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Plasma assisted and thermal atomic layer deposition of Al2O3 in the Oxford Instruments OpAL reactor

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Plasma assisted and thermal atomic layer deposition of \( \text{Al}_2\text{O}_3 \) in the Oxford Instruments OpAL reactor.

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Abstract

$\text{Al}_2\text{O}_3$ is a transparent, high-k dielectric material which can be used for different applications, e.g. as surface passivation film for c-Si solar cells and as dielectric in MOS trench capacitors. For these applications a deposition method is required, that provides good uniformity and conformality. Atomic layer deposition (ALD) is a low temperature (~RT-400 °C), deposition method that fulfills these requirements. ALD is based on two alternately executed half reactions, separated by purge steps. Because the two half reactions are self-limiting a sub-monolayer is deposited per cycle which offers precise thickness control. Two methods of ALD can be distinguished: plasma-assisted ALD and thermal ALD.

The Oxford Instruments OpAL reactor is a new ALD reactor that is suitable for both (remote) plasma-assisted ALD and thermal ALD. In this thesis both the plasma-assisted and thermal ALD process are characterized for deposition of $\text{Al}_2\text{O}_3$ at a substrate temperature of 250 °C in the OpAL reactor. By varying precursor dosing, purge times and plasma exposure time, true saturating ALD processes are developed for both plasma-assisted and thermal ALD with a cycle times of 8 s and 10 s respectively, while a good uniformity is obtained.

Temperature series for temperatures ranging from 50 °C to 400 °C are performed for both plasma assisted and thermal ALD. The material properties and the reaction mechanisms are investigated and compared. For plasma-assisted ALD the growth per cycle decreases monotonously for increasing temperature due to dehydroxylation. The activation energy for this dehydroxylation reaction is 0.216 eV, calculated using the Arrhenius equation. For thermal ALD >250 °C the growth per cycle also decreases due to dehydroxylation for increasing temperature. For <250 °C the growth per cycle increases for increasing substrate temperature. This could be explained by incomplete reactions during the oxidation step for low temperatures. An additional explanation might be a higher amount of recombination of OH-groups due to extended purge times.

For both plasma-assisted and thermal ALD stoichiometric $\text{Al}_2\text{O}_3$ is deposited at the high temperature (400 °C) while at lower temperatures a surplus of O is present. The mass density of the deposited films increases for increasing temperature, while the hydrogen concentration in the deposited layers decreases. Furthermore the refractive index of the deposited films shows correlation to the mass density and the hydrogen content of the deposited films. For increasing refractive index the mass density increases, while the hydrogen content decreases.
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Al₂O₃ is a versatile material that can be used in many applications. In industry Al₂O₃ is mostly produced by the Bayer process from bauxite. It is mostly used in the aluminum production, but because of its hardness and high melting point it can also be used as an abrasive. Al₂O₃ can also be used as a thin film. With properties, like high dielectric constant, transparency, thermal and chemical stability Al₂O₃ is researched for many applications, for example as passivation layer in solar cells, in trench MOS capacitors, as moisture barrier for organic light emitting diodes and for corrosion protection layers. In section 1.1 these applications of Al₂O₃ are discussed. In section 1.2 atomic layer deposition, a low temperature deposition method for Al₂O₃, is introduced. The goals of this work are explained in section 1.3, while in section 1.4 the outline of this work is given.

1.1 Applications of Al₂O₃

1.) Al₂O₃ for surface passivation in c-Si solar cells:

The surface of c-Si solar can be seen as a severe interruption of the crystalline structure. A high amount of defect states is present at the surface, offering recombination sites for the charge carriers. Al₂O₃ does not only provide chemical passivation (reduction of interface defects), but due to the large fixed negative charge density located at the c-Si/Al₂O₃ interface it also provides field-effect passivation for crystalline silicon (electrostatic shielding of minority charge carriers). Furthermore, Al₂O₃ is transparent, allowing transmission of solar radiation. Hoex et al.[2] and Agostinelli et al. [3] demonstrated that Al₂O₃ provides excellent surface passivation for p-doped c-Si.
CHAPTER 1. INTRODUCTION

Figure 1.1: $\text{Al}_2\text{O}_3$ as rear surface passivation layer for a PERC (passivated emitter and rear cell)-type crystalline silicon solar cell.[1]

Dingemans et al. [4] showed that the best passivation is obtained at a deposition temperature between 150 °C and 250 °C. For the use of $\text{Al}_2\text{O}_3$ as passivation layer, the thin films require good uniformity and a good chemical and thermal stability.

2.) $\text{Al}_2\text{O}_3$ in trench metal-oxide-semiconductor (MOS) capacitors:

Because of the constant drive in the semiconductor industry to miniaturization, $\text{SiO}_2$ does not satisfy the requirements anymore as oxide in MOS technologies, and replacement by another oxide is required. In MOS capacitors the performance improves when the thickness of the oxide dielectric is reduced. However the high-k dielectrics must maintain a low leakage current and a high breakdown voltage. $\text{Al}_2\text{O}_3$ combines the property of a high dielectric constant (~ 9), with a relative low leakage current and a relative high breakdown voltage. Hoogeland et al report low leakage currents and high breakdown voltages for thin $\text{Al}_2\text{O}_3$ films in TiN/$\text{Al}_2\text{O}_3$ stacks for MIMIM trench capacitor [5]. High conformality and uniformity are required for the fabrication of $\text{Al}_2\text{O}_3$ films for this application.

3.) $\text{Al}_2\text{O}_3$ as moisture permeation barrier for organic light emitting diodes (OLEDs):

The development of OLEDs may lead to inexpensive, efficient displays. However they require a good barrier against $\text{H}_2\text{O}$ and $\text{O}_2$ permeability. The deposition temperature should be below 110 °C, to remain below the glass temperature of polymers. Atomic layer deposition (ALD), see section 1.2) of $\text{Al}_2\text{O}_3$ is a low temperature deposition method that is known for its excellent uniformity and conformality. Furthermore the material deposited with ALD is generally dense and virtually defect-free. In combination with transparency and good water vapor transmission rate [6, 7] $\text{Al}_2\text{O}_3$ provides good permeation barrier performance for OLEDs.

4.) $\text{Al}_2\text{O}_3$ for corrosion protection

$\text{Al}_2\text{O}_3$ is a chemical resistant material with high hardness. These properties make $\text{Al}_2\text{O}_3$ capable for corrosion protection of steel materials. However the deposition tem-
1.2. ATOMIC LAYER DEPOSITION

Figure 1.2: OLEDs encapsulated in Al₂O₃ permeation barrier. In the inset the electroluminescence of a working OLED. The absence of black spots indicates a defect-free permeation barrier.

perature is required to be as low as possible, with a maximum deposition temperature of 160 °C, to avoid structural changes in the steel. Matero et al. reported that Al₂O₃ films and TiO₂-Al₂O₃ multilayer structures, grown by atomic layer deposition, provide reasonable protection to some extent [8].

1.2 Atomic layer deposition

A method of producing Al₂O₃ films is atomic layer deposition (ALD). ALD is a chemical vapor deposition method that is capable of growing high quality thin films. The deposition is controlled at the atomic level by self-limiting surface reactions of the substrate with reactive precursor gases, creating films providing precise thickness control, excellent uniformity over large areas, excellent conformality and low pinhole density. The temperature range of ALD of Al₂O₃ is from room temperature to ~ 400 °C.

The start of the development of ALD dates back to the 1960’s, when in Russia the group of Aleskovskii started growing TiO₂ and GeO₂[9]. In the 1970’s, Suntala and co-workers also developed an ALD process, separate from the Russian group. Their work started with the ALD process of growing ZnS, SnO₂ and GaP. During the starting years ALD was generally referred to as atomic layer epitaxy. The name atomic layer deposition dates back to the early 1990’s. From 1974 research was also started on the growth of Al₂O₃, for which Al(CH₃)₃ and H₂O were used as precursor gases. The growth of Al₂O₃ by ALD became, and still is, one of the most researched ALD processes and is usually considered as a model system for ALD. Over the years a lot of precursors were
used in ALD of Al₂O₃. Among others AlCl₃ and AlBr₃ were tested as precursor, while NO₂ was tested as precursor for the oxidation step. However the Al(CH₃)₃/H₂O process is considered an ideal process for thermal ALD, using highly reactive, but at the same time thermally stable, precursors and the gaseous reaction product CH₄ does not interfere with the process. An alternative for the oxidation step in the thermal process is the use of ozone (O₃) as precursor. O₃ is a more reactive precursor than H₂O, which can result in deposition of films with good properties at lower substrate temperatures.

Another development in ALD was the development of plasma-assisted ALD. In thermal ALD processes, the reactions between the precursor and the surface are thermally activated reactions between the precursor and the substrate surface. In oxidation reactions, the thermally activated reaction can be replaced by a reaction between radicals (O atoms) in a plasma and surface functional groups of the substrate. This is called plasma-assisted ALD. In the Plasma and Materials Processing Group at Eindhoven University of Technology a lot of experience exists with respect to plasma-assisted ALD. The research started with the home-built plasma-assisted ALD reactor “ALD-I”[10]. Later a beta-version of the Oxford Instruments FlexAL reactor was installed, which was co-developed by our group[11]. This reactor is capable of growing films by both plasma-assisted and thermal ALD. In July 2008, the Oxfords Instruments OpAL reactor was installed. The OpAL reactor is quite similar to the FlexAL reactor, although some features are omitted.

1.3 Goals

The applications discussed in section 1.1 require a low temperature deposition technique of Al₂O₃. Atomic layer deposition is a low temperature deposition technique that is capable of growing thin films with good uniformity and conformality. In July 2008, the Oxford Instruments OpAL reactor was installed at Eindhoven University of Technology. To deposit Al₂O₃ in a true ALD process while obtaining good uniformity, the process first should be fully characterized. The first goal of this thesis is to fully characterize the ALD process of Al₂O₃ for the newly installed OpAL reactor. For both plasma-assisted and thermal ALD true ALD processes were developed, providing good uniformity, while the process time was to remain as short as possible.

Different applications require different material properties, and different deposition temperatures. Another goal in this thesis is to compare the material properties and to gain information about the growth mechanisms of plasma-assisted and thermal ALD for various deposition temperatures. For various temperatures, in the range from 50 °C
to 400 °C, Al₂O₃ films were deposited. Growth rates and material properties, such as composition and mass density, were investigated and compared.

1.4 Outline

This work is structured as follows. In Chapter 2, the principles of both plasma-assisted and thermal ALD are explained. Furthermore other low temperature deposition techniques of Al₂O₃ are discussed in section 2.2. In chapter 3 the experimental procedures are discussed. An extensive description of the Oxford Instruments OpAL reactor is given and the diagnostics used for characterizing the ALD processes and the material properties are described. Furthermore an overview of the performed experiments is given. In chapter 4 the results are presented of the optimization of the ALD processes are optimized for a substrate temperature of 250 °C. In chapter 5 temperature series are performed and the material properties and growth mechanisms of both plasma-assisted and thermal ALD are compared for different temperatures. In chapter 6 the general conclusions of this thesis are summarized.
Atomic layer deposition (ALD) is a film deposition technique that is capable of growing ultra-thin films with precise thickness control. In section 2.1 the principles of ALD, and especially the growth of Al₂O₃, are explained. A distinction is made between plasma-assisted and thermal ALD. In section 2.2 the ALD process of Al₂O₃ is compared to other (low temperature) deposition techniques for Al₂O₃.

2.1 Atomic Layer Deposition of Al₂O₃

Chemical vapor deposition (CVD) is a chemical process to deposit thin film solid materials. In general, a wafer is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce a thin film. There are several different forms of CVD, e.g. plasma enhanced CVD (PECVD) and metal-organic CVD (MOCVD). One particular CVD technique for which interest has been growing since the late 1990’s is atomic layer deposition (ALD). ALD is capable of growing ultra-thin films. The deposition is controlled by self-limiting surface reactions through alternate exposure of the substrate surface to different gas-phase precursors. This enables precise thickness control.

ALD is a cyclic process that typically consists of two self-limiting half reactions (see figure 2.1). The substrate is first exposed to a gas phase reactant. This precursor reacts with a surface functional group, creating volatile product molecules that desorb from the surface leading to a new surface functional group that is not reactive with the precursor. Subsequently the first precursor and the reaction products are pumped away,
CHAPTER 2. ALD AND OTHER DEPOSITION TECHNIQUES FOR AL$_2$O$_3$

Figure 2.1: Schematic illustration of an ALD cycle. In the first half-cycle the surface is exposed to the first precursor, enabling a reaction between the precursor molecules and surface functional groups. After purging the reactor, the surface is exposed to a second reactant to enable a reaction for the newly formed surface functional groups and to regenerate the original type of surface functional groups. After pumping away the precursor and the reaction products the ALD cycle starts over.

after which the substrate is exposed to a second reactive precursor. This precursor reacts with the new surface functional groups, creating identical surface functional groups as the process started with. The volatile product molecules and the second precursor are pumped away, and one ALD cycle is finished. Ideally one sub-monolayer of material is grown during one ALD cycle. This provides the ability to increase the film thickness layer-by-layer by repeating ALD cycles, which enables precise thickness control. Furthermore excellent uniformity and conformality are provided, since the species at a certain surface site cannot react more than once, regardless of the incoming particle flux and size or shape of the surface. This is distinct from other CVD processes, where the reaction between the precursor molecules and the substrate is controlled by the precursor flux, i.e. more precursor flux leads generally to more growth.

The most common method of ALD is thermal ALD. In thermal ALD the substrate is positioned in a heated reactor and exposed to an alternating pulse of precursors, separated by intermittent purge gas flows. During the precursor exposure thermally activated chemisorption reactions between the surface functional groups and the precursors take place. In general a flux of precursor molecules flows through the reactor, passing the substrate. Two concepts of reactors exist: the cross flow concept, in which the precursors flow parallel to the substrate (often in a kind of “pulse-train” mode), and the perpendicular flow concept, in which the precursor is injected in the reactor from the top of the reactor flowing perpendicular to the substrate towards a pump situated
2.1. ATOMIC LAYER DEPOSITION OF AL$_2$O$_3$

Figure 2.2: Thermal ALD process of Al$_2$O$_3$: 1) The surface is exposed to the precursor Al(CH$_3$)$_3$. 2) The reactor is purged. 3) The surface is exposed to H$_2$O. 4) The reactor is purged.

below the substrate (e.g. through a showerhead-type electrode).

Another ALD method is the plasma-assisted ALD process. In a typical plasma-assisted ALD process a plasma is created in at least one of the half-reactions. The substrate is exposed to this plasma and the radicals in the plasma react with the substrate functional groups to create new substrate functional groups. In the plasma-assisted step the reactions occur due to the reactivity of the radicals, and thermal energy to activate the surface reactions is less important as compared to thermal ALD.

Three different concepts of plasma-assisted ALD exist: radical enhanced ALD, direct plasma ALD and remote plasma ALD. Radical enhanced resembles thermal ALD the closest. Radicals are generated in a plasma source located remotely from the reaction chamber itself and injected into the reactor. In the reactor the radicals react with the substrate. In radical enhanced ALD the surface mostly reacts with the afterglow of the plasma, because of the large distance between the source and the substrate. In direct plasma and remote plasma ALD an active plasma is used for the reaction. In both methods the plasma is created inside the reactor. In direct plasma the plasma is generated between two parallel placed electrodes by applying RF-power to the upper electrode. The substrate is placed on the lower electrode, and is directly involved in the creation of the plasma. In remote plasma ALD a plasma source is connected to the reactor and located at a distance (typically in the order of a couple of decimeters) from the substrate. The plasma diffuses from the plasma source towards the substrate. Remote plasma ALD is the plasma-assisted ALD method addressed in this thesis.
Chapter 2. ALD and Other Deposition Techniques for Al₂O₃

Thermal atomic layer deposition of Al₂O₃ is one of the most researched ALD processes. Figure 2.2 shows a schematic representation of the thermal ALD process. Al(CH₃)₃ is generally used as precursor for the first half cycle. Methyl groups in the precursor react with surface OH-groups in a ligand exchange reaction, creating O-Al bonds at the substrate surface. The reaction proceeds through the formation of an Al-O Lewis acid-base complex followed by CH₄ formation. The reaction is investigated using density functional theory [12] and the reaction path is drawn in figure 2.3a. The half-cycle is exothermic with an overall enthalpy of reaction of 1.70 eV.

The reaction in the first half cycle can be summarized as [9]:

\[
\text{AlOH}^* + \text{Al(CH₃)₃(g)} \rightarrow \text{AlOAl(CH₃)₂}^* + \text{CH₄(g)}
\]  

(2.1)

where the asterisks designate the surface groups. After the reaction the reactor is purged by a non-reactive gas to remove the excess precursor and the reaction products.

In the second half-cycle the methyl surface is exposed to an oxidant, to exchange the methyl groups for OH-groups. In thermal ALD the surface is exposed to the sec-
2.1. ATOMIC LAYER DEPOSITION OF AL$_2$O$_3$

Figure 2.4: Plasma-assisted ALD process of Al$_2$O$_3$: 1) The surface is exposed to the precursor Al(CH$_3$)$_3$. 2) The reactor is purged. 3) The surface is exposed to an O$_2$ plasma. 4) The reactor is purged.

For plasma-assisted ALD the reaction mechanisms is researched less extensively. In figure 2.4 the plasma-assisted ALD process is depicted. After the first half cycle mainly CH$_3$ surface groups are detected by infrared spectroscopy[13], indicating that the first half-reaction is the same reaction as for the first half-cycle of thermal ALD. The oxidation step however is different. As oxidant an O$_2$ plasma is used. Infrared spectroscopy showed that mainly OH surface groups are created during the reaction [13], while CO, CO$_2$ and H$_2$O were detected as reaction products by quadrupole mass spectroscopy [14]. Combustion-like reactions between oxygen radicals in the plasma and methyl-groups at the surface, in which OH-groups are formed at the surface and the volatile reaction products H$_2$O and CO$_2$ are produced, are proposed by Langereis et al.[13]. The proposed reaction is summarized by:

\[ \text{AlCH}_3^+ + 4O(g) \rightarrow \text{AlOH}^* + \text{CO}_2(g) + \text{H}_2\text{O}(g) \]  \(2.3\)
CHAPTER 2. ALD AND OTHER DEPOSITION TECHNIQUES FOR Al₂O₃

In the plasma-assisted ALD processes the volatile reaction products can react with electrons in the plasma to other reaction products. This will be discussed in section 3.2.2.

For both plasma-assisted and thermal ALD the reactor is purged by a non-reactive gas after the oxidation reaction.

2.2 Other deposition techniques

Deposition of Al₂O₃ by means of ALD, is a low temperature deposition method capable of depositing uniform films over large areas. Precise thickness control is provided, while the deposited films are stoichiometric Al₂O₃ and low contamination levels are reported[15]. The biggest disadvantage of ALD is the relative low deposition rate (~1 Å/cycle). In this section ALD is compared to other low temperature Al₂O₃ deposition techniques.

Table 2.1 shows a list of low temperature (<400 °C) deposition techniques of Al₂O₃. In this list most deposition techniques are CVD processes. In a CVD process the substrate is exposed to one or more volatile precursors which react and/or decompose on the surface. In general these reactions are thermally activated. However, there are CVD techniques in which the reactions are activated by other means, and the substrate temperatures can be lowered. In plasma-enhanced CVD (PECVD) radicals are created in a plasma, which react with the surface. In laser-assisted CVD (LACVD) radicals are created by directly above the substrate by a laser beam.

Another low temperature deposition technique Al₂O₃ is sputtering. In sputtering a solid target material is bombarded by energetic particles. Atoms are ejected from the target material and condense on the substrate. In RF-sputtering a plasma is created by a RF-source, and ions created in the plasma bombard the target material.

The growth rates for the CVD processes differ, due to the different reactors, deposition settings and precursors used. For all CVD processes however, the growth rates exceeds the growth rate of ALD processes (in general the growth rate ≥ 1 Å/s). In RF-sputtering the growth rate exceeds the growth rate of ALD as well (2.8 Å/s). For both sputtering and the CVD processes however the uniformity and conformity of films is worse then for films deposited by ALD. Unlike other CVD processes, in ALD the thickness is controlled by self-limiting reactions and the same amount of material is deposited everywhere, providing good uniformity and conformity. In CVD and sputtering processes the deposition rate is regulated by the flux of precursor on the surface. Only the uniformity and conformity in pulsed PECVD comes close to ALD. In this
PECVD process, the substrate is exposed to plasma pulses, while being exposed to both O\textsubscript{2} and precursor Al(CH\textsubscript{3})\textsubscript{3}. This results in a controlled growth per cycle, providing a fairly good uniformity and conformality [16].

The material properties of the different deposition methods are mostly dependent of the deposition settings. The O/Al ratio for all deposition techniques is around 1.5, corresponding to stoichiometric Al\textsubscript{2}O\textsubscript{3}. The mass densities of the different deposition techniques in general is between 2.4 and 3.2 g/cm\textsuperscript{3} which is lower than crystalline Al\textsubscript{2}O\textsubscript{3} (3.97 g cm\textsuperscript{-3}). In most processes low levels of carbon contamination is present in the films. Also hydrogen contamination was detected in some processes. In ALD and PECVD[4] the hydrogen concentration increased for decreasing substrate temperatures.
Table 2.1: Summary of low temperature (<400°C) deposition techniques for Al₂O₃. Deposition characteristics and the material properties of the deposited films are included in this table. In the first two rows the result for the OpAL reactor, obtained in this work, are included.

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>Precursors</th>
<th>Substrate</th>
<th>Temperature (°C)</th>
<th>Growth rate (Å/s)</th>
<th>Uniformity/Conformality</th>
<th>Refractive index</th>
<th>Mass density (g/cm³)</th>
<th>O/[Al] ratio</th>
<th>Carbon and Hydrogen content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma-assisted ALD (OpAL)</td>
<td>Al(CH₃)₃ and O₂</td>
<td>50-400</td>
<td>0.13-0.15</td>
<td>+</td>
<td>1.59-1.66</td>
<td>3.3-6.7</td>
<td>3.3-5.0</td>
<td>1.5-2.0</td>
<td>C (&lt;10 at%), H (1-13 at%)</td>
</tr>
<tr>
<td>Thermal ALD (OpAL)</td>
<td>Al(CH₃)₃ and H₂O</td>
<td>100-400</td>
<td>0.04-0.10</td>
<td>?</td>
<td>1.60-1.67</td>
<td>2.6-3.3</td>
<td>1.5-1.7</td>
<td>C (&lt;10 at%), H (2-12 at%)</td>
<td></td>
</tr>
<tr>
<td>Plasma-assisted ALD</td>
<td>Al(CH₃)₃ and O₂</td>
<td>25-300</td>
<td>0.25-0.43</td>
<td>++</td>
<td>?</td>
<td>2.6-3.0</td>
<td>1.5-2.1</td>
<td>C (&lt;1 at%), H (3-15 at%)</td>
<td></td>
</tr>
<tr>
<td>Thermal ALD</td>
<td>Al(CH₃)₃ and H₂O</td>
<td>100-300</td>
<td>~0.25</td>
<td>+++</td>
<td>?</td>
<td>2.6-2.9</td>
<td>1.5-1.6</td>
<td>C (&lt;1 at%), H (3-8 at%)</td>
<td></td>
</tr>
<tr>
<td>Thermal ALD</td>
<td>Al(CH₃)₃ and O₃</td>
<td>150-300</td>
<td>0.06-0.10</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>CVD</td>
<td>AlC₅H₇O₂</td>
<td>250-600</td>
<td>0.13-1.67</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>~1.5</td>
<td></td>
</tr>
<tr>
<td>PECVD</td>
<td>Al(CH₃)₃ and O₂</td>
<td>50-300</td>
<td>0.8-4.0</td>
<td>?</td>
<td>1.52-1.60</td>
<td>2.4-3.2</td>
<td>1.4-2.2</td>
<td>H (1-15 at%)</td>
<td></td>
</tr>
<tr>
<td>PECVD</td>
<td>Al(CH₃)₃ and O₂</td>
<td>300</td>
<td>16.7</td>
<td>?</td>
<td>1.61</td>
<td>3.2</td>
<td>1.67</td>
<td>C (4 at%)</td>
<td></td>
</tr>
<tr>
<td>Pulsed PECVD</td>
<td>Al(CH₃)₃ and O₂</td>
<td>&lt;150</td>
<td>~1</td>
<td>?</td>
<td>~1.58</td>
<td>2.85</td>
<td>1.5</td>
<td>C (0.3 at%), H (4 at%)</td>
<td></td>
</tr>
<tr>
<td>LACVD</td>
<td>Al(CH₃)₃ and N₂O</td>
<td>RT-450</td>
<td>33.3-66.7</td>
<td>+</td>
<td>1.54-1.66</td>
<td>?</td>
<td>1.44</td>
<td>C (&lt;1 at%)</td>
<td></td>
</tr>
<tr>
<td>RF-sputtering</td>
<td>Al and O₂</td>
<td>200</td>
<td>2.8</td>
<td>?</td>
<td>1.62</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>

---

As well, Table 2.1: Summary of low temperature (≤400°C) deposition techniques for Al₂O₃. Deposition characteristics and the material properties of the deposited films are included in this table. In the first two rows the result for the OpAL reactor, obtained in this work, are included.
3

Experimental procedures

In this chapter experimental procedures for the Al₂O₃ deposition process are described. In section 3.1 an extensive description of Oxford Instruments OpAL reactor is given and compared to the FlexAL reactor. Diagnostics used during and after experiments are described in section 3.2. Finally, in section 3.3 the experiments and the experiment settings are described.

3.1 ALD reactors

In July 2008 the Oxford Instruments OpAL reactor was installed in the clean-room at the University of Technology, Eindhoven. The ALD reactor resembles the Oxford Instruments FlexAL reactor, which is described by Heil et al[11] and which is also installed in the clean-room. Both reactors are capable of plasma-assisted ALD and thermal ALD. However there are some distinct differences between the reactors. In this section the OpAL reactor is described extensively and compared to the FlexAL reactor.

3.1.1 OpAL reactor

In 3.1a a schematic representation of OpAL is depicted, while a photo of the reactor is shown in 3.1b. The reactor consists of a deposition chamber to which a pump unit and a plasma source are connected through gate valves. The aluminum deposition chamber is optimized to minimize the volume and the presence of dead spaces while
Figure 3.1: a) Schematic representation of the Oxford Instruments OpAL reactor and b) picture of the Oxford Instruments OpAL reactor with a spectroscopic ellipsometer mounted on the reactor.
3.1. ALD REACTORS

Figure 3.2: The substrate stage with an 8” silicon wafer placed on it. In the reflection of the wafer the precursor inlets can be seen in the upper part of reaction chamber.

Figure 3.3: The OpAL reactor with the upper part of the reactor elevated.

maintaining a good film uniformity and pumping capacity. A 238 mm diameter substrate holder is located in the center of the deposition chamber and its temperature can be actively controlled between room temperature and 400 °C. The temperature of the walls of the reaction chamber can be controlled independently between room temperature and a maximum temperature of 180 °C. To facilitate cleaning of the walls the reaction chamber is fitted with removable liners, which can be cleaned by bead blasting. The OpAL reactor is an open-load system: the upper part of the reaction chamber can be elevated by a hoist to load substrates into the reactor.
A 63 m³/hr sliding vane rotary pump, which is situated one floor below the reactor (i.e., in the subfab of the clean-room), pumps the reaction chamber to a base pressure of approximately 0.5 mTorr. The operating pressure in the chamber during processing is in the range of 100-800 mTorr. A gate valve is positioned in between the reaction chamber and the pump in order to be able to isolate the pump from the chamber (e.g., for the case of venting to atmosphere of the reactor). The valve and the piping towards the pump are heated to prevent precursor condensation.

The plasma is generated by a remotely placed inductively coupled plasma source. The source can deliver up to 300 W of radio frequency power at 13.56 MHz and is controlled by an automated matching network. The source consists of a three turn water-cooled copper coil around a 65 mm Al₂O₃ ceramic plasma tube. Four gases, H₂, N₂, O₂, and NH₃, are connected to a common plasma source gas line. The flow of the plasma source gases is controlled independently by dedicated mass flow controllers (maximum range is 100 sccm) located in an extractable gas cabinet. There is no special gas mixing besides in the plasma source line when two or more source gases are used simultaneously. The source gases are fed axially into the plasma tube and the plasma species diffuse through the 100 mm gate valve into the conical shaped deposition chamber. When depositing conductive films the gate valve is closed during the precursor dosing to prevent film deposition inside the source. When using the reactor for thermal ALD, the gate valve can also remain closed to reduce the chamber volume. In that case the reducing or oxidizing gases can directly be injected into the chamber. Also Ar is connected as a purge gas, and is injected into the chamber below the gate valve. The Ar is also controlled by a dedicated mass flow controller and has a maximum flow of 50 sccm.

Vapor drawn liquid and solid precursors can be delivered into the process chamber from bubblers or precursor pots. Three precursor pots are situated in an extracted cabinet. The precursor is delivered into the chamber by fast ALD valves with a minimum opening time of 10 ms. Because the valves are located approximately 30 cm from the deposition chamber, the lines to the chamber can be purged by Ar gas after precursor dosing. The precursors are injected into the deposition chamber above the substrate stage through inlets positioned below the gate valve to the plasma source. Depending on the vapor pressure of the precursor, the delivery can be either vapor drawn or via bubbling with Ar carrier gas. The precursor pots, the delivery lines, and the ALD valves are separately heated (up to 180 °C).
3.1. ALD REACTORS

A separate water precursor pot, which enables thermal ALD (with H\textsubscript{2}O) whenever required, is situated in the main frame below the reaction chamber. However during initial experiments it turned out that the temperature of the water in the precursor pot was approximately 32 °C. This temperature corresponds to a vapor pressure of 5.4 kPa (calculated using the Clausius–Clapeyron equation[25]) . Because of this high vapor pressure a lot of water entered the reaction chamber during H\textsubscript{2}O dosing. High doses of water are difficult to remove completely from the reactor, creating an accumulation of water in the reactor during the process. This continuous presence of water during the reaction allowed unwanted CVD processes to take place, since both precursors were present in the reactor at the same time. This was solved by cooling the water precursor pot to a temperature of approximately 20 °C. This was done by a home made cooling system, in which cooling water flows around the precursor pot. Since the vapor pressure of H\textsubscript{2}O is 2.8 kPa at 20 °C, the water doses are smaller. This prevents parasitic CVD processes in the case that the reaction chamber is sufficiently purged after water dose.

The reactor operation is completely automated and computer controlled. In a graphical user interface different menus exist for setting up process recipes. Diagnostic ports with windows are mounted under a 70° angle to the substrate stage to allow in-situ spectroscopic ellipsometry measurements for real-time measurements of film thickness and optical properties of the films. The windows are valved off during deposition. An additional analytical port positioned above the plasma source allows optical emission spectroscopy of the plasma.
3.1.2 OpAL vs FlexAL

Although the OpAL reactor and the FlexAL reactor show a lot of similarities there are some differences. The main differences are:

- FlexAL is pumped by a turbo pump which is backed by a rotary vane pump which gives it a base pressure of ~ $10^{-6}$ mTorr in comparison to a base pressure of ~ 0.5 mTorr in OpAL which is only pumped by a rotary vane pump. The operating pressure in FlexAL is in the range of 10 - 80 mTorr, while for OpAL the operating pressure is in the range of 100 - 800 mTorr.

- In FlexAL the pressure is controlled independently by a butterfly valve, while for OpAL the pressure is flow dependent.

- While OpAL is an open load system, in FlexAL the wafers are loaded through a loadlock. This provides OpAL with two advantages: faster wafer loading, and the possibility of loading 3d objects. A disadvantage is that contamination can easier enter the reaction chamber.

- OpAL has a fixed water precursor pot next to the three precursor pots in the precursor cabinet. This enables thermal ALD whenever required. Currently,
3.2 Diagnostics

FlexAL only has two precursor pots and no fixed water precursor pot.

- FlexAL is connected to the process gases H\textsubscript{2}, N\textsubscript{2}, O\textsubscript{2}, NH\textsubscript{3} and SF\textsubscript{6} while OpAL is not connected to SF\textsubscript{6}. SF\textsubscript{6} can be used as a cleaning gas for the reactor. However, in OpAL the reactor walls are fitted with removable liners, which can be cleaned by bead blasting.

- In both FlexAL and OpAL the precursor is injected into the reaction chamber by direct vapor. However, for OpAL the ALD valve is located approximately 30 cm from the reactor. This makes it advisable to purge the lines by Ar after dosing.

3.2 Diagnostics

The diagnostics used to characterize the deposition of Al\textsubscript{2}O\textsubscript{3} process are:

- Spectroscopic ellipsometry.
- Optical emission spectroscopy.
- Rutherford backscattering spectrometry and elastic recoil detection.
- Fourier transform infrared spectroscopy.

3.2.1 Spectroscopic ellipsometry

Spectroscopic ellipsometry (SE) can be used to determine layer thickness and optical properties of deposited films. In-situ spectroscopic ellipsometry is used to determine the growth rate of the Al\textsubscript{2}O\textsubscript{3} during the deposition process and ex-situ spectroscopic ellipsometry are performed to determine the uniformity of the deposited films and to determine the thickness and the refractive index for the temperature series.

Ellipsometry measures the change of polarization of light which is reflected from the measured sample. Depending on the dielectric constants and the thicknesses of the layers in the sample, the polarization of the light changes because of the different reflection coefficients for the p-polarized and the s-polarized light. From the change in amplitude ratio \( \Psi \) and the phase difference ratio \( \Delta \) of the p-polarized and the s-polarized light material properties such as dielectric function, refractive index and thickness are determined. In spectroscopic ellipsometry, light with a broad range of photon energies is used which makes it possible to measure the optical constants as a function of photon energy, which allows more precise results. A more detailed explanation of spectroscopic ellipsometry can be found in reference [26].
CHAPTER 3. EXPERIMENTAL PROCEDURES

Three different spectroscopic ellipsometers, with different photon energies ranges (J.A. Woollam M2000U, 1.2-5.0 eV; M2000D with NIR extension, 1.2-6.5 eV; M2000U, 0.75-5.0 eV), have been used to determine the thicknesses and refractive indices of the deposited films. Each SE measurement consisted of 100 measurements to obtain a high signal-to-noise ratio. Analysis of the results was performed by the WVASE32 software. An optical model, defining the optical constants and the layers thickness, is required to analyze the results. The WVASE32 software program analyzes the results by calculating the $\Psi$- and $\Delta$-spectra from the model and comparing it to the measured $\Psi$- and $\Delta$-spectra in an iterative process minimizing the mean-squared error (MSE) of the fit.

The silicon substrate is modeled by a temperature dependent semi-infinite c-Si layer topped with a native oxide layer. Before deposition the temperature of the c-Si layer and the thickness of the native oxide are fitted. Because $\text{Al}_2\text{O}_3$ has an optical band gap $E_{\text{opt}} \approx 8.8$ eV it is non-absorbing in the wavelength range used by the ellipsometers. Therefore a standard Cauchy relation can be used to describe the dispersion of the refractive index $n$ [27]:

$$n = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4},$$

in which $A_n$, $B_n$ and $C_n$ represent the Cauchy fit parameters and $\lambda$ represents the wavelength in micrometers. The Cauchy fit parameters and the thickness are fitted to determine the refractive index and the thickness of the deposited film. In figure 3.6 the Cauchy relation is plotted for a typical $\text{Al}_2\text{O}_3$ film. The refractive index decreases rapidly for low wavelengths to stabilize at a constant level for wavelengths $\gtrsim 500$ nm. For measurements of refractive indices in this report the refractive index at 630 nm is used.

The growth per cycle is determined by measuring the thickness of the films by in-situ SE after a certain number of cycles are performed. Figure 3.7 shows the results of in-situ measurements for the deposition of a $\text{Al}_2\text{O}_3$ film. In general the growth per cycle is constant for ALD, since it is a self-limiting process. The growth per cycle is determined by dividing the thickness difference between two measurements by the number of cycles. In general the growth per cycle is determined by averaging the results of 4 series of 20 cycles.
3.2. DIAGNOSTICS

Figure 3.6: The refractive index measured as a function of the wavelength for a typical Al₂O₃ film. The refractive index is determined by the Cauchy relation (equation 3.1). The Cauchy parameters are \( A_n = 1.65, B_n = 2.7 \times 10^{-3} \mu m^2 \) and \( C_n = 2.7 \times 10^{-4} \mu m^4 \).

Figure 3.7: Thickness of an Al₂O₃ film by plasma-assisted ALD at a temperature of 250 °C. The growth is measured by in-situ SE.
CHAPTER 3. EXPERIMENTAL PROCEDURES

Uniformity measurements are performed by two different methods. For a global view of the uniformity, measurements are performed over two perpendicular axes and measurements are performed with intervals of 1 cm between the measurement points. For a better insight in the uniformity, the film thickness is mapped by ex-situ SE over the entire wafer, while the measurements points are separated by 1.5 cm. The mapping is performed on a automated stage by Q-cells SE. In general native oxide in the model is assumed to be 1.5 nm for the ex-situ SE measurements. However, for the mappings performed by Q-cells, no native oxide is taken into account in the model. This hardly effects the uniformity measurements.

3.2.2 Optical emission spectroscopy

Optical emission spectroscopy (OES) is a versatile technique to study, optimize and monitor plasma-assisted ALD processes [28]. It can be used to obtain insight into which atoms and molecules are present in the plasma during the plasma exposure step. In optical emission spectroscopy the wavelengths of photons emitted by atoms and molecules while decaying from excited states to lower energy states, are measured. It measures the intensity of photons as a function of the photon energy. During the plasma exposure different molecules and atoms are present in different excited states.

In plasma-assisted ALD the oxidation reaction that takes place during the plasma exposure on the surface of the wafer is:

\[
\text{AlCH}_3(s) + 4\text{O}(g) \rightarrow \text{AlOH}(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g) \quad (3.2)
\]

The reaction products of the reaction are mainly \(\text{CO}_2\) and \(\text{H}_2\text{O}\). However these reaction products can react with electrons in the plasma, for example by the following reactions:

\[
\begin{align*}
\text{H}_2\text{O} + e^- \rightarrow & \quad \left\{ \begin{array}{l}
\text{OH}^+ + \text{H} + e^- \\
\text{OH} + \text{H}^+ + e^- 
\end{array} \right.
\end{align*}
\]

\[
\begin{align*}
\text{CO}_2 + e^- \rightarrow & \quad \left\{ \begin{array}{l}
\text{CO}^* + \text{O} + e^- \\
\text{CO}^{**} + \text{O} + 2e^-
\end{array} \right.
\end{align*}
\]

where the asteriks designate the excites states.

Hence, during the plasma exposure step excited states of \(\text{OH}, \text{H}, \text{CO} \) and \(\text{CO}^+\) can be created[29].

During the oxidation reaction \(\text{CO}_2\) and \(\text{H}_2\text{O}\) are created as reaction products. How-
3.2. DIAGNOSTICS

![Graph showing the spectrum with peaks labeled OH*, H*, CO*, H2, H2O, O2, O2*. Intensity on the y-axis and Wavelength on the x-axis.]

Figure 3.8: A typical optical emission spectrum during the plasma step in plasma-assisted ALD of Al2O3. Peaks are identified at 309 nm (OH*), 486 nm (Hβ), 567 nm (CO*), 656 nm (Hα), 777 nm (O*) and 845 nm (O*).[30, 31]. The O peak at 777 nm shows an overload.

However, when insufficient Al(CH3)3 purging is applied, the Al(CH3)3 is still present in the reactor during the plasma exposure, resulting in parasitic CVD processes. These parasitic CVD reactions create an extra amount of CO2 and H2O molecules. In figure 3.8 a typical OES spectrum is shown. H, OH, and CO are created from the reaction products of the oxidation reaction in the ALD process. However the intensity will be higher when insufficient Al(CH3)3 purge is applied, since these byproducts are also created as a result of parasitic CVD processes. By measuring the intensity of these peaks as a function of the Al(CH3)3 purge the minimum purge can be determined.

3.2.3 Rutherford backscattering spectrometry and elastic recoil detection

Rutherford backscattering spectrometry (RBS) is used to determine the number of atoms of aluminum, oxygen and carbon (contamination) in the deposited film while elastic recoil detection (ERD) is used to determine the amount of hydrogen atoms. From these densities the stoichiometry and mass densities of the deposited films can be calculated.

In Rutherford backscattering spectrometry a beam of alpha particles (4He+) is accelerated towards the measured sample. The alpha particles are backscattered by the atoms in the film and the number of scattered ions and their energies are counted. Since the collisions in the substrate are elastic the masses of the atoms in the film are
CHAPTER 3. EXPERIMENTAL PROCEDURES

determined from the energy of the backscattered particles. From this data the con-
centrations of different kind of atoms in the film are determined. A detailed explanation
of Rutherford backscattering spectroscopy can be found in reference [32].

A drawback of RBS is that in substrates that mainly consists out of heavy particles,
like silicon, light elements are hard to detect. Due to their relative low cross section for
scattering and the low energy of the backscattered particles it is difficult to detect the
light elements. With elastic recoil detection however, light elements can be detected.
A beam of \( ^4\text{He}^+ \) particles is directed towards the substrate and an elastic collision takes
place in which light atoms in the film scatter. Since hydrogen is the only light element
present in the Al\(_2\)O\(_3\) film, the hydrogen concentration is calculated by counting the
scattered atoms. A more elaborate description of ERD can be found in [33].

Both RBS and ERD measurements are performed by AccTec B.V. In the mea-
asurements a 2 MeV \( ^4\text{He}^+ \) beam is used. Since particles for Rutherford backscattering
spectrometry and elastic recoil detection are scattered by different angles, both mea-
surements can be performed using the same beam.

3.2.4 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is used to determine the bonding struc-
ture of Al\(_2\)O\(_3\) films. This gives information about the composition of the deposited
films.

In Fourier transform infrared spectroscopy a beam of infrared radiation (ranging in
wavenumbers from 370 to 7500 cm\(^{-1}\)) is directed towards the substrate. In the substrate
radiation is absorbed for specific wavenumbers. These wavenumbers correspond to e.g.
stretching modes corresponding to specific bonds in the material. The intensity of the
transmitted radiation is measured as a function of the wavenumbers. The absorbance
in a film is determined by measuring the transmission of the substrate with and without
deposited film and calculated by:

\[
A = -10 \log \left( \frac{T_{\text{sample}}}{T_{\text{reference}}} \right)
\]  \hspace{1cm} (3.3)

in which \(A\) is absorbance, \(T_{\text{sample}}\) refers to the transmission of the substrate with
film deposited on it, and \(T_{\text{reference}}\) refers to the transmission of the bare substrate. The
FTIR measurements are performed by a dry N\(_2\) purged Bruker Optics VECTOR 22
with 4 cm\(^{-1}\) resolution. The measurements are averaged over 600 measurements.
3.3 Experimental settings

The first goal during the depositions is to obtain a true and saturating ALD process for plasma-assisted and thermal ALD. To obtain these conditions, measurements are performed at a substrate temperature of 250 °C. After obtaining the conditions the uniformity is tested. After this samples for a temperature series are deposited for both thermal and plasma-assisted ALD. For these temperature series material properties are determined to compare the plasma-assisted and thermal ALD methods.

All experiments are executed in the Oxford Instruments OpAL reactor. For the experiments some standard conditions are used. Al(CH₃)₃ is used as precursor and is placed in a precursor pot in the precursor cabinet. The precursor pot is heated to temperature of 30 °C, while the delivery lines and the ALD valve is heated to 50 °C. The temperature of wall of the reaction chamber are regulated to 180 °C, while the exhaust towards the pump is regulated to 120 °C. During plasma-assisted ALD the plasma power used during the plasma exposure is regulated to 200 W.

In plasma-assisted ALD O₂ is used to purge the reaction chamber, while in thermal ALD Ar is also used to purge the reaction chamber. During the plasma-assisted ALD process an additional Ar flow is used after the Al(CH₃)₃ dose, to purge the line between the ALD valve and the reaction chamber. To make sure there are no delays in the regulation of the flow during the process, the Ar flow is kept constant during the entire process. The Ar flow is diverted through the H₂O line when no Al(CH₃)₃ purge takes place. The flows and the specific lines the Ar enters the reactor chamber for both plasma assisted ALD and thermal ALD are shown in 3.1 and 3.2 respectively, unless mentioned otherwise.

3.3.1 Saturation curves

First several depositions are performed to optimize the ALD processes for both plasma-assisted and thermal ALD. Each step in the process, discussed in 2.1, are optimized time wise. For each step the time is varied separately, while all other deposition settings are kept constant. In-situ spectroscopic ellipsometry is used to monitor the growth of the films. From these measurements the growth per cycle is determined as a function of the time, for each step separately, creating so-called saturation curves. In the
CHAPTER 3. EXPERIMENTAL PROCEDURES

Table 3.1: The Ar and the O\(_2\) purge flows and the lines through which the gases enter the chambers during the plasma-assisted ALD process. Also the lines Ar enters the chamber is shown. The Ar enters the chamber through the H\(_2\)O line when it is not purging the Al(CH\(_3\))\(_3\) line. This is done because the fill line is not equipped with a fast ALD-valve, but with a slower valve. The opening time of this valve would not be fast enough.

<table>
<thead>
<tr>
<th>Step</th>
<th>O(_2) flow (sccm)</th>
<th>Ar flow through Al(CH(_3))(_3) lines (sccm)</th>
<th>Ar flow through H(_2)O lines (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(CH(_3))(_3) dose</td>
<td>50</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>Purge after Al(CH(_3))(_3) dose</td>
<td>50</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td>Plasma exposure</td>
<td>50</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>Purge after plasma exposure</td>
<td>50</td>
<td>0</td>
<td>14</td>
</tr>
</tbody>
</table>

Table 3.2: The Ar purge flow and the lines through which the Ar enters the room during the thermal ALD process.

<table>
<thead>
<tr>
<th>Step</th>
<th>Ar flow through Al(CH(_3))(_3) lines (sccm)</th>
<th>Ar flow through H(_2)O lines (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(CH(_3))(_3) dose</td>
<td>0</td>
<td>144</td>
</tr>
<tr>
<td>Purge after Al(CH(_3))(_3) dose</td>
<td>144</td>
<td>0</td>
</tr>
<tr>
<td>H(_2)O dose</td>
<td>144</td>
<td>0</td>
</tr>
<tr>
<td>Purge after H(_2)O dose</td>
<td>0</td>
<td>144</td>
</tr>
</tbody>
</table>

optimization of the purge after Al(CH\(_3\))\(_3\) dosing, also optical emission spectroscopy measurement are performed.

If a precursor dose or plasma exposure is not sufficient, not all surface groups react and the process does not saturate. This is demonstrated by a lower growth per cycle. If the purges after precursor doses are insufficient parasitic CVD processes occur as discussed in section 3.2.2. Parasitic CVD manifests itself by a higher growth per cycle than for true ALD processes. For the purge after Al(CH\(_3\))\(_3\) dose parasitic CVD processes are also demonstrated by an higher emission intensity of radiation of reaction products during the plasma exposure.

Single side polished silicon wafers (4 " diameter) are used for these depositions. In general one wafer is used to determine one saturation curve.
3.3. EXPERIMENTAL SETTINGS

3.3.2 Uniformity measurements

To check if with the conditions determined in section 3.3.1 uniform films are deposited, nonuniformity is measured for these conditions. Films of approximately 50 nm are deposited. Ex-situ spectroscopic ellipsometry is used to measure the thickness of the deposited layers. The thickness is measured at different spots on the wafer. From this data the nonuniformity is calculated as defined by [15]:

\[
\text{nonuniformity} = \frac{d_{\text{max}} - d_{\text{min}}}{2d_{\text{average}}} \times 100\%,
\]

in which \(d_{\text{max}}\) is the maximum thickness, \(d_{\text{min}}\) is the minimum thickness and \(d_{\text{average}}\) is the average thickness over the entire wafer.

For the uniformity measurement Al₂O₃ films are deposited on 8” single side polished silicon wafers.

3.3.3 Temperature series

After optimizing the ALD processes temperature series are performed for both ALD processes. For plasma-assisted ALD, films are deposited at substrate temperatures ranging from 50 °C to 400 °C. For thermal ALD the substrate temperature ranged from 100 °C to 400 °C. To avoid extensive purge times necessary to remove H₂O, a substrate temperature of 50 °C is not considered for the thermal ALD method. Films of approximately 50 nm are deposited on single side polished silicon wafers (4” diameter). The growth per cycle for these films is determined by in-situ spectroscopic ellipsometry, while the refractive index and the thickness are measured by ex-situ SE at room temperature. Rutherford backscattering spectrometry and elastic recoil detection measurements are performed to measure the material properties of the deposited films.

For Fourier transform infrared spectroscopy measurements separate temperature series are performed. For plasma-assisted ALD films are deposited using substrate temperatures ranging from 25 °C to 200 °C. For these measurement 4” double side polished silicon wafers are used. The wafers first received a 1 minute 2 % HF treatment just prior to the depositions. For thermal ALD films are deposited at substrate temperatures ranging from 100 °C to 250 °C. For these depositions also 4” double side polished wafers are used, but no HF treatment is applied. For both plasma-assisted and thermal ALD the wafers are positioned vertical in the reactor to allow deposition of approximately 50 nm on both sides of the wafer.
Characterization of ALD processes for Al₂O₃ deposition

In this chapter, the characterization of the plasma-assisted and thermal ALD methods for the deposition of Al₂O₃ will be presented. In section 4.1 and 4.2 the results on the optimization of the plasma-assisted ALD and thermal ALD processes are given and discussed. A substrate temperature of 250 °C is used for these depositions. Also the uniformity will be addressed in these sections.

4.1 Process characterization plasma assisted ALD

To develop a truly saturating ALD process, without CVD components or sub-saturated growth, all four steps comprising the plasma-assisted ALD cycle should be optimized. In this section these (sub-cycle) steps are optimized by varying the time period for every step at a temperature of 250 °C, while keeping the other conditions constant. Optical emission spectroscopy will also be used to characterize the process.

4.1.1 Saturation curves

Saturation curves, in which the growth-per-cycle is plotted against the Al(CH₃)₃ dose, Al(CH₃)₃ purge, plasma time and plasma purge, are obtained by monitoring the film growth using in-situ SE. Each step in the ALD-cycle requires a certain amount of time to stabilize to a growth-per-cycle indicative of a saturated process. Since in-situ SE only measures the growth on one spot in the center of the wafer, only on this spot the process is certainly a saturating ALD process. However, as will be addressed in section
4.1.3, excellent uniformity is generally obtained using the ALD process, and therefore the measured properties are found to be representative for the growth process.

First the Al(CH$_3$)$_3$ dose and the purge after the Al(CH$_3$)$_3$ dose were varied. In figure 4.1b the growth per cycle is measured as a function of the Al(CH$_3$)$_3$ dose. Technically 10 ms is the smallest dose that can be used. For doses of at least 20 ms it is observed that the growth per cycle is constant, indicating a saturating process. For a dose of 10 ms the growth per cycle is slightly lower indicating that the process might not be fully saturated. This implies that the injected Al(CH$_3$)$_3$ is not sufficient yet to react with all surface OH-groups.

In figure 4.1b the growth per cycle is measured as a function of the purge after Al(CH$_3$)$_3$ dosing. The growth per cycle is constant for purges longer than 3.5 s. For shorter purges a higher growth per cycle is observed, indicating that the purge is not sufficient. When the purge is not sufficient, Al(CH$_3$)$_3$ is still present in the reactor during the plasma exposure, with the consequence that a parasitic CVD-like process can occur in which precursor molecules can react with newly created surface OH groups or in which the precursor is decomposed in the plasma. This results in a higher growth per cycle than for ALD processes without parasitic CVD processes.
4.1. PROCESS CHARACTERIZATION PLASMA ASSISTED ALD

The minimum purge required to remove is determined here for a reactor pressure of 170 mTorr. The pressure in the reactor changes however when the purge flow is altered. In appendix A the reactor pressure is varied and the minimum purge time is determined for these pressures. It appears that the minimum purge time increases for decreasing reactor pressure. In appendix A it is also shown that a calculated residence time is a good indication for the minimum purge time.

In figure 4.2a the growth per cycle is measured as a function of the plasma exposure. The growth per cycle is constant for exposures longer than 4 s. For shorter exposures lower growth per cycle values are observed, indicating not all surface CH$_3$ groups have reacted. In figure 4.2b the growth per cycle is measured as a function of plasma purge. For purges longer than 0.2 s or longer the growth per cycle is observed to be constant. However, when no purge is applied the growth per cycle is only slightly higher. This can be attributed to two parasitic CVD-like processes. The first process occurs because the plasma is not immediately extinguished when the plasma is turned off. When radicals are still present in the reactor when the precursor is injected the radicals might react with newly formed surface CH$_3$ groups or precursor molecules, resulting in a CVD-like process. The second process occurs because some H$_2$O is created during the oxidation reaction (equation 2.3). If not all H$_2$O is removed from the reactor when the precursor is injected a CVD like reaction can take place between the H$_2$O and the Al(CH$_3$)$_3$. The higher growth rate when no purge is applied can probably be attributed to the first process, since the little amount of H$_2$O created can easily be removed at a substrate temperature of 250 °C. For lower temperatures this reaction channel should be taken into account however.

Table 4.1 shows an optimized recipe for the deposition of Al(CH$_3$)$_3$ in the OpAL reactor at 250 °C, based on the saturation curves. In this recipe the minimum time periods required to obtain a truly saturating ALD process are used, while maintaining a cycle time as short as possible. The plasma purge is slightly extended to 0.5 s with respect to the 0.2 s determined from figure 4.2b, but this hardly affects the total time. Using this recipe a growth per cycle of 1.1 Å/cycle is obtained, which is similar to the growth per cycle in FlexAL [15], using the same substrate temperature. Studies using direct plasma reported a slightly higher growth with approximately 1.2 Å/cycle [34].
CHAPTER 4. CHARACTERIZATION OF ALD PROCESSES FOR AL₂O₃ DEPOSITION

Figure 4.2: Saturation curves for plasma exposure and the plasma purge. An Al(CH₃)₃ dose of 20 ms is used, while a purge of 2.5 s is used after the Al(CH₃)₃ dose. In a) the growth per cycle is measured as a function of plasma exposure. The plasma purge is kept constant at 0.5 s. In b) the growth per cycle is measured as a function of the plasma purge, while the plasma exposure time is kept constant at 4 s.

Table 4.1: Standard recipe, extracted from the saturation curves, for plasma-assisted ALD at a temperature of 250 °C.

<p>| | |</p>
<table>
<thead>
<tr>
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<th></th>
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</thead>
<tbody>
<tr>
<td>Al(CH₃)₃ dose</td>
<td>0.020 s</td>
</tr>
<tr>
<td>Purge after Al(CH₃)₃ dose</td>
<td>3.5 s</td>
</tr>
<tr>
<td>Plasma exposure</td>
<td>4 s</td>
</tr>
<tr>
<td>Purge after plasma exposure</td>
<td>0.5 s</td>
</tr>
<tr>
<td>Total time</td>
<td>8.0 s</td>
</tr>
</tbody>
</table>

4.1.2 Optical emission spectroscopy measurements

OES is a powerful tool to study, monitor and control the growth process of plasma-assisted ALD. OES measurements can be used to minimize the purge time after Al(CH₃)₃ dosing, without measuring the growth per cycle. Furthermore OES can measure radiation from reaction products created anywhere in the reaction, allowing it to minimize the purge time for the entire wafer. This in contrast to SE measurements, which only determines a true saturating ALD process for one spot on the wafer.

Figure 4.3 shows the total radiation emitted by H, OH and CO during the plasma exposure as a function of the duration of the preceding purge step. The intensity of the peaks is integrated over the entire plasma exposure time (a plasma exposure time of 4 s is used). When the purge after Al(CH₃)₃ dosing is longer than 3.5 s the total radiation for these three reaction products is constant. For shorter purges however a larger
Figure 4.3: The intensity of the total radiation emitted during the plasma exposure as a function of the Al(CH$_3$)$_3$ dose for OH (at a wavelength of 309 nm), H (656 nm) and CO (567 nm). The radiation is measured using OES and integrated over the plasma exposure time.

emission signal is present for these reaction products. This indicates that additional reactions occur during the plasma exposure, which can be attributed to the parasitic CVD reactions, as discussed in section 4.1.1. These reactions occur due to insufficient purging after Al(CH$_3$)$_3$ dosing. This confirms the results obtained in the saturation curves, indicating all Al(CH$_3$)$_3$ is removed from the reactor for purges of at least 3.5 s long.

In figure 4.4 the integrated intensity is shown for the radiation emitted by O as a function of the duration of the preceding purge step. The intensity of O radiation is constant, indicating that the O concentration is constant for most purge times. However, for short purge times the O radiation seems a increase slightly. This is an interesting observation. For short purges, when additional CVD components occur, more oxygen would be consumed during the reactions. Although this is a minor effect, this would at least result in a lower intensity for O emission directly created from O$_2$ dissociation. However, the higher intensity for shorter purges could be explained by generation of
CHAPTER 4. CHARACTERIZATION OF ALD PROCESSES FOR AL₂O₃ DEPOSITION

Figure 4.4: The intensity of the total radiation emitted during the plasma exposure as a function of the Al(CH₃)₃ dose at a wavelength of 845 nm (O). The radiation is measured using OES and integrated over the plasma exposure time.

O particles from the reaction products. The reaction products CO₂ and H₂O can react in the reactor creating excited states of O radicals as well. This can result in a higher intensity of the radiation:

\[ CO₂ + e^- \rightarrow O^* + CO + e^- \]

\[ H₂O + e^- \rightarrow O^* + 2H + e^- \]

Another explanation for the additional O radiation visible in the reactor could be a change in the electron temperature. Because of a different composition of the particles in the plasma, the electron temperature might have changed. This could result in a slightly higher rate of creation of excited O radicals from O₂ molecules.

4.1.3 Uniformity

Uniformity does not only show whether a uniform film is deposited, but for ALD it also indicates if a the ALD process is a saturating process without parasitic CVD processes. In 3.3.1 a recipe for ALD was determined by measuring growth per cycle by in-situ SE. These measurement only show, however, that the obtained recipe is saturating and without parasitic CVD components at the measured spot. ALD provides excellent uniformity, since it is a self-limiting process in which only the surface functional groups react. However, if the process is not saturating or contains parasitic CVD processes,
4.1. PROCESS CHARACTERIZATION PLASMA ASSISTED ALD

Figure 4.5: a) The thickness profile of an Al$_2$O$_3$ film, deposited on a 8” silicon wafer by plasma-assisted ALD, measured by ex-situ SE. The thickness is measured at intervals of 1.5 cm over the entire wafer. b) The nonuniformity of the deposited film as a function of the radius of the wafer.

this can result in varying growth per cycle for different positions on the wafer.

Approximately 50 nm Al$_2$O$_3$ is deposited on an 8” silicon wafer, using the recipe extracted from 4.2.1. The thickness of the deposited layer is mapped by ex-situ SE over the entire wafer in a grid (intervals of 1.5 cm between measurement points). The results in figure 4.5a show that in the middle of the wafer the thickness is homogeneous, while at the edges the thickness decreases rapidly. The nonuniformity calculated for this wafer is 4.31 %. For wafers with smaller radii however, the nonuniformity is obviously much smaller. Figure 4.5b shows that for a radius smaller than 7 cm the nonuniformity is less than 1 %.

Since Al(CH$_3$)$_3$ is injected into the reaction chamber radially, nonuniformity caused by the injection of precursor would probably show non-symmetrical irregularities. The O$_2$ plasma however enters the reaction chamber from the top of the chamber perpendicular to the substrate. A probable reason for the rapid decrease of thickness at the edges of the wafer is an insufficient exposure to the plasma species. Longer plasma time is necessary for the plasma to reach the edges of the reactor. Since not all surface functional groups react the ALD process is not saturating there. This is solved by using a longer plasma exposure (as shown by other experiments in the Plasma & Materials Processing group). In the center of the substrate the uniformity is good however, so for wafers with radii smaller than 7 cm a plasma exposure of 4 s is sufficient.
Figure 4.6: Saturation curves for Al(CH$_3$)$_3$ dose and the purge after Al(CH$_3$)$_3$ dose. The H$_2$O dose and purge are kept constant at 20 ms and 10 s respectively. In a) the growth per cycle is measured as a function of the Al(CH$_3$)$_3$ dose. The purge after the Al(CH$_3$)$_3$ dose is kept constant at 7.5 s. In b) the growth per cycle is measured as a function of the Al(CH$_3$)$_3$ purge, while the Al(CH$_3$)$_3$ dose is kept constant at 20 ms.

### 4.2 Process characterization thermal ALD

In this section the thermal ALD process is investigated at a temperature of 250 °C. The process is optimized by varying the time period for all four (sub-cycle) steps, compromising the thermal ALD process, independently, while keeping other deposition conditions constant. The uniformity of several deposited films will also be addressed.

#### 4.2.1 Saturation curves

In figure 4.6a the growth per cycle is measured as a function of the Al(CH$_3$)$_3$ dose. The growth per cycle is constant for all doses tested indicating that the smallest dose technically possible (10 ms) is sufficient to obtain a saturating process. In figure 4.6b the growth per cycle is measured as a function of the Al(CH$_3$)$_3$ purge. For purges longer than 4 s the growth per cycle is constant, and no parasitic CVD processes occur.

In figure 4.7 the H$_2$O dose and the purge time after the H$_2$O dose are optimized. In figure 4.7a the growth per cycle is measured as a function of the H$_2$O dose. The growth per cycle increases for increasing H$_2$O dose, indicating that the growth still is not completely saturated for a dose of 80 ms. Matero et al.[35] reports similar results
4.2. PROCESS CHARACTERIZATION THERMAL ALD

Figure 4.7: In a) the growth per cycle is measured as a function of the H$_2$O dose for different H$_2$O doses. The H$_2$O purge is kept constant at 10 s. In b) the growth per cycle is measured as a function of the H$_2$O dose. For both graphs a Al(CH$_3$)$_3$ dose of 20 followed by a purge of 2.5 s.

A standard recipe, shown in table 4.2, is determined for the thermal ALD process at 250 °C. An Al(CH$_3$)$_3$ dose of 20 ms is used, similar to plasma-assisted ALD, to assure the dose is high enough for all OH-groups on the entire substrate surface to react. Although a purge of 4 s would be sufficient according to figure 4.6b, the purge is extended to 5 s to ensure all Al(CH$_3$)$_3$ is removed from the entire reactor, and not only the spot where in-situ SE measurement was executed. Figure 4.7b shows that a purge of 5 s is sufficient for a H$_2$O dose of 20 ms, to remove all H$_2$O from the reactor. This recipe gives a growth per cycle of 1.0 Å/cycle, which is also obtained in FlexAL[15], and is consistent with results in the literature [34, 35].
CHAPTER 4. CHARACTERIZATION OF ALD PROCESSES FOR AL$_2$O$_3$ DEPOSITION

Table 4.2: Standard recipe, extracted from the saturation curves, for thermal ALD at a temperature of 250 °C.

<p>| | |</p>
<table>
<thead>
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<tbody>
<tr>
<td>Al(CH$_3$)$_3$ dose</td>
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</tr>
<tr>
<td>Purge after Al(CH$_3$)$_3$ dose</td>
<td>5 s</td>
</tr>
<tr>
<td>H$_2$O dose</td>
<td>20 ms</td>
</tr>
<tr>
<td>Purge after H$_2$O dose</td>
<td>5 s</td>
</tr>
<tr>
<td>Total time</td>
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Table 4.3: The nonuniformity calculated for different deposition conditions. For wafer 1 the recipe determined in 4.2.1 is used, while for the other wafers all steps in a thermal ALD process are varied. The nonuniformity is calculated from thickness measurements performed by ex-situ SE over 2 axis perpendicular to each other with intervals of 1 cm between the measurement points.

<table>
<thead>
<tr>
<th>Wafer</th>
<th>Al(CH$_3$)$_3$ dose (ms)</th>
<th>Purge after Al(CH$_3$)$_3$ dose (s)</th>
<th>H$_2$O dose (ms)</th>
<th>Purge after H$_2$O dose (s)</th>
<th>Nonuniformity (%)</th>
</tr>
</thead>
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<tr>
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<td>20</td>
<td>5</td>
<td>20</td>
<td>5</td>
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</tr>
<tr>
<td>2</td>
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<td>20</td>
<td>5</td>
<td>2.95</td>
</tr>
<tr>
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</tr>
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<td>5</td>
<td>50</td>
<td>5</td>
<td>20</td>
<td>5</td>
<td>1.94</td>
</tr>
</tbody>
</table>

4.2.2 Uniformity

The recipe composed in section 4.2.1 provides a saturating ALD process. In the recipe quite some margins are taken into account to ensure doses are not too low and not too high and purges are long enough to remove all precursor gases from the entire reactor. To verify if those margins are not taken too broad uniformity measurements are performed, while the precursor doses are increased and the purges are shortened. For this experiment films of approximately 50 nm are deposited on 8” wafers. The thickness is measured by ex-situ SE over two axis perpendicular to each other (x-axis and y-axis) with intervals of 1 cm. Uniformity is calculated using 3.4. Table 4.3 displays the deposition conditions and the results of the nonuniformity measurements. These results indicate that increasing the Al$_2$O$_3$ dose to 50 ms deteriorates the uniformity of the wafer. Reducing the purges after the H$_2$O and the Al(CH$_3$)$_3$ dose deteriorates the uniformity. Increasing the H$_2$O dose does not seem to affect the nonuniformity. The nonuniformities are comparable with 1.52 % for a dose of 40 ms and 1.53 % for a dose of 20 ms.
In Figure 4.8 thickness is displayed over the entire wafer (with intervals of 1.5 cm) for both wafers (wafer 1 and wafer 4). When the nonuniformity is calculated for those measurements however, wafer 1 has a nonuniformity of 1.55%, while for wafer 4 a higher nonuniformity of 2.64% is calculated. The uniformity of the films decreases when the H$_2$O dose is increased from 20 ms to 40 ms. The recipe corresponding to wafer 1 shows a good uniformity, while increasing doses or shortening purge times results in worse uniformities.

Figure 4.8 also shows that the thickness profile of both wafers are quite similar. The thickness has a maximum around the coordinates (-3 cm, 7 cm), while the thickness decreases when moving over the wafer in all directions. The position of the the inlets of the precursor gases with respect to the wafer orientations in figure 4.8 are displayed in figure 4.9. A possible cause for this maximum thickness might be that injected H$_2$O is directed to the reactor wall reflects at the wall into the direction of the wafer where the maximum film thickness is observed. When Al(CH$_3$)$_3$ enters the reaction chamber it reacts with this H$_2$O residue and is deposited on the wafer, causing extra thickness. A solution might be a longer purge after H$_2$O dosing.
CHAPTER 4. CHARACTERIZATION OF ALD PROCESSES FOR Al₂O₃ DEPOSITION

Figure 4.9: Positions of the gas inlets in the reactor with respect to the wafer orientations shown in figure 4.8.

4.3 Conclusions

In section 4.1 and sections 4.2.1 and 4.2.2 the plasma-assisted and thermal ALD process was characterized for deposition at a substrate temperature of 250 °C. As a result recipes are obtained for true ALD processes. For plasma-assisted ALD a recipe was determined with a cycle time of 8.0 s, resulting in a growth per cycle of 1.1 Å/cycle. The cycle time for the thermal ALD process was slightly longer with 10 s, resulting in a slightly lower growth per cycle of 1.0 Å/cycle (the longer cycle time can be attributed to the longer purge times necessary in the thermal ALD process).

In thermal ALD a nonuniformity of 1.55 % is obtained over an 8” wafer. The nonuniformity is attributed to the fact that the H₂O is not completely removed locally, resulting in a small parasitic CVD component in the growth at one position of the wafer. For the plasma-assisted ALD process a nonuniformity of 4.31 % is obtained. This nonuniformity however reduces quickly when smaller wafers are used, to less than 1 % for wafers with a radius of less than 7 cm. This symmetrical nonuniformity is attributed to an insufficient exposure of the wafer edge by the plasma, which diffuses from the top of the reactor, perpendicular to the wafer.
Material properties and deposition temperature variation for ALD of Al$_2$O$_3$

In this chapter the influence of the deposition temperature on the growth process and Al$_2$O$_3$ material properties is investigated and compared for plasma-assisted ALD and thermal ALD. Films were deposited in the OpAL reactor at different substrate temperatures ranging from 50 °C to 400 °C. In section 5.1 growth per cycles, as determined by SE, are shown, while in section 5.2 Al, O, H and C concentrations in Al$_2$O$_3$ are shown as determined by RBS and ERD measurements. In section 5.3 the number of “monolayers” deposited per cycle is calculated. In section 5.4 the refractive index of the deposited films is compared to material properties, while in section 5.5 FTIR is used to determine the bonding configuration of the Al$_2$O$_3$ films. In section 5.6 the dehydroxylation reactions are discussed. Finally, in section 5.7 the material properties and the reaction mechanisms are interpreted and discussed.

5.1 Growth per cycle

Plasma-assisted and thermal ALD films of approximately 50 nm were deposited using substrate temperatures ranging from 50 °C to 400 °C. For plasma-assisted ALD the recipe displayed in table 4.1 is used, except for the depositions at substrate temperatures of 50 and 150 °C. For substrate temperatures 50 °C and 150 °C the purge times after plasma exposure are extended to 5 s and 2.5 s, respectively. For these lower substrate temperatures longer purge times are chosen to remove the H$_2$O that is created during the plasma exposure, and for decreasing temperatures it is harder to remove all H$_2$O. With thermal ALD, films are deposited at substrate temperatures ranging from 100 °C
CHAPTER 5. MATERIAL PROPERTIES AND DEPOSITION TEMPERATURE VARIATION FOR ALD OF Al2O3

Figure 5.1: Growth per cycle, determined by in-situ SE, measured as a function the substrate temperature for both plasma-assisted and thermal ALD for depositions in the OpAL reactor. Also the results obtained in FlexAL by Van Hemmen et al. are included [15].

to 400 °C. Apart from depositions at substrate temperature of 100 °C and 150 °C the recipe displayed in table 4.2 is used. For substrate temperatures of 100 °C and 150 °C purge times of 15 s and 10 s respectively are used after H2O dosing, to allow the removal of all H2O from the reactor.

Figure 5.1 shows the growth per cycle as a function of substrate temperature for both plasma-assisted and thermal ALD. Also the results obtained in FlexAL by van Hemmen et al. [15] are included (however, an erroneous setting in the reactor software caused the substrate temperatures in FlexAL to be slightly higher than shown in figure 5.1.)

For plasma-assisted ALD the growth per cycle decreases for increasing temperature from 1.74 ± 0.05 Å at 50 °C to 0.94 ± 0.05 Å at 400°C. The decreasing trend in the OpAL corresponds to the decrease in growth per cycle observed in FlexAL. This decreasing trend is also observed in radical enhanced [36] and direct plasma ALD [34], but the growth per cycle reported for those methods is higher for the lower substrate temperatures.

For thermal ALD the growth per cycle decreases from of 0.99 ± 0.05 at 250 °C to 0.89 ± 0.05 at 400 °C. This corresponds to the results obtained in FlexAL and other results reported in the literature [17, 34, 35]. For lower temperature the growth per cycle decreases to 0.87 ± 0.05 at 100 °C, corresponding to results obtained in the FlexAL and reported by Matero et al. [35]. In other literature reports however the
5.2. MATERIAL PROPERTIES

Composition: RBS measurements were performed on the films to determine the amount of Al, O and C atoms, while the amount of H atoms was determined by ERD measurements. Carbon is not detected in any of the films. The presence of carbon contamination in the films is not excluded however, since the detection limit of the RBS measurements is 10 at%. In figure 5.2 the results of the RBS and ERD measurements are displayed. For plasma-assisted ALD the number of aluminum atoms per cm$^3$ slightly increased for increasing temperatures, while the oxygen concentration remained constant. For thermal ALD both the amount of aluminum and oxygen atoms per cm$^3$ increased for increasing temperature. The amount of hydrogen atoms per cm$^3$ decreased significantly for increasing temperatures and finally reaches virtually 0 at% at 400 °C for both plasma-assisted and thermal ALD.

Mass density: From the RBS/ERD measurements, in combination with ex-situ SE measurements of the thickness of the films, the density of the films was calculated. In figure 5.3a the mass density of the deposited films is displayed as a function of the substrate temperature. For plasma-assisted ALD the density increases from 2.7 ± 0.2

Figure 5.2: The density of aluminum, oxygen and hydrogen atoms in the deposited films for a) plasma-assisted ALD and b) thermal ALD.

decrease of growth per cycle with increasing substrate temperatures > 200 °C is not observed [34] as will be discussed in section 5.7.

5.2 Material properties
CHAPTER 5. MATERIAL PROPERTIES AND DEPOSITION TEMPERATURE VARIATION FOR ALD OF Al₂O₃

g cm⁻³ at 50 °C to 3.2 ± 0.2 g cm⁻³ for temperatures over 250 °C. This corresponds well with the results obtained with the FlexAL [15]. Niskanen et al[36] also report the same results for lower temperatures. However for a substrate temperature of 300 °C a higher mass density was reported. The results for thermal ALD show an increasing mass density as well, but in general the mass density is lower than for plasma-assisted ALD. The density increases from 2.6 ± 0.2 g cm⁻³ at 100 °C to 3.3 ± 0.2 g cm⁻³ at 400 °C. This corresponds to results reported in literature [15, 37]. The mass density amounts to approximately 80 % of the mass density of crystalline Al₂O₃ (3.97 g cm⁻³).

**Stoichiometry:** From the RBS measurements the ratio between the concentration of oxygen and aluminum is calculated. In figure 5.3b the ratio is shown as function of the substrate temperature. For both plasma-assisted and thermal ALD at a substrate temperature of 400 °C the films are stoichiometric ([O]/[Al]=1.5). For decreasing temperature the ratio increases to 2.0 at 50 °C for plasma-assisted ALD. Thermal ALD shows similar results but the ratio decreases less than for plasma-assisted ALD. The ratio increases from stoichiometric Al₂O₃ at 150 °C to 1.7 at 100 °C. In literature similar results are reported [15, 36]. Groner et al [37] however reports ratios ranging from 1.34 to 1.70 for substrate temperatures from 25 °C to 200 °C, while there was no systematic trend with substrate temperature.

**Hydrogen content:** In figure 5.3c the hydrogen content in the deposited film, determined by ERD, is shown as a function of the substrate temperature. In both plasma-assisted and thermal ALD the hydrogen content increases for decreasing temperature. In thermal ALD the hydrogen concentration exceeds the hydrogen concentration for plasma-assisted ALD for all temperatures. These observations will be discussed in more detail with reference to the growth mechanism in section 5.7. The decreasing hydrogen concentration for increasing substrate temperature is also reported in literature[15, 37, 36].

**Oxygen excess:** The increasing excess of oxygen atoms and the increasing hydrogen content for decreasing substrate temperatures suggests these are incorporated in the film as OH groups. However for plasma-assisted ALD the surplus of oxygen is higher than for thermal ALD, while for thermal ALD a higher hydrogen concentration is obtained. In figure 5.4 the surplus of oxygen (assuming all Al is bonded in stoichiometric Al₂O₃) is compared to the hydrogen content. For plasma-assisted ALD there is a surplus of oxygen atoms for most substrate temperatures, while for thermal ALD there is a surplus of hydrogen atoms. Since during plasma-assisted ALD CO-bonds are created (e.g. CO2/CO is a reaction product, section 2.1 and section 3.2.2) the surplus
5.2. MATERIAL PROPERTIES

Figure 5.3: The a) mass density, b) O/Al ratio and c) H content as a function of the substrate temperature.
CHAPTER 5. MATERIAL PROPERTIES AND DEPOSITION TEMPERATURE VARIATION FOR ALD OF Al₂O₃

Figure 5.4: The difference between the surplus of oxygen atoms (oxygen atoms not bonded in Al₂O₃, assuming all Al is bonded in stoichiometric Al₂O₃) and the number of hydrogen atoms, as a function of the substrate temperature.

of oxygen can be explained by the incorporation of COₓ in the deposit films. This will be addressed in section 5.5, using FTIR. Thermal effusion measurements have also confirmed the presence of COₓ related impurities in plasma assisted ALD of Al₂O₃ films[38]. For thermal ALD the only reaction products in both reactions is CH₄. The excess of hydrogen atom could be explained by incorporation of CHₓ in the films.

Al deposited per cycle: In section 5.1 the growth per cycle is measured for the different substrate temperatures. However in the growth per cycle, the density of the material is not taken into account. Another measure for the growth is the number of aluminum atoms deposited per cycle, in which the amount of Al₂O₃ material per cycle is measured. In figure 5.5 the number of aluminum atoms deposited per cycle is shown as a function of the substrate temperature. For plasma-assisted ALD the number of aluminum atoms increases from 3.4 · 10¹⁴ cm⁻² at 400 °C to 4.0 · 10¹⁴ cm⁻² at 250 °C. For lower temperatures the number of deposited aluminum atoms further increases to 4.5 · 10¹⁴ at 50 °C. For thermal ALD the number of Al atoms deposited per cycle increases from to 3.4 · 10¹⁴ at 400 °C to 4.1 · 10¹⁴ at 250 °C. For decreasing temperature <250 °C the number of aluminum atoms decreases to 3.4 · 10¹⁴ at 250 °C. These results correspond to the growth per cycle measured in figure 5.1. The decreasing number of aluminum atoms deposited for higher temperatures is in agreement with the dehydroxylation reaction occurring. Due to the thermally activated recombination of surface OH-groups less OH-groups are available to react with Al(CH₃)₃ for increasing temperature, which causes less Al atoms to be deposited per cycle.
5.3 Reaction Mechanisms

Only in the ideal case one “monolayer” is deposited per cycle. However in reality less than one monolayer is deposited per cycle. In this section the amount of monolayer deposited in one cycle is determined for different substrate temperatures. Here, a monolayer is considered as the thickness of one layer of Al₂O₃ units [39]. Since section 5.2 shows that the density is not constant for different substrate temperature the thickness of one monolayer is not constant.

The thickness of one monolayer is determined from the Al concentration [Al]⁻¹. The volume in which one Al atom can be found is the reciprocal of the concentration: [Al]⁻¹. Since there are two Al atoms present in one Al₂O₃ unit, the volume of one Al₂O₃ unit is 2 x [Al]⁻¹. The thickness of one monolayer is then be estimated as (2[Al]⁻¹)¹/₃. In figure 5.6a and figure 5.6b the monolayer is shown as a function of the substrate temperature for plasma-assisted and thermal ALD respectively. For both methods the thickness of a monolayer is approximately 4 Å (for crystalline Al₂O₃ the thickness of one monolayer is 3.5 Å). Also the growth per cycle, as determined in section 5.1 by SE, are plotted. Comparing the growth per cycle and the monolayer thickness, it is observed that the growth per cycle is much less than one monolayer.

The number of monolayers deposited per cycle is determined by dividing the growth
per cycle by the monolayer thickness. In figure 5.6c the number of monolayers deposited per cycle is measured as a function of the substrate temperature. In general the number of monolayers deposited per cycle for plasma-assisted ALD is slightly higher than for thermal ALD and decreases from 0.41 for a substrate temperature of 50 °C to 0.26 at 400 °C. For thermal ALD the number of monolayers deposited per cycle varies from 0.21 to 0.27 for different substrate temperatures.

5.4 Refractive index vs. material properties

In section 5.2 material properties were determined by RBS measurements. In this section it is investigated whether the refractive index correlates with these material properties. The Al₂O₃ films deposited in the temperature series were measured by ex-situ SE to determine the refractive index of the films, using equation 3.1 (see section 3.2.1). In figure 5.7 the refractive index (determined at a wavelength of 630 nm) is shown as a function of the substrate temperature, both for plasma-assisted and thermal ALD. For both methods the refractive index increases with increasing substrate temperature.

Figure 5.8 shows the mass density of the deposited films as a function of the refractive index. The mass density increases for increasing refractive index, independent of the ALD method. This trend corresponds to the mass Clausius-Mossotti equation, as derived by Feynman in his lectures [40]:

\[ N\alpha = 3 \cdot \frac{n^2 - 1}{n^2 + 2}, \]  \hspace{1cm} (5.1)\]

in which \( N \) is the particle density, \( \alpha \) is the atomic polarizability and \( n \) is the refractive index. In equation 5.1 the particle density increases for increasing refractive index.

In figure 5.9a the mass density is shown as a function of the hydrogen content. Since hydrogen is mainly incorporated as OH groups in the films [41], we can conclude that not all OH groups at the surface have reacted during the ALD process. As a result the deposited film is less dense, explaining the lower mass density. Figure 5.9b shows the hydrogen content as a function of the refractive index, and the expected trend is observed in which the refractive index decreases for increasing hydrogen concentration. This is also in agreement with the results obtained by Otterman et al [42].
Figure 5.6: a) Growth per cycle, determined by in-situ SE, and the thickness of a monolayer measured as a function of the substrate temperature for plasma-assisted ALD. b) Growth per cycle, determined by in-situ SE, and the thickness of a monolayer measured as a function of the substrate temperature for thermal ALD. c) The number of monolayers deposited per cycle plotted as a function of the substrate temperature for both plasma-assisted and thermal ALD.
that the refractive index decreases for increasing H concentration for thin oxide films using different deposition techniques, such as sol-gel processes, reactive evaporation, sputtering and ion plating on glass substrates.

From the observed correlation between the mass density, the hydrogen content and the refractive index, the refractive index can be used as a “qualitative measure” of the mass density and the hydrogen content.
Figure 5.9: a) Mass density shown as a function of the hydrogen content determined by RBS measurements. b) Hydrogen content plotted as a function of the refractive index (determined at a wavelength of 630 nm). For both figures data are given for plasma-assisted and thermal ALD.
CHAPTER 5. MATERIAL PROPERTIES AND DEPOSITION TEMPERATURE VARIATION FOR ALD OF Al₂O₃

5.5 FTIR measurements

FTIR measurements give insight into the bonds present in the deposited films which gives information on the composition of the films. For the FTIR measurements films of approximately 50 nm were deposited on both sides of a silicon wafer. Film thicknesses were measured by ex-situ SE and small thickness differences were corrected in the FTIR results (the absorbance is divided by the thickness, as measured by SE, and multiplied by 50 nm).

There are three regions of interest in the absorption spectrum of Al₂O₃ [41]. The absorbance region between 400 and 1000 cm⁻¹ is related to Al-O stretching vibrations, while the absorption peak region between 1200 and 1800 cm⁻¹ can be assigned to C-O stretching vibrations. The third region of interest is between 2800 and 3900 cm⁻¹ which is assigned to O-H stretching modes.

In figure 5.10a the absorbance in the region between 400 and 1000 cm⁻¹ is shown for plasma-assisted ALD. The maximum of the peak related to Al-O stretching modes increases for increasing substrate temperature. In figure 5.10b the absorbance in this region is shown for thermal ALD. Here, the absorbance is similar for substrate temperatures of 200 and 250 °C, while for a substrate temperature of 100 °C the absorbance peak of the Al-O stretching modes is lower. Furthermore when comparing plasma-

Figure 5.10: Absorbance measured as a function of the wavenumber in the wavenumber region related to Al-O stretching modes for a) plasma-assisted and b) thermal ALD for different substrate temperatures.
5.5. FTIR MEASUREMENTS

assisted and thermal ALD, the peak for plasma-assisted ALD is broader than for thermal ALD. This suggests that in thermal ALD the Al-O bonds are more similar (in terms of bond lengths and angles) than in plasma-assisted ALD. This could indicate that the structure of the Al₂O₃ deposited by thermal ALD is less amorphous.

Since generally all Al atoms in the deposited films are bonded to O atoms, the absorbance of the Al-O stretching modes can give an indication of the amount of Al atoms in the films. To verify this, the absorbance is integrated over the wavenumber in figure 5.11a for the peak related to Al-O stretching vibrations. The integrated absorbance increases as a function of the substrate temperature. This agrees with the Al concentration measured by RBS (section 5.2), which is also included in the figure. In figure 5.11b the integrated absorbance is shown as a function of the substrate temperature for thermal ALD. Also here the integrated absorbance increases as a function of the substrate temperature. This also agrees with the results obtained by RBS measurements. Since for both plasma-assisted and thermal ALD the integrated absorbance correspond to the Al concentration, it might be interesting to plot the integrated absorbance as a function of the Al concentration, to check whether FTIR is a reliable indicator for Al concentrations. In figure 5.11c the integrated absorbance is measured as a function of the Al concentration. In general the integrated absorbance increases for increasing Al concentration, but the correlation is not sufficient to allow a quantitative determination.

In figure 5.12a the absorbance region from 1200 to 1800 cm⁻¹, which is related to C-O stretching modes, is shown for plasma-assisted ALD. Three peaks at approximately 1480, 1550 and 1600 cm⁻¹ are related to C-O bonding. However it is not straightforward to assign these peaks individually. The peaks at 1550 cm⁻¹ and 1600 cm⁻¹ are likely due to carboxylate (CO₂⁻), carbonate (CO₃⁻) and formate (COOH) groups[41]. The peak at 1480 cm⁻¹ might be assigned to asymmetric deformation of CH₃ or the presence of O-CH₃[41]. In RBS the C concentration was found to be below the detection limit. However, because of the large infrared absorption cross section it is possible to detect C-O bonds even for low concentration of COₓ. For plasma-assisted ALD the maximum of the peaks decreases for increasing substrate temperature. In figure 5.12b the absorbance for the peaks is integrated over the wavenumber. It shows that the amount of C-O bonds decreases for increasing substrate temperature. The detection of C-O bonds confirms the presence of COₓ, as suggested in section 5.2. This is explained by incomplete reactions during the oxidation step. Gaseous CO₂ is a reaction
Figure 5.11: The absorbance peak related to Al-O stretching modes integrated over its wavenumber range measured as a function of the substrate temperature for a) plasma-assisted and b) thermal ALD. The Al concentrations, determined by RBS measurements (section 5.2), are measured as a function of the substrate temperature in the same figures. c) The integrated absorbance for the Al-O stretching modes measured as a function of the Al concentration. The results for both plasma-assisted and thermal ALD are included in this graph.
5.5. FTIR MEASUREMENTS

Figure 5.12: a) Absorbance related to C-O stretching modes for plasma-assisted. b) The absorbance peaks related to C-O stretching modes integrated over its wavenumber range as a function of the substrate temperature for plasma assisted ALD.

product in the combustion-like reaction and the presence of the bonds can be interpreted as an intermediate state of this reaction. These detection of C-O bonds confirms the presence of CO$_x$, as suggested in section 5.2.

The wavenumber region between 1200 and 1800 cm$^{-1}$ was also researched for thermal ALD. However basically no absorbance was detected in this region indicating that no C-O bonds are present in the films. Most probably this can be explained by the fact that during the thermal ALD process no C-O bonds are created during both half reactions. However CH$_x$ groups can be created during the thermal ALD process.

In figure 5.13 the absorbance region between 2800 and 3900 cm$^{-1}$, assigned to OH bonds, is shown. In figure 5.13a the absorbance for plasma-assisted ALD is shown. The peak intensity decreases for increasing substrate temperature. Superimposed on the broad O-H peak is a small contribution of C-H stretching vibrations from -CH$_x$ groups at 2945 cm$^{-1}$. For thermal ALD the absorbance is shown in figure 5.13b. For substrate temperatures 200 °C and 250 °C hardly any absorbance is detected while for a substrate temperature of 100 °C a small peak of O-H stretching modes are detected. Comparing the results of plasma-assisted ALD and thermal ALD, the amount of O-H bonds detected for thermal ALD is negligible compared to plasma-assisted ALD. This could indicate that hardly any OH groups are present in the deposited films for thermal ALD. However, ERD measurements (section 5.5) show that the H content for thermal ALD is bigger than for plasma-assisted ALD. Although H can be incorporated in CH$_x$.
CHAPTER 5. MATERIAL PROPERTIES AND DEPOSITION TEMPERATURE VARIATION FOR ALD OF Al₂O₃

Figure 5.13: Absorbance measured as a function of the wavenumber in the wavenumber region related to O-H stretching modes for a) plasma-assisted and b) thermal ALD for different substrate temperatures. Note that the scaling of the absorbance is significantly different for the two figures. c) The absorbance peak related to O-H stretching modes integrated over the wavenumber measured as a function of the substrate temperature for plasma-assisted ALD. The H concentration, determined by RBS measurements (section 5.2), as a function of the substrate temperature is shown in the same figure. d) The integrated absorbance for the O-H stretching modes plotted as a function of the H concentration for plasma-assisted ALD.
or other structures, most H is expected to be incorporated in the films as OH and the absorbance of O-H for thermal ALD should of the same magnitude as for plasma-assisted ALD. The exact reason for this is unknown and more research is required to investigate it.

For plasma-assisted ALD the absorbance is integrated over the wavenumber for the OH-peak. In figure 5.13c the integrated absorbance is measured as a function of the substrate temperature. The integrated absorbance decreases for increasing substrate temperature. Since most H atoms are incorporated in the deposited films in OH bonds, the H concentration, measured by ERD (section 5.2), is also plotted as a function of the substrate temperature. In figure 5.13d the integrated absorbance is plotted as a function of the hydrogen concentration. It shows that a linear correlation between the H concentration and the OH absorbance. However, this only accounts for plasma-assisted ALD, since the results for thermal ALD are different. Furthermore only 3 data points are plotted, which is insufficient to conclude that the absorbance of OH stretching modes is a good indication for the hydrogen concentration.

5.6 Arrhenius plot dehydroxylation

In section 5.1 it was observed that for plasma-assisted ALD the growth per cycle decreases for increasing substrate temperature. This can be attributed to two factors. In section 5.2 it is shown that the mass density of the deposited films decreases for increasing substrate temperature. This indicates that the deposited material is less densely stacked, resulting in a higher growth per cycle. In section 5.1 it is also shown that for increasing substrate temperature the number of Al atoms deposited per cycle decreases. This indicates that for increasing substrate temperature less material is grown. This is generally attributed to dehydroxylation reactions[15, 43]. Due to thermally activated recombination, surface OH-groups, created during the oxidation step disappear from the surface and the amount of available reaction spots for Al$_2$(CH$_3$)$_3$ adsorption reduces. In this section the activation energy of this dehydroxylation reaction is calculated.

In dehydroxylation reactions surface OH-groups react in thermally activated recombination reactions creating H$_2$O molecules:

$$2(\text{Al} - \text{OH}^*)(s) \rightarrow \text{Al} - \text{O} - \text{Al}(s) + \text{H}_2\text{O(g)}$$

To calculate the activation energy it is necessary to calculate the reaction constant $k$ of the dehydroxylation reaction. The relation between reaction constant of the dehy-
droxylation and the amount of surface OH-groups \([\text{OH}^*]\) is expressed as [25]:

\[
\frac{d[\text{OH}^*]}{dt} = -k[\text{OH}^*]^2
\]  

(5.2)

Rearranging equation 5.2 results in:

\[
k \, dt = -\frac{d[\text{OH}^*]}{[\text{OH}^*]^2}
\]  

(5.3)

Integrating results in:

\[
k \int_0^t dt = -\int_{[\text{OH}^*]_0}^{[\text{OH}^*]} \frac{d[\text{OH}^*]}{[\text{OH}^*]^2}
\]  

(5.4)

\[
k t = \frac{1}{[\text{OH}^*]} - \frac{1}{[\text{OH}^*]_0}
\]  

(5.5)

In which \([\text{OH}^*]_0\) is the amount of surface OH-groups at the end of the oxidation reaction.

Since during the first half-cycle the surface OH-groups react with the Al(CH\(_3\)\(_3\))\(_3\) precursor, the number of Al atoms deposited per cycle can be seen as the number of surface OH-groups created per cycle. However during the purge time the dehydroxylation reaction takes place. In figure 5.5 in section 5.2 the number of Al atoms deposited per cycle are measured as a function of the substrate temperature. Since for low temperatures no dehydroxylation occurs, the amount of surface OH-groups can be assumed to be \([\text{OH}^*]_0\). The number of Al atoms deposited per cycle extrapolates to approximately \(5.0 \times 10^{14} \text{ cm}^{-2}\), so \([\text{OH}^*] = 5.0 \times 10^{14} \text{ cm}^{-2}\). In figure 5.14 the reciprocal of \([\text{OH}^*]\) is plotted as a function of the time for different temperatures. From this the reaction constant can be calculated using equation 5.5.

As can be seen from the results in figure 5.14 the reaction constant varies for different substrate temperatures. The reaction constant increases from \(4.44 \times 10^{-17} \text{ cm}^2\text{s}^{-1}\) for a substrate temperature of 323 K to \(1.91 \times 10^{-15} \text{ cm}^2\text{s}^{-1}\) for 673 K. The relation between the substrate temperature and the reaction constant is often given by the Arrhenius equation:

\[
k = A \cdot \exp\left(-\frac{E_a}{k_b T}\right)
\]  

(5.6)

\(^2\)Here, it is assumed that no bifunctional (two CH\(_3\) groups in one Al(CH\(_3\)\(_3\)) molecule react with surface OH-groups) takes place, and that all surface OH groups react.
5.6. ARRHENIUS PLOT DEHYDROXYLATION

![Arrhenius plot diagram]

Figure 5.14: $1/[\text{OH}^+]$ measured as a function of the time purge time for different substrate temperatures. From the gradients the reaction constant is calculated.

![Logarithm of reaction constant vs reciprocal substrate temperature]

Figure 5.15: The logarithm of reaction constant for the dehydroxylation reaction measured as a function of the reciprocal substrate temperature. The gradient gives a activation energy of 0.216 eV.

In which $A$ is a pre-factor, $E_a$ is the activation energy, $k_b$ is the Boltzmann’s constant and $T$ is the substrate temperature. The Arrhenius equation can also be written as:

$$\ln(k) = \ln(A) - \frac{E_a}{k_bT} \tag{5.7}$$

In figure 5.15 the logarithm of the reaction constant is plotted as a function of the reciprocal of the substrate temperature. The activation energy is calculated from the gradient of the plot, resulting in an activation energy of 0.216 eV. This is relatively low in comparison to literature, where activation energies of approximately 2 eV are calculated for different materials[44, 45]. The pre-factor $A$ has a value of $9.2 \times 10^{-14}$ cm$^2$ s$^{-1}$. 

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5.7 Discussion

In section 5.1 the growth per cycle for plasma-assisted and thermal ALD is shown. The growth per cycle for the plasma-assisted ALD exceeds for all temperatures the growth per cycle for thermal ALD. Especially at low temperatures this is clearly noticeable. In thermal ALD saturation is not reached since only a H\textsubscript{2}O dose of 20 ms is injected, as explained in 4.2.1. For longer H\textsubscript{2}O doses the growth per cycle increases. This explains why the growth per cycle of plasma-assisted ALD consistently exceeds the growth per cycle for thermal ALD. An additional explanation could be that O\textsubscript{2} is a more effective oxidant than H\textsubscript{2}O.

For plasma-assisted ALD the growth per cycle decreases for increasing substrate temperature. In section 5.6 it is discussed that this can be attributed to two factors. The first factor is the decrease of the mass density indicating that the material is less densely stacked. The second factor was the dehydroxylation reactions. Due to thermally activated recombination, surface OH-groups, disappear from the surface and the amount of available reaction spots for Al\textsubscript{2}O\textsubscript{3} adsorption reduces. Another small factor could be that for the substrate temperature of 50 °C the possibility exists that a small amount of parasitic CVD-reactions occur as well. Although the purge after plasma exposure is extended, it might still not be sufficient to remove all the H\textsubscript{2}O created during the plasma exposure step (equation 3.1). However, this only contributes to the higher growth per cycle for the substrate temperature of 50 °C.

For thermal ALD the growth per cycle can be divided in two regions: substrate temperatures higher than 250 °C and substrate temperatures lower than 250°C. In the region >250°C the growth per cycle decreases for increasing substrate temperature. This can generally be attributed to the dehydroxilation reaction, as discussed for plasma-assisted ALD. In the region <250°C, the growth per cycle decreases for decreasing temperature. Since for both plasma-assisted and thermal ALD the similar reaction mechanism occurs during the Al(CH\textsubscript{3})\textsubscript{3} exposure, the difference between the increasing growth in plasma-assisted ALD and the decreasing growth in thermal ALD cannot be attributed to reactions taking place in the first half-cycle. In plasma-assisted ALD the oxidation step is not likely to be influenced by temperature, since the reaction energy is supplied by plasma power. In thermal ALD the oxidation step is influenced by the substrate temperature, since thermally activated reactions takes place.

Puurunen[9] indicates it is possible that the decrease in growth per cycle is an arti-
5.7. DISCUSSION

fact caused by incomplete reactions. For lower temperatures, with lower reaction rates and slower mass transport, the reaction might have not completed. The possibility of a
the ligand exchange reaction between precursor H2O and surface methyl-groups might
decrease for decreasing temperature, since it is a thermally activated reaction. Since
the H2O dose is not changed for decreasing temperatures less reactions occur resulting
is a lower amount of surface OH-groups. A different approach to explain the decrease
in growth per cycle with decreasing temperature is an increase of recombination of
surface OH-groups for decreasing temperature. For lower temperatures the H2O purge
time is extended. During a longer purge time more recombination reactions of surface
OH-groups occur, resulting in a smaller amount of surface OH-groups. Both mecha-
nisms result in lower amount of surface OH-groups, causing less reaction spots to react
with Al(CH3)3. This is also shown in figure 5.5, which shows that less Al atoms are
deposited per cycle, resulting in a lower growth per cycle.

As mentioned in 5.2 the increasing hydrogen concentration for decreasing tempera-
tures for both thermal and plasma ALD (as shown in figure 5.3c) indicates a larger
amount of OH-groups is incorporated in the deposited films. This indicates that not
all surface OH-groups react with the Al(CH3)3 precursor. Since this reaction is a ther-
rnally activated reaction, the reaction rate decrease for lower temperatures. Since the
Al(CH3)3 dose is not altered for decreasing temperatures, not all surface OH-groups
react with an Al(CH3)3 molecule. Figure 5.5 shows that for thermal ALD the amount
of aluminum atoms deposited per cycle decreases for decreasing substrate temperatures
<250°C. For plasma-assisted ALD, however, the number of aluminum atoms deposited
per cycle increases for decreasing temperature <250°C. An explanation can be that less
surface OH-groups recombine for decreasing temperature, resulting in an increasing
amount of surface OH-groups. This is in agreement with the results of the FTIR mea-
surements in 5.5, indicating a larger amount of OH groups in plasma-assisted ALD.
The larger amount of OH-groups increases the reaction rate of the reaction between
surface OH-groups and the Al(CH3)3 precursor.
Conclusions

In this thesis the optimization of the ALD processes for Al\(_2\)O\(_3\) for both plasma-assisted and thermal ALD in the Oxford Instruments OpAL reactor at a substrate temperature of 250 °C were described. Recipes were obtained for saturating ALD processes, without parasitic CVD components. A total cycle-time of 8 s was determined for plasma-assisted ALD. The nonuniformity was <1% for wafers with radii smaller than 7 cm. However at the edges of the reactor the uniformity decreased rapidly due to insufficient plasma exposure. For thermal ALD a recipe was determined with a total cycle time of 10 s. The nonuniformity for a wafer with a radius of 10 cm is 1.55 %.

Furthermore in this thesis a comparison was made between the plasma-assisted and the thermal ALD process for Al\(_2\)O\(_3\) while varying substrate temperatures. Observing the growth per cycle three different regions can be distinguished. In the first region (plasma-assisted and thermal ALD >250°C) the growth per cycle decreases for increasing temperatures due to dehydroxylation reactions. The activation energy of these dehydroxylation is calculated to be 0.216 eV. In the second region (plasma-assisted ALD >250°C) the growth per cycle increases for decreasing substrate temperatures because of the same dehydroxylation reactions. An additional cause is the lower density of the films for decreasing substrate temperature. In the third region (thermal ALD <250°C) the growth per cycle decreases for decreasing substrate temperatures. This could be explained by incomplete reactions during the oxidation step. Another explanation might be a higher amount of recombination of OH-groups due to extended purge times. The number of “monolayers” deposited per cycle ranges from 0.21 to 0.41.

The refractive index of the deposited Al\(_2\)O\(_3\) films was observed to be correlated to the mass density, independently of the deposition method. The mass density increases for increasing refractive index. The mass density is also correlated to the hydrogen
content, since hydrogen is mainly incorporated as OH in films, which reduces the density. Since the mass density is correlated to the hydrogen content, the refractive index is also correlated to the hydrogen content. The refractive index decreases for an increasing hydrogen content. From the correlation between the mass density, the hydrogen content and the refractive index, the refractive index can be used as a “qualitative measure” of the mass density and the hydrogen content.

FTIR measurements show a correlation between the absorbance of the Al-O bonds and the Al concentration. The absorbance increases for an increasing Al concentration. For plasma-assisted ALD the absorbance of the O-H bonds increases for increasing H concentration. However, for thermal ALD no significant absorbance is detected for O-H bonds.

It was also observed that the material properties improved for increasing substrate temperatures. The deposited films became more stoichiometric, while the mass density increased for increasing temperature. The hydrogen content decreased for increasing temperature, indicating a reduction of the amount of incorporated OH groups.
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Residence time

The residence time is the average time particles are present in the reactor. The purge time is the minimum time necessary to remove all the precursor gases from the reactor. It is expected therefore that there exists a correlation between the purge time and the residence time. In this appendix the correlation is investigated using a simple model to determine the residence time and experimental data. In section A.1 the residence time is calculated as a function of the reactor pressure. In section A.2 the minimum purge time after Al(CH$_3$)$_3$ is measured as a function of the reactor pressure and compared to the calculated residence time.

A.1 Residence time

The residence time $\tau$ of a gas in the OpAL reactor is calculated by dividing the volume $V$ of the reactor by the pump speed $S$:

$$\tau = \frac{V}{S}$$  \hspace{1cm} (A.1)

This suggests that the residence time is constant, if we assume that the pump speed for the OpAL reactor is constant, e.g. 63 m$^3$/hr, as mentioned in section 3.1.1.

However, if the pump speed depends on the pressure the residence time can be determined from the particle flow through the reactor. The change in the number of particles in the reactor over time is the difference between the number of particles entering the reactor and the number of particles leaving the reactor. The amount of particles leaving the reactor is given by the total amount in the reactor, divided by the residence time. When divided by the reactor volume, this gives:
APPENDIX A. RESIDENCE TIME

\[ \frac{dn}{dt} = \frac{Q}{V} - \frac{n}{\tau}, \quad (A.2) \]

in which \( n \) is the particle density in the reactor and \( Q \) is the number of particles entering the reactor per second.

During the depositions the particle density in the reactor will reach an equilibrium and the particle density will be constant:

\[ \frac{dn}{dt} = 0 \quad (A.3) \]

As a consequence the residence time is determined by:

\[ \tau = \frac{nV}{Q} \quad (A.4) \]

Using the ideal gas law \[25\] the particle density can be written as:

\[ n = \frac{P}{RT}, \quad (A.5) \]

in which \( P \) is the pressure in the reactor, \( R \) is the gas constant, and \( T \) is the reactor temperature.

The amount of particles entering the reactor is determined by the purge gas flow. Since the gas flow is given in sccm (standard cubic centimeter per minute), \( Q \) is given by:

\[ Q = \frac{1}{60} \frac{qP_0}{RT_0} \quad (A.6) \]

in which \( q \) is the gas flow in sccm, \( T_0 \) is the standard temperature (293.15 K), \( P_0 \) is the standard pressure (1 atm).

Substituting equation A.5 and A.6 into equation A.4 yields:

\[ \tau = 60 \cdot \frac{VT_0}{P_0T} \cdot \frac{P}{q} \quad (A.7) \]

When the temperature is kept constant\(^1\) in the reactor the first part of equation A.7 is constant and the residence time is dependent of the reactor pressure and the gas flow entering the reactor. In figure A.1 the pressure in the reactor is measured as a function of the gas flow entering the reactor (the reactor temperature was 180 °C and the gate valve was open). For low gas flows, the relation between the gas flow and the reactor

\(^1\)Note that \( V \) was estimated at 10,000 cm\(^3\).
A.2 PURGE TIME VS RESIDENCE TIME

Figure A.1: Pressure in the reactor as a function of the gas flow. The ratio between argon flow and oxygen flow is kept constant (7:25). The gate valve is open during these measurements, while the wall temperature is regulated to 180 °C.

<table>
<thead>
<tr>
<th>Flow (sccm)</th>
<th>Pressure (mTorr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
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<tr>
<td>120</td>
<td>200</td>
</tr>
<tr>
<td>150</td>
<td>250</td>
</tr>
</tbody>
</table>

Equation A.7 and the results obtained in figure A.1, allow us to calculate the residence time as a function of the reactor pressure (a reactor volume of 10,000 cm$^3$ is estimated, in this estimation the gate valve is considered to be open). The results of these calculations are shown in figure A.2, in which the residence time decreases for increasing pressure to a steady residence time of approximately 2.2 s. This indicates that for the lowest pressures the pump speed is not constant. Furthermore, when a constant pump speed of 63 m$^3$/hr is considered, equation A.1 gives a residence time of 0.57 s, which is lower than the residence time stabilizes to in figure A.2. This is explained by the long piping between the reactor and the pump, in which some pumping capacity is lost.

A.2 Purge time vs residence time

In the calculations of the residence time in section A.1 the gate valve is considered to be open, like in plasma-assisted ALD. In section 3.3.1 the purge after Al(CH$_3$)$_3$ is determined for the plasma-assisted ALD process. A purge flow of 64 sccm is applied, corresponding to a reactor pressure of 170 mTorr. A purge of at least ~3.5 s was required to remove all Al(CH$_3$)$_3$ from the reactor. Figure A.2 shows the residence time.
is influenced by the pressure. In this section the minimum purge time for obtaining pure ALD processes is determined for various pressures.

Apart from the purge time determined at 170 mTorr the minimum purge time is measured for two different pressures: 106 mTorr and 269 mTorr (which corresponds to total gas flows of 32 sccm and 108 sccm, respectively). The purge time is varied for both pressures while all other deposition settings are kept constant. In figure A.3 the growth per cycle is measured as a function of the growth per cycle, for three different pressures (including 170 mTorr). The growth per cycle is normalized by dividing the growth per cycle by the growth for a stabilized growth. Figure A.3 shows that for higher pressures a shorter purge is required for the growth per cycle to stabilize to a constant level, indicating that for that minimum time all Al(CH$_3$)$_3$ is removed from the reactor as explained in section 4.1.1. For a pressure of 106 mTorr a minimum purge of 5 s is required to remove Al(CH$_3$)$_3$ from the reactor, while for a pressure of 269 mTorr a minimum purge 2.5 s is required.

OES measurement are performed during the plasma exposure during these measurements to confirm the obtained results. In figure A.4a the intensity of the radiation emitted by excited H and OH species, integrated over the plasma exposure time, is measured as a function of the Al(CH$_3$)$_3$ purge for a reactor pressure of 269 mTorr. The radiation emitted by these reactor products is constant for purges longer than 2.5 s, indicating that all the purge is long enough to remove all Al(CH$_3$)$_3$ from the reactor. This confirms the results obtained in the growth per cycle measurements. Figure A.4b shows the radiation emitted by excited H and OH species for a reactor pressure of 106 mTorr. The radiation is constant for purges longer than 5 s, which also confirms the
A.2. PURGE TIME VS RESIDENCE TIME

Figure A.3: a) The growth per cycle measured as a function of the Al(CH$_3$)$_3$ purge time for three different reactor pressures: 106 mTorr, 170 mTorr and 269 mTorr. The growth per cycle is normalized by dividing it by the growth per cycle it stabilizes to when sufficient purge is used. In all depositions the Al(CH$_3$)$_3$ dose is 20 ms, the plasma exposure is 4 s, and the plasma purge is 0.5 s.

Figure A.5 shows a comparison of the measured Al(CH$_3$)$_3$ purge times and the residence times calculated in section A.1. The residence time and the purge time are shown as a function of the pressure in the reactor. Both the residence time and the purge time decrease for increasing pressure. The purge time decreases faster than the residence time. However, the calculated residence time gives a good indication of what the minimum Al(CH$_3$)$_3$ purge time should be.
Figure A.4: The radiation emitted by OH (309 nm) and H (656 nm) during the plasma exposure measured as a function of the Al(CH$_3$)$_3$ purge time for reactor pressures of a) 107 mTorr, and b) 269 mTorr. During the depositions the Al(CH$_3$)$_3$ dose is 20 ms, the plasma exposure is 4 s, and the plasma purge is 0.5 s.

Figure A.5: The calculated residence time and the measured Al(CH$_3$)$_3$ measured as a function of the pressure in the reaction chamber. The OpAL reactor is configured for plasma-assisted ALD with a reactor temperature of 180 °C.