursor choice?

   In order to answer that question, alternative inhibitors (Hacac, aniline) and Al precursors (TMA, DMAI, TDMAA) were investigated. The FTIR studies for a single thermal BC cycle on $\text{Al}_2\text{O}_3$ powder suggested that TMA and DMAI adsorb in a self-limiting way. In contrast, the adsorbed TDMAA decomposed on the powder, which indicates CVD-like behaviour. Moreover, the $\text{H}_2\text{O}$ dose applied after the
TDMAA dose resulted in formation of OH groups in the region of hydrogen bonded OH groups (3600-3100 cm$^{-1}$), even though these species were not consumed during the TDMAA step. This behaviour could be related to the TDMAA decomposition on the Al$_2$O$_3$ powder.

Furthermore, the FTIR studies for precursor blocking (i.e. on Hacac-functionalized powders) showed that TMA blocking is very challenging. The small size of the TMA molecule allowed it to readily reach and adsorb on OH sites not consumed by Hacac (e.g. hydrogen bonded OH groups), resulting in poor blocking. Additionally, 24% of Hacac adsorbates were removed upon a saturated TMA dose, indicating that TMA is not suitable for area-selective ALD, when Hacac is employed as inhibitor. This conclusion was in line with the XPS and in-situ SE measurements performed on CoO$_x$ and HfO$_x$ samples, since the A+BC type cycles with TMA showed no nucleation delay. In contrast, exceptional blocking was observed with FTIR for DMAI and TDMAA, which was accompanied with significantly smaller inhibitor removal (3% for DMAI and 1.7% for TDMAA). The use of DMAI in A+BC type cycles resulted in a 4-cycle nucleation delay on CoO$_x$ and a 10-cycle delay on HfO$_x$, indicating that DMAI is more suitable when Hacac is used as inhibitor.

Additionally investigations with aniline as inhibitor were performed by using ABC type cycles with aniline (step A), TMA or DMAI (step B) and H$_2$O (step C). These studies showed a longer nucleation delay when employing aniline for both precursors, as compared to Hacac. A 10-cycle nucleation delay was achieved on Co with TMA, thereby enabling selective deposition of $\sim$9 Å Al$_2$O$_3$ film on SiO$_2$. Although the delay on Co with DMAI was approximately 20 cycles, this case allowed for selective deposition of $\sim$6.5 Å Al$_2$O$_3$ on SiO$_2$, due to a reduced GPC obtained with DMAI. Lastly, these experiments indicated that aniline adsorbs to some extend on Al$_2$O$_3$ and SiO$_2$, and therefore, similarly to Hacac, aniline does not show ideal selective adsorption on the non-growth area.

Interestingly, the comparative studies of alternative inhibitors and precursors showed that the inhibitor selection can determine which precursor is more suitable for the process. DMAI was more suitable when employed in combination with Hacac, whereas area-selective ALD with aniline and TMA resulted in the best results reported in this project.

Overall, the results of this work provide essential information on the fundamental mechanisms of area-selective ALD, and give insight into the factors that influence the selectivity. Area-selective ALD could be utilized to replace top-down fabrication schemes, and/or mitigate the effects resulting from bad alignment during top-down patterning. However, further investigation is required before the process can be implemented in the semiconductor industry. In future work, various alternative inhibitors and precursors could be explored, to expand the selection of different compounds and enable selective deposition of various materials. These studies can also provide further understanding on the mechanisms limiting selectivity, and therefore bring area-selective ALD closer to the applications.
8 Outlook

The findings of this work have provided deeper understanding into the area-selective Al₂O₃ ALD process. What is also important, is that through the discussion of these results new ideas for future work have been generated. In this section, additional experiments to provide further insight into Al₂O₃ area-selective ALD are discussed and suggestions for process improvement are given.

8.1 Does water remove Hacac adsorbates?

Although the removal of Hacac adsorbates by various precursors was studied in detail in this project (see section 6.2), the effect of the H₂O step on a Hacac functionalized substrate has not been investigated. Taking into account that Hacac can be applied only prior to the ALD process (see section 2.2), Hacac removal during the H₂O steps might also contribute significantly to the loss of selectivity after a few cycles. Especially for DMAI and TDMAA, where Hacac removal was found to be less than 3%, the H₂O step might be the dominant cause of Hacac removal.

Further insight into this question could be provided by performing an experiment similar to the process depicted in Figure 5.10. Instead of TMA pulses, consecutive H₂O pulses could be applied with an FTIR measurement in between. Significant removal of Hacac adsorbates during the H₂O would suggest that Hacac is not suitable for Al₂O₃ area-selective ALD, since H₂O is milder oxidizing agent compared to O₂ plasma and O₃. In such a case, alternative inhibitors should be investigated, as discussed in more detail in section 8.3.

8.2 Temperature optimization for aniline

As discussed in section 3.1.3, aniline has been reported to undergo hydrogenolysis reactions near 80 °C and dehydrogenation in a wide temperature range (70-325 °C) [102, 103]. These processes could take place to some extent during our experiments (see section 6.5), but their effect on precursor blocking requires further research. To gain more insight into that topic, precursor blocking could be studied by applying ABC type cycles on SiO₂ and Co substrates (growth and non-growth area) at various temperatures. The temperature investigation should be mostly focused on the lower temperatures, for mainly two reasons: (a) TMA and aniline decompose at a temperature of ~330 °C [15, 102], and (b) fabrication of interconnections in the BEOL should not be performed at temperatures above 400 °C to maintain the chip’s integrity [140]. These experiments would indicate the optimal process temperature and therefore can potentially improve selectivity.

Moreover, the effect of hydrogenolysis and dehydrogenation reactions on precursor blocking could be further investigated with in-situ FTIR. Aniline adsorption on metal surfaces (e.g. on Co) and precursor blocking could be studied at various temperatures, by adopting experimental procedures similar to those shown in Figures 5.6 and 5.10, with aniline doses instead of Hacac. For these experiments reflectance FTIR spectroscopy should be utilized instead of transmittance FTIR, since the free-carriers in the metal surface absorb the incident radiation [141].

8.3 Investigation of alternative inhibitors

The area-selective Al₂O₃ ALD process could be further improved with the investigation of alternative inhibitors and precursors, as shown in sections 6.3, 6.4 and 6.5. These findings suggested that the choice of inhibitor can predominantly influence the selectivity, and therefore investigation of different inhibitor molecules should be prioritized.

Aromatic molecules could be further explored, since their ring structure exhibits very high stability, while offering physico-chemically interaction pathways with substrate surfaces through their π-electrons in their aromatic ring. Based on the discussion in section 3.1.3, aromatics can typically bond on the metal surface through their functional groups (e.g. NH₂ in Figure 3.8) and/or their π-electrons. When bonding through the π-electrons, the inhibitor functional group is available for precursor adsorption. In case that these functional groups facilitate precursor adsorption, precursor blocking would be very challenging. Therefore, the inhibitor candidate should have functional groups that do not react with the precursor. For instance, benzene derivatives such as the compounds depicted in Figure 8.1b-8.1f can be considered, since TMA does not react with their functional groups [13, 82]. Moreover, benzene, which is depicted in Figure 8.1, has no functional groups, and therefore should demonstrate efficient precursor blocking, assuming a high coverage on the non-growth area. In contrast, TMA adsorption might take place on the OH group of phenol, shown in Figure 8.1g, and therefore this compound might not demonstrate efficient blocking on metal surfaces. Nevertheless, phenol has a pKₐ-value of 9.9 [142], which means that it is a weak acid (similarly to Hacac). This suggests that phenol will show only small adsorption on SiO₂ (growth-area),
and can lose the OH functional group through acid-base reactions with other dielectric surfaces (e.g. Al₂O₃). Thus, phenol could be exploited for other application possibilities of area-selective ALD. The selective inhibitor adsorption on the non-growth area could be investigated with in-situ SE and/or FTIR, similar to the Hacac and aniline studies discussed in Figures 3.4 and 3.9.

Figure 8.1: Schematic illustration of alternative aromatic inhibitor candidates for area-selective ALD of Al₂O₃.

8.4 Investigation of alternative precursors

The comparative studies in sections 6.3 and 6.5 showed that different Al precursors match better with different inhibitors, since DMAI is more suitable with Hacac, while TMA with aniline. Therefore, investigation of alternative precursors can extend the precursor options and could reveal more effective inhibitor-precursor combinations, which can improve selectivity. The Al precursor choice could be based on (but not restricted to) the requirements discussed in chapter 3. Such an example is aluminum triisopropoxide (ATIP), which is depicted in Figure 8.2. It has been utilized for Al₂O₃ deposition at a temperature range of 150-175 °C and demonstrated a GPC of 1.8 Å/cycle [143]. ATIP is bulkier than TMA and shows less reactivity towards OH and H₂O groups on a Al₂O₃ surface, as suggested by a DFT study [143]. This is attributed to the higher adsorption and dissociation energy of ATIP, as compared to TMA. The large molecular size of ATIP, paired with its lower reactivity suggest that this compound could be a more suitable precursor for area-selective ALD of Al₂O₃.

Figure 8.2: Schematic illustration of ATIP molecule. The Al center is bonded to three propoxide ligands [144].
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Appendices

A FTIR measurements for ALD processes using TMA, DMAI and TDMAA

Figure A.1: *In-situ* FTIR saturation spectra for (a) TMA, (b) DMAI and (c) TDMAA adsorption on Al₂O₃-coated powder.
Figure A.2: In-situ FTIR saturation spectra after \( \text{H}_2\text{O} \) pulses on adsorbed (a) TMA, (b) DMAI and (c) TDMAA on Al\(_2\)O\(_3\)-coated powder.

**B  XPS measurements for A+BC type cycles with Hacac**

Figure B.1: Al 2p signal related to Al\(_2\)O\(_3\) for A+BC type thermal cycles on CoO\(_x\) samples with (a) TMA and (b) DMAI. The black curves show the signal from 1 BC cycle on CoO\(_x\) sample without inhibitor.
C XPS measurements for ABC type cycles with aniline

Figure C.1: Al2p signal related to Al2O3 for ABC type cycles with (a) TMA and (b) DMAI.