Low-Temperature Plasma-Enhanced Atomic Layer Deposition of Silicon Dioxide and Aluminum Oxide

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Atomic layer deposition (ALD) is a powerful deposition technique for the fabrication of highly conformal and precise thickness-controlled films. Recently, there has been a growing interest in low-temperature (<100 °C) ALD because of the emerging applications made of organic and polymeric materials, which are known to be thermally sensitive materials. Due to the inherent disadvantages of low-temperature thermal ALD, such as slow reaction rate, long cycle time, poor film density, high impurity level and poor encapsulation properties of ultra-thin films (<5nm), the plasma-enhanced atomic layer deposition (PEALD) becomes an attractive alternative. However, there is only limited data available to show the effect of plasma parameters on film properties at low process temperatures and thus its full potential remains largely unexplored. This thesis presents the process development for low-temperature PEALD SiO₂ and Al₂O₃ aiming to have a deeper understanding of plasma parameters vs. film properties.

The work started with a study on PEALD SiO₂ thin film growth, where oxygen and carbon dioxide were used as oxidizing agents. The results showed that process temperature, plasma power and exposure time used in the deposition had a strong impact on the film growth rate as well as the film properties. For example, the growth-per-cycle (GPC) increased from 0.78 to 1.15 Å/cycle with a decrease of process temperature from 200 to 90 °C, plasma power from 300 to 50 W or plasma exposure time from 6 to 3 s, respectively. Although the high growth rate of ALD film is highly desired in the industry, the film quality should not be neglected. As shown in this work, there is a trade-off between the film properties and film growth rate during SiO₂ thin film deposition. In order to balance the throughput and quality of PEALD SiO₂ thin film, the plasma power of 180 W and plasma exposure of 3 s was suggested.

The studied low-temperature ALD Al₂O₃ processes included either O₂-based PEALD or a process that combines H₂O-based thermal ALD with in-situ N₂ plasma treatment. For O₂-based PEALD, the moisture barrier properties of Al₂O₃ films were found to be improved with increasing plasma power when the plasma exposure time was relatively short (1 and 3 s). The best water vapor transmission rate of 4-nm thick Al₂O₃ film was 5×10⁻⁹ gm⁻²day⁻¹. However, a degradation in the moisture barrier properties was observed if the plasma exposure time reached 6 s. This degradation did not occur in the combined process of H₂O-based thermal ALD with in-situ N₂ plasma treatment. In addition to the moisture barrier properties of Al₂O₃ thin films, the growth, refractive index, density, roughness and elemental composition were also investigated. Overall, the results demonstrate that with proper PEALD process optimization, it is possible to fabricate high-quality SiO₂ and Al₂O₃ films for thermally sensitive materials/applications.
Preface

When I was a second-year student of Master program in Department of Micro- and Nanosciences at Helsinki University of Technology (Presently: Aalto University school of electrical engineering) in 2008, I heard a new technology of “atomic layer deposition” in a lecture. Out of curiosity, I did some research on this keyword and noticed that it is a powerful technique of the thin film deposition which was firstly industrialized by Finnish researchers. More following this technology, I become more interested in it and hoped to be a part of this field someday.

Thanks to Beneq Oy, I started my journey in the world of “atomic layer deposition” in 2011. After a few years working as a process specialist in Beneq Oy, I got an opportunity of continuous my scientific research at Aalto University as a part-time student from 2015 to 2019.

The work presented in this thesis has been performed under the supervision of Prof. Hele Savin in the Electron Physics Group of Department of Electronics and Nanoengineering at Aalto University. I wish to express my utmost gratitude toward Prof. Hele Savin who offered excellent guidance to my scientific research during the last years. I would like to thank Dr. Chiara Modanese and Dr. Saoussen Merdes for their encouragement, advice and discussion on the scientific publications.

During the years, I have also had a chance to work closely with many experts for thin film characterization, Prof. Marisa Di Sabatino (from Norwegian University of Science and Technology), Dr. Perttu Sippola (from Aalto University school of electrical engineering), Oili M.E. Ylivaara (from VTT Technical Research Centre of Finland Ltd.), Mikko J. Heikkilä (from University of Helsinki) and Dr. Kenichiro Mizohata (from University of Helsinki). I am very grateful for their valuable contributions during my scientific research. Also, I want to acknowledge Prof. Harri Lipsanen, Haibing Huang, Yameng Bao, Dr. Päivikki Repo, Dr. Guillaume von Gastrow, Dr. Iris Mack and Dr. Ville Vähänissi from Aalto University and Dr. Emma Salmi, Dr. Markus Bosund, Kari Härkönen, Pekka J. Soininen, Ville Malinen, Kalle Niiranen, Mikael Saarni-heimo, Sami Sneck, Dr. Mikko Söderlund, Dr. Lei Dong, Zhenzi Chen, Rongxu Bai, Chunliang Liu and Sauli Virtanen from Beneq Oy for the warm discussion and support.

I want to thank some of my former colleagues, Shuo Li, Liang Qiao, Jiahua Chang, Jarmo Maula, Olli Jylhä, Prof. Matti Putkonen, Ismo Heikkinen, Heli Seppänen, whom I spent a great deal of time working together.
Finally, I give my heartfelt appreciation to my wife Cuiwen Chen and my lovely daughter Zhixuan (Amy) Zhu for their loving support. Lastly, I thank my parents, Tiansheng Zhu and Shuling Wang, for their love and support throughout my life.

Espoo, 14 July 2019
Zhen Zhu
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This thesis consists of an overview and the following publications which are referred to in the text by their Arabic numerals.


Author’s Contribution

**Publication 1:** Nanometer-scale depth-resolved atomic layer deposited SiO₂ thin films analyzed by glow discharge optical emission spectroscopy

The author designed the experiments, fabricated the samples and performed the measurements of ellipsometry and spectrometry. The author contributed to the data analysis of rf-GDOES. The author interpreted the majority of the results and wrote the manuscript.

**Publication 2:** Low-temperature plasma-enhanced atomic layer deposition of SiO₂ using carbon dioxide

The author designed the experiments, fabricated the samples and performed the measurements of ellipsometry and spectrometry. The author contributed to the data analysis of rf-GDOES and ATR-FTIR. The author interpreted the majority of the results and wrote the manuscript.

**Publication 3:** Influence of plasma parameters on the properties of ultrathin Al₂O₃ films prepared by plasma enhanced atomic layer deposition below 100 °C for moisture barrier applications

The author designed the experiments, fabricated the samples and performed the measurements of ellipsometry and WVTR. The author interpreted the majority of the results and wrote the manuscript.

**Publication 4:** Al₂O₃ thin films prepared by a combined thermal-plasma atomic layer deposition process at low temperature for encapsulation applications

The author designed the experiments, fabricated the samples and performed the measurements of ellipsometry. The author analyzed and interpreted the results, wrote the manuscript and presented the results in the conference of “EuroCVD 22-Baltic ALD 16”.

**Publication 5:** Residual stress study of thin films deposited by atomic layer deposition

The author designed the experiments, fabricated the samples and performed the measurements of ellipsometry. The author analyzed and interpreted the results, wrote the manuscript and presented the results in IEEE 12th International Conference on ASIC (ASICON).
Additionally, outside the scope of this thesis, the author has contributed to the published work in References [1–4].
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflection Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>BTBAS</td>
<td>Bis(tertiary-butylamino)silane</td>
</tr>
<tr>
<td>CCP</td>
<td>Capacitively coupled plasma</td>
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<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
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<tr>
<td>DRAMs</td>
<td>Dynamic random-access memories</td>
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<tr>
<td>ERDA</td>
<td>Elastic recoil detection analysis</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<tr>
<td>GD</td>
<td>Glow discharge</td>
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<td>GDOES</td>
<td>Glow discharge optical emission spectroscopy</td>
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<tr>
<td>GPC</td>
<td>Growth-per-cycle</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
</tr>
<tr>
<td>MEMS</td>
<td>Microelectromechanical systems</td>
</tr>
<tr>
<td>MOSFET</td>
<td>Metal oxide semiconductor field effect transistors</td>
</tr>
<tr>
<td>OES</td>
<td>Optical emission spectrometer</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light-emitting diode</td>
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<tr>
<td>PEALD</td>
<td>Plasma-enhanced atomic layer deposition</td>
</tr>
<tr>
<td>PEN</td>
<td>Polyethylene naphthalate</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
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<tr>
<td>RBS</td>
<td>Rutherford backscattering spectrometry</td>
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<tr>
<td>RF</td>
<td>Radio frequency</td>
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<tr>
<td>SIMS</td>
<td>Secondary ion mass spectrometry</td>
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<tr>
<td>TFEL</td>
<td>Thin film electroluminescent</td>
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<tr>
<td>Acronym</td>
<td>Term</td>
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<td>---------</td>
<td>-------------------------------------------</td>
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<tr>
<td>TMA</td>
<td>Trimethylaluminum</td>
</tr>
<tr>
<td>TOF-ERDA</td>
<td>Time-of-flight elastic recoil detection analysis</td>
</tr>
<tr>
<td>WVTR</td>
<td>Water vapor transmission rate</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>XRR</td>
<td>X-ray reflectivity</td>
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</table>
List of Symbols

\( A \)  \hspace{1cm} \text{Atoms or radicals}
\( A^* \)  \hspace{1cm} \text{Atoms in an excited state}
\( A^{\pm(\cdot)} \)  \hspace{1cm} \text{Positive or negative ions}
\( AB \)  \hspace{1cm} \text{Molecules}
\( e \)  \hspace{1cm} \text{Electron}
\( \Psi \)  \hspace{1cm} \text{Amplitude ratio}
\( \Delta \)  \hspace{1cm} \text{Phase difference}
\( \Phi \)  \hspace{1cm} \text{Incident angle of ellipsometer}
\( \theta \)  \hspace{1cm} \text{Critical angle of X-rays incidence during the measurement of X-ray reflectivity}
\( E_s \)  \hspace{1cm} \text{Elastic modulus of the substrate}
\( N \)  \hspace{1cm} \text{Number of ALD cycles}
\( R_o \)  \hspace{1cm} \text{Substrate curvature radius before the film deposition}
\( R_i \)  \hspace{1cm} \text{Substrate curvature radius after the film deposition}
\( t \)  \hspace{1cm} \text{Waiting step between the H_2O pulse and the N_2 plasma exposure}
\( t_f \)  \hspace{1cm} \text{Thickness of ALD thin film}
\( t_s \)  \hspace{1cm} \text{Thickness of the substrate}
\( V_s \)  \hspace{1cm} \text{Poisson’s ratio of substrate}
\( \sigma_f \)  \hspace{1cm} \text{Stress of thin film}
1. Introduction

Atomic layer deposition (ALD) is a thin film growth method which can be considered to belong to a subclass of chemical vapor deposition (CVD), and which offers the exceptional advantages in the form of precise film thickness control combined with pinhole free, high uniformity, and conformal film growth.

ALD was invented independently twice by Prof. Aleskovskii and Prof. Suntola in the 1960s and in 1970s, respectively. [5–7] Prof. Tuomo Suntola firstly introduced this thin film growth method to a specific industrial application, namely a flat panel thin film electroluminescent (TFEL) display that was based on ALD processes of ZnS:Mn, Al₂O₃ and TiO₂ films. [7,8] Nowadays, ALD technology has been widely used in the semiconductor applications, e.g. high-κ dielectric ALD thin films are used as gate oxides in the metal oxide semiconductor field effect transistors (MOSFET) and capacitor dielectrics in dynamic random-access memories (DRAMs). [8] In the field of microelectromechanical systems (MEMS), ALD also attracts a lot of attention since ALD layers can be utilized as wear resistant, [9] anti-stiction, [10] and insulating [11] coatings to enhance the performance of MEMS components. Moreover, ALD has been successfully adapted to the applications of photonics, [12–14] photovoltaics, [1,2,15] sensors, [16,17] catalysts, [18] and protective coatings. [19,20]

Recently, the request for low-temperature ALD has grown rapidly because of the emerging applications for organic and polymeric materials. For example, during the fabrication of organic light-emitting diodes (OLED) and flexible displays, the process temperature of ALD is often limited to 100 °C as the organic emitter and polymeric substrate do not tolerate higher temperatures. However, conventional low-temperature thermal ALD processes are known to suffer from shortcomings such as a slow reaction rate, long cycle time, poor structural quality and high impurity levels. [21]

To overcome those challenges, plasma-enhanced atomic layer deposition (PEALD) is potentially an advantageous method to grow high-quality ALD films at low temperatures, considering that the surface chemistry involved in the process is driven by the plasma species rather than the thermal energy. This merit of PEALD has recently attracted a lot of attention in the industrial applications, e.g. the spacer-defined double-patterning method in DRAM manufacturing and thin film encapsulation for OLED display. [22] In these industrial applications, PEALD offers excellent film uniformity, high throughput and low process temperature < 100 °C. However, the use of plasma species can also lead to complex surface reactions and degradation of films or substrates. [23] Therefore, further
development and optimization of PEALD processes as well as deeper understanding of the PEALD reactions are highly desired.

The two most common ALD oxide materials are SiO$_2$ and Al$_2$O$_3$ which are amorphous and pinhole free. SiO$_2$ thin films are studied and developed mostly in the field of microelectronics [8,24–26] and optics [27–29] while Al$_2$O$_3$ thin films show good performance in the surface passivation of Si-based solar cells, [1,15] as well as in the moisture barrier for encapsulation applications. [30–32] In this thesis, these common ALD films (SiO$_2$ and Al$_2$O$_3$) were selected to study the impact of low-temperature PEALD process parameters on the resulting film properties aiming to broaden the applications of SiO$_2$ and Al$_2$O$_3$ films to thermally sensitive materials.

The structure of this dissertation consists of five chapters. In the following, the principles of the thermal and plasma-enhanced ALD are presented in Chapter 2, together with the configurations of different reactors. Chapter 3 describes the experimental techniques of film growth and characterization utilized in this thesis. In Chapter 4, the main results of low-temperature PEALD oxides, such as SiO$_2$ (reported in Publication 1 and 2) and Al$_2$O$_3$ (reported in Publication 3 and 4 as well as Publication 5) are summarized. Finally, the conclusion of this thesis is given in Chapter 5.
2. Atomic Layer Deposition (ALD)

Atomic layer deposition is a chemical deposition method, closely related to CVD. Unlike to CVD, in ALD the gas phase precursors are not applied to the reactor simultaneously, and thus no gas phase reactions are involved. ALD film growth occurs through sequential self-terminating gas-solid reactions. An example of one ALD-cycle is shown in Figure 1, illustrating the following four steps:

i. The self-terminating reaction of the first precursor
ii. Purge to remove the unreacted precursors and by-products
iii. The self-terminating reaction of the second precursor
iv. Purge to remove the unreacted precursors and by-products

As a result of one ALD-cycle, one monolayer is formed. By repeating the ALD-cycle, a film with the desired thickness can be grown. This proportional relationship between film thickness and numbers of ALD-cycle is generally expressed as growth-per-cycle (GPC) which can be obtained by

\[ GPC = \frac{t_f}{N} \]

where \( t_f \) is the thickness of ALD thin films and \( N \) is the number of ALD cycles. Moreover, the above four steps are often divided into two “ALD half-cycles”, shown in Fig. 1.

<table>
<thead>
<tr>
<th>First ALD half-cycle</th>
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<td>(a)</td>
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<th>ALD cycle</th>
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<td>(c)</td>
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<th>Second ALD half-cycle</th>
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<td>(d)</td>
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<td>(e)</td>
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**Figure 1.** Schematic of one ALD-cycle (a) pulse of the first precursor, (b) purge, (c) pulse of the second precursor and (d) purge. The steps of (a) and (b) can be referred to the “first ALD half-cycle”, while (c) and (b) belong to the “second ALD half-cycle”.

Generally, ALD can be divided into thermal ALD and plasma-enhanced ALD based on the driven energy of surface reactions. For thermal ALD, the substrate
temperature is a key factor since the surface reactions are mainly driven by thermal energy. For plasma-enhanced ALD, the surface chemistry involved in the process is driven by plasma species, which allows more freedom in the process conditions as compared to thermal ALD. [23] More details of thermal and plasma-enhanced ALD are shown below.

## 2.1 Thermal ALD

In thermal ALD, the surface reactions are driven by the thermal energy. The process temperature, which is also called as substrate temperature, reactor temperature or growth temperature, is one of the most important key parameters for film growth, thus, emphasizing the need for finding a suitable ALD temperature window in process optimization.

### 2.1.1 Temperature window

For ideal ALD thin film growth, the GPC is independent on the certain process temperature range and remains a constant. In Figure 2, the schematic of the ALD window is presented as well as some non-ALD growth phenomena. When process temperature is lower than the limit of ALD temperature window, the GPC either increases or decreases depending on the condensation or low reactivity of precursors. At temperatures above the ALD window, the precursor decomposition might lead to a CVD component and results in an increase of GPC, whereas the precursor desorption can lead to a decreased GPC.

![Figure 2. Schematic of ALD temperature window. Some non-ALD growth phenomena, such as condensation, low-reactivity, decomposition and desorption of precursor, are illustrated as well.
](image)

### 2.1.2 Precursor pulse and purge time

In order to achieve the desired ALD process, each half-reaction has to be irreversible and saturated. Growth saturation ensures the self-limiting growth mechanism of ALD and has a close relationship with precursor pulse time which is shown in Figure 3. When the pulse time of precursor is long enough, the film growth reaches saturation where the GPC remains a constant and is not dependent on the precursor dose. [33] Otherwise, the unsaturated growth occurs because of the insufficient precursor dose.
In addition to the GPC vs. precursor pulse time, Fig. 3 presents the GPC as a function of the precursor purge time. To prevent the co-existence of two precursors, which leads to an undesired CVD-like film growth, a sufficient purge time is required for the residual removal of unreacted precursors, particularly during the low-temperature process. [21]

**Precursor purge time**

Figure 3. GPC as a function of precursor pulse and purge time. The insufficient pulse and purge time of precursor lead to the unsaturated and CVD-like growth, respectively.

### 2.1.3 Low-temperature thermal ALD

In general, thermal ALD processes are conducted at modest temperatures which are often lower than 350 °C. [34] However, for thermal-sensitive materials, such as organic and polymeric materials, the temperature range between room temperature and 100 °C is highly preferred. In order to achieve the requested low-temperature, highly reactive precursors are preferred. For example, trimethylaluminum (TMA) and water enable the growth of Al₂O₃ at room temperature without a significant decline in GPC (~1.1 Å/cycle). [21] Furthermore, the use of catalyst is an effective solution to decrease the process temperature of thermal ALD. [35–37]

At low temperature, due to the lack of thermal energy, the precursor reactivity is relatively low compared to the one at high temperature. As reported in an earlier study of low-temperature ALD Al₂O₃ thin films, [38] the reactivity of the first half ALD-cycle is not enough at low temperature, and thus causes an inefficient removal of -CH₃ surface groups. The residual of -CH₃ groups impact on the reaction in the second half ALD-cycle. This persistent negative effect limits the growth of ALD thin films. Another major issue of low-temperature ALD is CVD-like reactions which are caused by the incomplete removal of “precursor A” before the pulse of “precursor B”. Particularly, for the H₂O-based low-temperature thermal ALD, a long purge time of water, which is often in the range of minutes, is requested. [21,39]
2.1.4 Thermal ALD reactors

Thermal ALD reactors can be divided between temporal and spatial-ALD configurations. In the temporal-ALD reactors, as shown in Figure 4 (a) and (b), the substrates are stationary and the precursor delivery is separated in time with inert gas purge step. Contrary to temporal-ALD, in the spatial-ALD reactors (Fig. 4 (c) and (d)) there is a motion or relative-motion of substrates and the precursors are separated in space.

Depending on the throughput, the temporal-ALD reactors can also be divided into the single-substrate reactor (Fig. 4 (a)) and the batch reactor (Fig. 4 (b)). [40,41] For the batch reactor, multiple substrates can be coated in one run. Although the relatively long cycle-time is needed to prevent the CVD components or chemical side-effects, the deposition-speed-per-substrate, defined by the ratio of total ALD process time and the number of substrates, is much higher than the one of the single-substrate reactor. On the other hand, the large volume and complex configuration of the batch reactor have a larger influence on the control of film thickness uniformity, making it more difficult for process optimization.

Instead of separating the precursor pulsing step, Fig. 4 (c) and (d) show that the precursors are continuously and separately delivered into zone A and B in the spatial-ALD reactors. [42,43] In order to expose the substrate to the precursors, the motion or relative-motion of substrates is needed. For instance, when the substrate travels to zone A, the first ALD half-reaction is taking place. After the substrate passes zone B, the full ALD-cycle is done. Therefore, the GPC of thin films is strongly linked to the travelling or relative-travelling speed of the substrate. If the flexible substrates (i.e. polymers) are placed in a spatial-ALD reactor (Fig. 4 (d)), this special configuration is often named as “roll-to-roll ALD”. [44,45]

![Figure 4. Schematic of the ALD reactors (a) single-substrate reactor, (b) batch reactor, (c) spatial reactor and (d) roll-to-roll reactor.](image-url)
2.2 Plasma-enhanced atomic layer deposition (PEALD)

2.2.1 Plasma processing

Plasma processing has been widely applied for many industrial applications, e.g. plasma ashing for photoresist removal, [46] cleaning for surface contamination, [47,48] surface activation, [49] etching, [50,51] film densification [52,53] and film deposition, which includes physical vapor deposition (PVD) [54,55] and CVD. [56,57]

Plasma-enhanced atomic layer deposition is one of the plasma-based film depositions, belonging to the category of CVD. Compared to thermal ALD, the surface reactions of the second ALD half-cycle during PEALD process are activated in a plasma environment. Figure 5 presents an example of one ALD-cycle for Al2O3 growth using PEALD. Due to the involvement of the plasma species, the surface reactions of PEALD are more complex than the ones of thermal ALD. However, plasma enhancement yields to several potential benefits:

- Improved film properties related to film growth, density and impurity level;
- Reduced film deposition temperature without compromising the film quality;
- Decreased ALD cycle time during the low-temperature process;
- Added possibilities of plasma treatments, including pre-treatment, in-situ treatment and post-treatment;

![Figure 5. A schematic of one ALD-cycle for PEALD Al2O3 growth using TMA and O2 plasma as precursors.](image)

2.2.2 Gas discharge

As mentioned above, the plasma reactions are complex. In order to understand the surface reactions of PEALD, the gas discharges during the process have to be discussed. In this section, the discharges of O2 (reported in Publication 1, 3 and 5), CO2 (reported in Publication 2), H2O vapor (reported in Publication 4), and N2 (involved in all processes of reported publications) are briefly described.

Plasma is a gas composed of charged species (i.e. electrons, negative and positive ions), radicals, atoms and molecules in their neutral and excited states. The
plasma can be created by providing sufficient kinetic energy to gases in order to exceed their ionization potential, \(i.e.\) 12.07 eV for \(\text{O}_2\), \([58]\) 13.78 eV for \(\text{CO}_2\), \([59]\) 12.7 eV for \(\text{H}_2\text{O}\), \([59,60]\) and 15.7 eV for \(\text{N}_2\). \([58,59]\) The kinetic energy can be provided by external sources, such as high-frequency electromagnetic fields (radio frequency (RF), microwave), electric fields, lasers, etc. Table 1 shows the main reactions during a plasma discharge.

For the excitation process, electron collision with an atom or molecule can lead to elevation of the electron to a higher energy level but will still orbit the nucleus. In the process of ionization, ions are formed by gain or loss of an electron from an atom or a molecule. When the atom or molecule gains the electron from the electron collision, it becomes a negatively charged ion. Otherwise, it forms positively charged ion due to the loss of the electron. Electron-impact detachment can be important in destroying atomic or molecular negative ions. After the electron collision, the negative charged atom or molecule becomes neutral. During the dissociation process, the \(\text{AB}\) molecule can be separated into two reactive atoms of \(\text{A}\) and \(\text{B}\) by electron collision. The dissociation products \(\text{A}\) and \(\text{B}\) are called radicals which have a significant role in the process of PEALD. During the reaction, the dissociation and ionization can appear simultaneously, and thus lead to a dissociative ionization. For dissociative recombination, the electron collision can destroy the positive charged molecular and lead to the productions of an atom with an excited state and a radical. The process of dissociative attachment produces a negative ion as well as a radical due to the collision between the electron and molecular. As shown in Table 1, the charge transfer corresponds to an electron transfer from a neutral particle to a positive ion. If the reaction has no defect of electronic energy, \(i.e.\) \(\text{O}^+\) to \(\text{O}\), it is called a resonant charge transfer; otherwise, it is referred to nonresonant charge transfer, \(i.e.\) the electron transfer between \(\text{O}^+\) and \(\text{N}\) has an energy defect of 1 eV.\([61]\)

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation</td>
<td>(\text{A} + \text{e} \rightarrow \text{A}^* + \text{e})</td>
</tr>
<tr>
<td>Ionization</td>
<td>(\text{A} + \text{e} \rightarrow \text{A}^+ + 2\text{e})</td>
</tr>
<tr>
<td>Electron-impact detachment</td>
<td>(\text{A}^* + \text{e} \rightarrow \text{A} + 2\text{e})</td>
</tr>
<tr>
<td>Dissociation</td>
<td>(\text{AB} + \text{e} \rightarrow \text{A} + \text{B} + \text{e})</td>
</tr>
<tr>
<td>Dissociative ionization</td>
<td>(\text{AB}^* + \text{e} \rightarrow \text{A} + \text{B}^* + 2\text{e})</td>
</tr>
<tr>
<td>Dissociative recombination</td>
<td>(\text{AB}^* + \text{e} \rightarrow \text{A} + \text{B}^*)</td>
</tr>
<tr>
<td>Dissociative attachment</td>
<td>(\text{AB} + \text{e} \rightarrow \text{A} + \text{B})</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>(\text{A}^* + \text{B} \rightarrow \text{A} + \text{B}^*)</td>
</tr>
</tbody>
</table>
**Oxygen discharges**

In **Publication** 1, 3 and 5, O$_2$ plasma was used for the growth of SiO$_2$ and Al$_2$O$_3$ thin films, and therefore the examples of reactions in oxygen discharge are listed in Table 2.

**Table 2. Examples of reactions in oxygen discharge.** [63–66]

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation</td>
<td>O + e → O$^+$ + e</td>
</tr>
<tr>
<td>Ionization</td>
<td>O + e → O$^+$ + 2e</td>
</tr>
<tr>
<td>Electron-impact detachment</td>
<td>O$^+$ + e → O + 2e</td>
</tr>
<tr>
<td>Dissociation</td>
<td>O$_2$ + e → O + O + e</td>
</tr>
<tr>
<td>Dissociative ionization</td>
<td>O$_2$ + e → O + O$^+$ + 2e</td>
</tr>
<tr>
<td>Dissociative recombination</td>
<td>O$_2$ + e → O + O</td>
</tr>
<tr>
<td>Dissociative attachment</td>
<td>O$^+$ + O$_2$ → O + O$_2$$^+$</td>
</tr>
</tbody>
</table>

**Carbon dioxide discharges**

In **Publication** 2, CO$_2$ plasma was used for the growth of SiO$_2$ thin films, and therefore the examples of reactions in carbon dioxide discharge are listed in Table 3.

**Table 3. Examples of reactions in carbon dioxide discharge.** [67,68]

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation</td>
<td>CO$_2$ + e → CO$_2$$^+$ + e</td>
</tr>
<tr>
<td>Ionization</td>
<td>CO$_2$ + e → CO$_2$$^+$ + 2e</td>
</tr>
<tr>
<td>Dissociation</td>
<td>CO$_2$ + e → CO + O + e</td>
</tr>
<tr>
<td>Dissociative ionization</td>
<td>CO$_2$ + e → CO + O$^+$ + 2e</td>
</tr>
<tr>
<td>Dissociative recombination</td>
<td>CO$_2$ + e → CO + O$^*$</td>
</tr>
<tr>
<td>Dissociative attachment</td>
<td>CO$_2$ + e → CO + O$^-$</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>CO$_2$ + CO$^+$ → CO$_2$$^+$ + CO</td>
</tr>
</tbody>
</table>

**Water discharges**

In **Publication** 4, H$_2$O plasma was involved in the growth of Al$_2$O$_3$ thin films, and therefore the examples of reactions in water vapor discharge are listed in Table 4.

**Table 4. Examples of reactions in water vapor discharge.** [66,69]

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation</td>
<td>OH + e → OH$^+$ + e</td>
</tr>
<tr>
<td>Ionization</td>
<td>OH + e → OH$^+$ + 2e</td>
</tr>
<tr>
<td>Electron-impact detachment</td>
<td>OH$^+$ + e → OH + 2e</td>
</tr>
<tr>
<td>Dissociation</td>
<td>H$_2$O + e → H + OH + e</td>
</tr>
<tr>
<td>Dissociative ionization</td>
<td>H$_2$O + e → H$^+$ + OH + 2e</td>
</tr>
<tr>
<td>Dissociative recombination</td>
<td>H$_2$O$^+$ + e → H + OH$^+$</td>
</tr>
<tr>
<td>Dissociative attachment</td>
<td>H$_2$O + e → OH$^+$ + H</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>H$^+$ + OH → OH$^+$ + H</td>
</tr>
</tbody>
</table>
**Nitrogen discharges**

In this work, N\(_2\) was used as the carrier and purge gas for the growth of all mentioned oxide films. Thus, the examples of reactions in nitrogen discharge have to be considered and are listed in Table 5.

**Table 5. Examples of reactions in nitrogen discharge.** [63,70,71]

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation</td>
<td>N(_2) + e \rightarrow N(_2^*) + e</td>
</tr>
<tr>
<td>Ionization</td>
<td>N + e \rightarrow N(^+) + 2e</td>
</tr>
<tr>
<td>Dissociation</td>
<td>N(_2) + e \rightarrow N + N + e</td>
</tr>
<tr>
<td>Dissociative ionization</td>
<td>N(_2) + e \rightarrow N + N(^+) + 2e</td>
</tr>
<tr>
<td>Dissociative recombination</td>
<td>N(_2^+) + e \rightarrow N + N(^+)</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>N(^+) + N(_2) \rightarrow N + N(_2^+)</td>
</tr>
</tbody>
</table>

**2.2.3 Surface chemistry of PEALD**

**Silicon dioxide**

In this thesis, the bis(tertiary-butylamino)silane (BTBAS) was used as a Si precursor. The O radicals, which can be generated during the O\(_2\) and CO\(_2\) plasma dissociation reactions as shown in Table 2 and 3, dominated ALD surface reactions as the oxidizing agents. In this case, the reactions of the first and second ALD half-cycle for SiO\(_2\) thin films reported in *Publication* 1 and 2 can be described by:

\[ \text{||–} \text{OH} + \text{SiH}_2[\text{NHtBu}]_2 (g) \rightarrow \text{||–} \text{O–SiH}_2[\text{NHtBu}]_{2–x} + \text{t-butylamine (g)} \quad (2) \]

\[ \text{||–} \text{O–SiH}_2[\text{NHtBu}]_{2–x} + 4\text{O (g)} \rightarrow \text{||–} \text{O–OH} + \text{H}_2\text{O (g)} + \text{CO}_2 (g) + \text{N-containing species (g)} \quad (3) \]

where only one (x=1) or both (x=2) of -NHtBu ligands, which are shown in the reaction of first ALD half-cycle, can react with the surface -OH groups forming t-butylamine molecules into the gas phase. [72]

**Aluminum oxide**

Based on earlier studies, [73] the surface reactions of PEALD Al\(_2\)O\(_3\) using TMA (as Al source) and O\(_2\) plasma (as the oxidant) reported in *Publication* 3 and 5 can be written as:

\[ \text{||–} \text{OH} + \text{Al(CH}_3)_3 (g) \rightarrow \text{||–} \text{O–Al(CH}_3)_2 + \text{CH}_4 (g) \quad (4) \]

\[ \text{||–} \text{O–Al(CH}_3)_2 + 4\text{O (g)} \rightarrow \text{||–} \text{O–Al–OH} + \text{CO}_2 (g) + \text{H}_2\text{O (g)} \quad (5) \]

Nevertheless, the surface chemistry of the H\(_2\)O plasma involved ALD Al\(_2\)O\(_3\) process is more complex since both H\(_2\)O molecule [74–76] and OH radicals, [77–80] which are generated during H\(_2\)O plasma dissociation reactions (in Table 4), can be regarded as oxidants. The reaction of the first ALD half-cycle can be described as Equation (4), while the reaction of the second ALD half-cycle can be considered as a combination of Equation (6) and (7).

\[ \text{||–} \text{O–Al(CH}_3)_2 + \text{H}_2\text{O (g)} \rightarrow \text{||–} \text{O–Al–OH} + \text{CH}_4 (g) \quad (6) \]

\[ \text{||–} \text{O–Al(CH}_3)_2 + \text{OH (g)} \rightarrow \text{||–} \text{O–Al–OH} + \text{hydrocarbon (g)} \quad (7) \]
2.2.4 PEALD reactors

There are several different reactor configurations for PEALD, which differ from the design of plasma source and the solution of plasma species delivery. Four common PEALD reactor configurations, the radical-enhanced ALD, direct plasma ALD, inductively coupled plasma (ICP) ALD, and capacitively coupled plasma (CCP) ALD, are shown in Figure 6.

In the radical-enhanced ALD (Fig. 6 (a)), the plasma species have to travel through a long distance to reach the substrate. Consequently, many ions and electrons are lost due to their recombination in the delivery path, and only radicals participate in the film deposition process. However, the flux of radicals can also be reduced by recombination reactions. To reach the saturated surface reaction, long plasma exposure is often required. [23]

![Figure 6. Schematic of the PEALD reactors. (a) radical-enhanced ALD, (b) direct plasma ALD and remote plasma ALD with (c) ICP and (d) CCP. Reproduced with permission from [23]. Copyright 2011 American Vacuum Society.](image)

In Figure 6 (b), the reactor configuration presents a direct plasma ALD with a CCP setup, containing two planar electrodes. The discharge between the electrodes is driven by the RF source. The upper electrode is typically powered, while the lower one is grounded. The substrate is located on the lower electrode. Depending on the delivery path of plasma gases, the reactor can also be divided into a “shower-flow reactor”, where gases are introduced into the reactor through the powered electrode, and a “cross-flow reactor”, where the gases are introduced from the side of the electrodes.
Remote plasma ALD often integrates an ICP source which is located remotely from the substrate stage (Fig. 6 (c)). In remote plasma ALD, the flux of radicals and ion bombardment can be tuned by the distance between source and substrate as well as the pressure in the reactor. An alternative approach of remote plasma ALD is shown in Figure 6 (d). In this reactor, a grounded mesh plate is placed between two electrodes. This configuration allows plasma radicals to diffuse to the substrate, while it limits the ion energy and flux towards the deposition surface. [23] In this plasma setup, the operating pressure of the ALD process is of the order of 1 hPa. Due to the short distance between the two electrodes, the high power of the plasma generator is not necessary while a few hundred watts can be satisfied. However, there is a drawback of the short distance between two electrodes, which makes the PEALD process of conducting or metal films more complicated than the one in the ICP plasma setup because of the precursor diffusion. In this case, the flow of shower gas and hole size of the mesh plate have to be well controlled and selected.
3. Experimental

This chapter introduces the methods of fabrication and characterization for SiO₂ and Al₂O₃ thin films used by the author of this thesis. The plasma-enhanced atomic layer deposition equipment will be described in Section 3.1. In addition to that, the characterization analyses, such as ellipsometry, X-ray reflectivity (XRR), thin film stress analysis, moisture permeation analysis, Fourier transform infrared spectroscopy (FTIR), glow discharge optical emission spectroscopy (GDOES), and time-of-flight elastic recoil detection analysis (TOF-ERDA) used for the publications will be introduced in Section 3.2.

3.1 Sample fabrication

The SiO₂ and Al₂O₃ thin films were grown by a commercial Beneq TFS 200 ALD equipped with a capacitively coupled 13.56 MHz RF plasma source. The process temperature was mainly kept at 90 °C. The schematic of the plasma configuration of TFS 200 ALD is shown in Figure 7. The plasma discharge region was above the substrate. A grounded metal grid was located between the plasma discharge and substrate to prevent the plasma damage of the substrate. N₂ was used as a carrier and purge gas with a through reactor flow of 300-600 sccm and a through plasma system flow of 50-200 sccm. During the processes, the pressure in the reactor was about 1 hPa. Furthermore, the container temperature of precursor A and B was set to 21 °C. The precursor was pulsed into the reactor either by own vapor pressure or with 0.1 s N₂ boost (See Figure 8). The sequence of precursor pulse and plasma exposure depended on the selected precursors. The details of ALD-cycle for SiO₂ and Al₂O₃ growth are shown below.

Figure 7. Schematic representation of the remote plasma configuration in Beneq TFS 200 ALD.
3.1.1 ALD-cycle sequence of SiO₂

When BTBAS was used as the precursor A, the N₂ boost was required. O₂ or CO₂ was used as the precursor C with a constant gas flow, the ALD-cycle sequence consists of

\[ \text{precursor A pulse (0.05-0.5 s)} \rightarrow \text{purge (0.5-3 s)} \rightarrow \text{plasma on (1-15 s)} \rightarrow \text{plasma off} \rightarrow \text{purge (0.5-3 s)}. \]

![Figure 8](image)

Figure 8. Precursor pulse with (a) own vapor pressure and (b) N₂ boost of 0.1 s.

3.1.2 ALD-cycle sequence of Al₂O₃

For O₂-based PEALD, TMA and a constant flow of O₂ were introduced into the reactor through precursor A and C, respectively. The ALD-cycle sequence consists of

\[ \text{precursor A pulse (0.2 s)} \rightarrow \text{purge (3 s)} \rightarrow \text{plasma on (1-6 s)} \rightarrow \text{plasma off} \rightarrow \text{purge (2 s)}. \]

For the combined process of thermal-plasma ALD, TMA and H₂O were used as the precursor A and B, respectively. The ALD-cycle sequence consists of

\[ \text{precursor A pulse (0.2 s)} \rightarrow \text{purge (3 s)} \rightarrow \text{precursor B pulse (0.15 s)} \rightarrow \text{plasma on (1-6 s)} \rightarrow \text{plasma off} \rightarrow \text{purge (7 s)} \]

or

\[ \text{precursor A pulse (0.2 s)} \rightarrow \text{purge (3 s)} \rightarrow \text{precursor B pulse (0.15 s)} \rightarrow \text{waiting step (0.5-2 s)} \rightarrow \text{plasma on (6 s)} \rightarrow \text{plasma off} \rightarrow \text{purge (7 s)}. \]

3.2 Characterization methods

3.2.1 Ellipsometry

Ellipsometry is a powerful method to determine the thickness of thin films with sub-nm scale precision. The instrument of this technique is called an ellipsometer which often consists of the light source, polarizer, compensators, analyzer and detector. As shown in Figure 9, the light beam, which is emitted by a
light source and linearly polarized by a polarizer, passes through a compensator and irradiates the sample. After surface reflection, the light beam passes another compensator and analyzer, then finally falls into the detector. The measurement of ellipsometry is based on the change in polarization which can be represented as an amplitude ratio ($\Psi$) and the phase difference ($\Delta$). During the data analysis, the calculated values of $\Psi$ and $\Delta$, which match the experimental data best, determine the film optical constants and thickness. [81]

In this thesis, SENTECH SE400adv ellipsometer, which employs a HeNe laser with a wavelength of 632.8 nm at a 70 ° angle of incidence ($\Phi$), was used to determine the film thickness and reflective index. Furthermore, the thickness uniformity of thin film was obtained by a wafer scan with statistical data.

![Figure 9. The schematic of the ellipsometer.](image)

### 3.2.2 X-ray reflectivity

X-ray reflectivity (XRR) is a contact-free measurement to obtain film information of thickness, density and roughness. The basic idea behind this technique is to measure the intensity of reflected X-rays from the sample when the reflected angle is equal to the incident angle. Philips X’pert Pro diffractometer was used in this thesis, and the schematic of XRR measurement is shown in Figure 10 (a). When the incident angle is above the critical angle $\theta$, the radiation can penetrate the deposited film. Due to the different density of materials, the reflective and refractive conditions for X-ray beams are unique. On the other hand, if the incident angle is below $\theta$, all X-ray beams will be only reflected on the surface. After the data record, a proper simulation has to been done based on the reflectance curve (see Fig. 10 (b)) to extract the information of film thickness (from the spacing of the oscillations), density (from the location of the critical angle) and surface roughness (from the slope of the oscillations). In this thesis, most of the XRR data were simulated with an in-house developed fitting software which is based on Parratt’s formalism and Nevot-Croce roughness approximation. [82]
Experimental

![Figure 10](image.png)

Figure 10. (a) Schematic representation of XRR measurement and (b) the example of the XRR curve.

### 3.2.3 Thin film stress analysis

Residual stress is often determined together with the wafer curvature measurement [83] and Stoney’s equation [84]

\[
\sigma_f = -\frac{E_s}{6(1-V_s)} \frac{t_s^2}{t_f} \left(\frac{1}{R_1} - \frac{1}{R_0}\right)
\]  

(8)

where \(\sigma_f\) is the thin film stress; \(E_s\) is the elastic modulus of the substrate; \(V_s\) is the Poisson’s ratio of the substrate; \(t_s\) and \(t_f\) are the thickness of the substrate and the film, respectively; \(R_0\) and \(R_t\) are the substrate curvature radius measured before and after the film deposition. In order to obtain accurate film stress, the film thickness nonuniformity over the wafer has to be minimized. Moreover, the backside coating of the thin film should also be avoided due to the effect on curvature measurement. In Publication 2, 4 and 5, the TOHO FLX-2320-S was used for wafer curvature measurement and the schematic of the measurement is shown in Figure 11. The 150 mm wafers were scanned in two directions of parallel and perpendicular to the wafer flat using a 120-mm scan length.

![Figure 11](image.png)

Figure 11. Schematic representation of wafer curvature measurement to determine thin film stress.
3.2.4 Moisture permeation analysis

Water vapor transmission rate (WVTR) is a key criterion for describing the moisture permeation barrier properties of thin films. Nowadays, the WVTR measurements are typically conducted by either calcium tests based on the optical and electrical methods [85,86] or using a commercial tool. [87,88] In this thesis, a commercial tool of Systech Illinois 7001 water vapor permeation analyzer was used. This analyzer complies with ASTM standard F-1249. [89] For this method, the maximum active test area on the sample is 50 cm² and the measurement range is from 0.002 to 18 gm⁻²day⁻¹ at temperatures of 5-50 °C. The principle of operation is shown in Figure 12. The sample is clamped to a diffusion chamber and a wet N₂ flow is then introduced into the upper half of the chamber while a dry N₂ flows through the lower half chamber. The water molecules diffuse through the sample into the lower chamber and are conveyed to the sensor. Finally, the detected moisture implies WVTR. The WVTR of Al₂O₃ coated Polyethylene naphthalate (PEN) shown in this thesis (Publication 3 and 4) was measured under the test conditions of 38 °C (for temperature), 90 % (for relative humidity) and 50 cm² (for detecting area).

![Figure 12. Sample test chamber of Systech Illinois 7001 water vapor permeation analyzer.](image)

3.2.5 Compositional analysis

Composition characterization methods for Al₂O₃ and SiO₂ thin films were carried out with FTIR (Publication 1, 2 and 3), TOF-ERDA (Publication 2 and 4) and GDOES (Publication 1 and 2).

*Fourier transform infrared spectroscopy*

Fourier transform infrared spectroscopy is a qualitative compositional technique used to identify and provide insight into the chemical bonds of the materials. An FTIR instrument, as shown in Figure 13, consists of the IR source, laser, interferometer, sample compartment, and detector. In the ALD community, FTIR has been often used both *in-situ* and *ex-situ* for thin film chemistry analysis due to its three major advantages over a typical dispersive infrared spectrometer, i) Multiplex advantage: this arises from the fact that relevant information corresponding to wavelength can be collected simultaneously; ii) Throughput advantage: there are no slits needed in the FTIR instrument meaning that more energy reaches the sample and improves the signal-to-noise ratio; and iii) Wavelength accuracy advantage: the wavelength scale is calibrated by a controlled laser beam which provides the reference for both precision and accuracy of the infrared spectrometer.
In this thesis, the modified FTIR, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was used. The measurements were done by using a Thermo Electron Corporation Nicolet 380 ATR-FTIR spectrometer with a diamond crystal as an internal reflection element. A 2 cm\(^{-1}\) resolution over the 500–4000 cm\(^{-1}\) wavenumber range was used.

**Time-of-flight elastic recoil detection analysis**

Ion beam analysis techniques, Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA), are very useful for the quantitative determination of the elemental composition in materials. Compared to RBS, ERDA is more sensitive for light elements, such as H, N and C, especially for impurity level analysis. However, the drawbacks of ERDA are the depth resolution and mass separation. To improve the performance of ERDA, the configuration based on the time-of-flight detection was developed. [90,91]. This method is called to time-of-flight elastic recoil detection analysis (TOF-ERDA).

In TOF-ERDA, the sample surface is bombarded with high energy ion beams, such as \(^{35}\text{Cl}\), \(^{63}\text{Cu}\), \(^{75}\text{Br}\) or \(^{127}\text{I}\). [92] The surface ion collision results in energetic recoils. An energy detector measures the velocity and kinetic energy of recoiled atoms which later can be converted to an elemental depth profile. [93] The SiO\(_2\) and Al\(_2\)O\(_3\) thin films in this thesis (Publication 2 and 4) were measured by using 40 MeV energy \(^{75}\text{Br}\) ions which obtained from a 5 MV tandem accelerator with a detection angle of 40\(^\circ\). The schematic of TOF-ERDA is shown in Figure 14.

**Figure 13.** Schematic of a FTIR instrument.

**Figure 14.** Schematic of TOF-ERDA setup used for SiO\(_2\) and Al\(_2\)O\(_3\) thin film characterization.
Glow discharge optical emission spectroscopy

As the acronym suggests, GDOES is a technique that combines a glow discharge (GD) with an optical emission spectrometer (OES). It is an analysis method which can be used for either qualitative or quantitative measurement depending on the calibration materials. The schematic of GDOES is presented in Figure 15 (a). During the measurement, Ar gas is used as a glow discharge source and delivered through the anode towards the sample. Due to the high direct voltage between the anode and sample, Ar is dissociated into electrons and cations (Ar+) which are accelerated towards the sample surface due to the high negative potential. Some atoms are ejected from the sample by Ar cations. After the state change of these ejected sample atoms, the emitted light is generated with a characteristic wavelength spectrum, which contributes to the further chemical composition analysis.

GDOES can provide both the depth profile and the bulk elemental composition of solid materials and thin films. Compared to other analytical techniques, such as secondary ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS) or ERDA, GDOES has the advantage of high sputtering rate and throughput, short specimen preparation time, high analytical depth (several nm to ~100 μm) and large analysis area. [94]

In this thesis, the composition analysis of the SiO₂ thin films was done by a Horiba GD-Profiler 2 instrument. A 4-mm diameter anode and RF power of 35 W in the pulsed mode were used. The spectral information was acquired as an intensity vs time profile of the characteristic emission line for each element (as shown in Fig. 15 (b)). During the element analysis, the measured emission intensity was integrated over the whole layer thickness, where the time at the SiO₂/Si interface transition was calculated at 50% of the maximum height. Lacking reference samples, the reported values were not calibrated for compositional depth profiling. The element-dependent emission rate was not considered and thus reported intensities of the given element could be compared among different samples, but comparison among different elements was not feasible.

Experimental
4. Results and Discussion

4.1 PEALD of SiO\(_2\): impact of process parameters

This section discusses the results from Publication 1 and 2, where PEALD SiO\(_2\) thin films were prepared by using O\(_2\) plasma and CO\(_2\) plasma as oxidants. The effect of plasma parameters (power and exposure time) on film growth was studied, as well as the effect of the process temperature. Furthermore, the correlation between the film properties of SiO\(_2\) thin films and plasma parameters was investigated.

4.1.1 Plasma power

This section presents the results related to Publication 1, where the growth behavior of PEALD SiO\(_2\) thin films grown with BTBAS and O\(_2\) plasma at 90 °C were investigated. In order to study the dependence of the film properties (i.e. refractive index, density, composition and residual stress) on plasma power, a fixed plasma exposure time of 1 s was applied.

Figure 16 shows the GPC and refractive index of PEALD SiO\(_2\) thin film as a function of plasma power. The refractive index slightly increased with an increase in plasma power, while there was a negative correlation between plasma power and GPC. Since the cycle number was controlled for all power conditions, the relatively low GPC and high refractive index of films grown with higher plasma power can be attributed to the better film quality, e.g. a higher mass density and lower impurity content.

Figure 16. GPC and refractive index of PEALD SiO\(_2\) thin film as a function of plasma power.
As described in Section 3.2.5, the measured values from GDOES were not calibrated for compositional depth profiling. Therefore, the elements shown in Figure 17 (a) and (b) can only be compared among different samples, and comparison among different elements is not feasible.

![Figure 17](image-url)

**Figure 17.** The element composition of 150-nm thick SiO₂ thin films: (a) main contents of Si and O and (b) impurities of H, C and N. Reproduced with permission from Z. Zhu, C. Modanese, P. Sippola, M. Di Sabatino and H. Savin, Phys. Status Solidi A. 215 (2018) 1700864. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

As shown in Fig. 17 (a), the plasma power does not influence the Si intensity, that is, the possible differences among the SiO₂ matrices do not lead to a significant change in the Si emission rates. Moreover, the intensities of the detected impurities, H, C and N, are presented in Fig. 17 (b). Although the higher emission intensity for C and H at the beginning of the sputtering was a known surface effect, [95] their qualitative evaluation allowed for an analytical comparison between the different samples. The hydrogen content was mostly contributed as OH-groups in the film. [57,96,97] Also, the emission intensity change of H among the three SiO₂ films grown by plasma powers of 50, 180 and 300 W was within the accuracy of the GDOES method, which is estimated to be within ±15%. Based on the findings of Si and H, the similar O intensity level among three different samples can be well understood.

There was an identifiable effect of plasma power on the film impurity levels of C and N. The intensity of the analytes seems to decrease when the plasma power was increased to a level of ≥ 180 W. This suggests that the high power can promote the completion of surface reactions while reducing film impurities due to the contribution of plasma enhancement during the ALD process as reported earlier by Langeris et al. [73]

During the measurement of GDOES, different sputtering rates of 11.68, 11.11 and 10.98 nm/s were observed for the SiO₂ thin films grown by three power conditions. The results are shown in Figure 18 and as can be seen, there is a strong power dependence. Furthermore, the density of SiO₂ thin films as a function of plasma power is presented in Fig. 18 as well, where the film density increases with power increasing. The observations of lower sputtering rate and higher density were in good agreement, indicating a better film quality when higher plasma power is used for PEALD SiO₂ thin film deposition.
Residual stress of 50-nm thick SiO$_2$ films was measured as a function of plasma power and the results are shown in Figure 19. The film stress shifted from the tensile stress of 16±9 MPa to the compressive stress of 87±16 MPa with a plasma power increase from 50 to 300 W. This trend could be credited to the plasma activity, film density and impurity level.

Based on the above results that were made with a fixed plasma exposure time of 1 s, in order to achieve a low-temperature PEALD SiO$_2$ thin film with the high growth rate (1.46 Å/cycle), low impurity level, high density (2.1 g/cm$^3$) and low compressive residual stress (25 MPa), the plasma power of 180 W is the recommended choice.

4.1.2 Process temperature

This section discusses the results related to Publication 2, where the growth behavior of PEALD SiO$_2$ thin films grown with BTBAS and CO$_2$ plasma at a temperature range of 90-200 °C were investigated. To the best of the author's
knowledge, this is the first demonstration of SiO₂ thin films grown by CO₂-based PEAALD at such low temperatures.

Before the investigation of process temperature effects, the BTBAS pulse and purge time were optimized. During the processes, a fixed plasma power of 180 W, a CO₂ plasma exposure time of 3 s and a CO₂ plasma purge time of 2 s were applied. Figure 20 (a) and (b) show GPC values as a function of BTBAS pulse and purge time at 90 °C, respectively. For the dependence on pulse time, the BTBAS purge time was set to 3 s, whereas for the dependence on purge time, the BTBAS pulse time was set to 0.3 s. During the parameter optimization, a BTBAS pulse time of 0.1 s was found to be sufficient to reach a self-limiting growth with a GPC of 1.15 Å/cycle, however, for the pulse time of 0.3 s, there was an improvement of the film thickness uniformity in SiO₂ films. Furthermore, there is no significant change in GPC shown in Fig. 20 (b), although the purge time was shortened from 3 to 0.5 s. This indicates that the applied short purge time of BTBAS was sufficient to prevent CVD components. Note however that the uniformity of film thickness was improved with increasing purge time. Based on these findings, the pulse and purge time of BTBAS for further investigations was set to 0.3 s and 3 s, respectively.

Figure 20. GPC of SiO₂ thin films as a function of BTBAS (a) pulse time and (b) purge time. The applied plasma power and process temperature were 180 W and 90 °C, respectively.

Figure 21 shows the effect of the process temperature between 90 and 200 °C on the GPC of SiO₂ thin films which were grown with a plasma power of 180 W, a plasma exposure time of 3 s and a plasma purge time of 2 s. There was a clear decrease of GPC from 1.15 to 0.78 Å/cycle with process temperature increasing from 90 to 200 °C. As shown in Section 2.2.3, the presence of -OH surface groups plays an important role in ALD surface reactions. Therefore, the decrease of the GPC with increasing temperature can be attributed to the surface-coverage loss of -OH groups due to the thermally activated dehydroxylation reaction. [33,57,98,99] Furthermore, the trend of GPC vs. process temperature shown in Fig. 21 is in good agreement with the earlier report from Dingemans et al.. [57]
4.1.3 Plasma exposure time

The plasma exposure time played a dominant role in tuning the film growth and properties in this work. The GPC, density and element composition of PEALD SiO₂ thin films grown at 90°C are presented in Figure 22 (a) and (b). When plasma exposure time increased from 1 to 6 s, an “inverse V” trend of the GPC is shown in Fig. 22 (a). The highest value of 1.15 Å/cycle was obtained in the SiO₂ thin films grown with a plasma exposure time of 3 s. For 6 s plasma exposure, the lowest GPC of 0.98 Å/cycle was observed.

The density of SiO₂ thin films vs. the CO₂ plasma exposure time is also shown in Fig. 22 (a). Although the values were within the measurement error margin, the lowest and highest mean values of film density were obtained in SiO₂ thin films grown with an exposure time of 1 and 6 s, respectively. This indicates that the film density slightly increased with an increase in plasma exposure time. The results of film density support the findings of film growth, that GPC dropped at 6 s, and was most likely related to film densification during the long-time plasma exposure.

Figure 22. (a) GPC and density of SiO₂ thin films as a function of plasma exposure time, and (b) qualitative elemental composition of films grown with the plasma time of 1, 3 and 6 s measured by GDOES. The measurement has an accuracy of ±15% and the cross-elemental comparison of the intensities is not possible (no calibration factor is available). The applied process parameters of the process temperature, plasma power and purge time were 90 °C, 180 W, and 2 s, respectively.
The elemental composition of SiO$_2$ thin films was measured by GDOES. The detected elements of Si, O, H, N and C are shown in Fig. 22 (b). As displayed on the figure, no significant effects of plasma exposure time on the Si, O, and H contents are observed in any of the samples. This finding is similar to the plasma power effects reported in Section 4.1.1, where the SiO$_2$ thin films were prepared by using O$_2$-based PEALD. For nitrogen, the intensities of the samples prepared by 1 and 3 s CO$_2$ plasma exposure were rather constant, whereas a lower intensity was measured for the films prepared by a plasma exposure time of 6 s. This suggests that N impurity removal was more effective during the film densification. Note that, independently of sample growth conditions, all the measured samples showed the same intensity for C content. This is most likely due to the surface contamination since the C impurity was not found by the cross-check of TOF-ERDA measurement.

As shown in this study, there was a trade-off between the film growth rate and process temperature. Considering the throughput and quality of PEALD SiO$_2$ thin film grown at 90 °C, the plasma power of 180 W and the plasma exposure time of 3 s is suggested. Table 6 presents the film properties of PEALD SiO$_2$ thin film grown under the process condition optimized in this work and the corresponding values reported in the literature. [57]

Table 6. The film properties of PEALD SiO$_2$ reported in this work with suggested process condition and from a previous study of Dingemans et al. [57]

<table>
<thead>
<tr>
<th>Film properties</th>
<th>This work</th>
<th>Ref. [57]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPC (Å/cycle)</td>
<td>1.15</td>
<td>1.4</td>
</tr>
<tr>
<td>Residual stress (MPa)</td>
<td>30±10</td>
<td>-</td>
</tr>
<tr>
<td>(tensile)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>2.11±0.05</td>
<td>2.0±0.1</td>
</tr>
<tr>
<td>Element (at.%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>31.4±1.0</td>
<td>29.1±0.8</td>
</tr>
<tr>
<td>O</td>
<td>66±1.1</td>
<td>61.3±1.5</td>
</tr>
<tr>
<td>H</td>
<td>2.4±0.6</td>
<td>9.6±0.9</td>
</tr>
<tr>
<td>N</td>
<td>0.17±0.05</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>&lt;0.05'</td>
<td>-</td>
</tr>
<tr>
<td>O/Al ratio</td>
<td>2.1</td>
<td>2.1</td>
</tr>
</tbody>
</table>

4.2 Al$_2$O$_3$ for encapsulation: O$_2$-based PEALD process

This section discusses the results from Publication 3, where the growth behavior of PEALD Al$_2$O$_3$ thin films prepared by O$_2$ plasma at 90 °C with 20% O$_2$ concentration was investigated. The dependence of the moisture barrier properties on plasma parameters, including power and exposure time, are presented, as well as other film properties, such as refractive index, density and composition. In addition, the same GPC of Al$_2$O$_3$ thin films was present in Publication 5 where the same process conditions were applied.

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1 Below the detection limit of TOF-ERDA
4.2.1 Film growth and material properties

The dependence of the GPC and refractive index of Al₂O₃ thin films on Si substrates as a function of the plasma power is shown in Figure 23 (a) and (b). The film thickness was in the range of 35-50 nm, which was obtained using the same ALD cycle number of 300 for all the samples. The plasma power was varied from 50 to 300 W with three plasma exposure time of 1, 3 and 6 s. As shown in Fig. 23 (a), for 1 s plasma exposure the GPC increases with the increased plasma power and achieves the highest value (1.57 Å/cycle) when power reaches 100 W or more. For the plasma exposure time of 3 and 6 s, the GPC of Al₂O₃ thin films is found to decrease with an increase of plasma power.

Figure 23. (a) GPC and (b) refractive index of Al₂O₃ thin films, for various plasma exposure time, as a function of plasma power.

Fig. 23 (b) shows the refractive index dependence of Al₂O₃ thin films on plasma power and exposure time. As a general observation, the refractive index is found to increase from 1.6 to 1.66 with increasing exposure time. While the highest refractive index was obtained with a plasma exposure time of 6 s, the lowest one was obtained for films grown with an exposure time of 1 s and a power of 50 W. Note that, independently of plasma exposure time, the constant values (within the error margins) were obtained with a plasma power above 100 W.

To study the effect of plasma power on film properties, the plasma exposure time was fixed at 1 s. The film density, surface roughness and chemical composition were carried out by the XRR and ATR-FTIR measurements. In Figure 24, the density and surface roughness of Al₂O₃ thin films as a function of plasma power are shown. Although the rather constant value of ~2.85 g/cm³ was found for higher powers, the 50 W process led to films with a lower density of 2.6 g/cm³. This lower density of Al₂O₃ thin films was most likely caused by the insufficient plasma power that resulted in a shortage of O radicals and therefore led to an incomplete surface reaction. For surface roughness, the highest value of 1.22 nm was obtained for a plasma power of 50 W, while the sub-nanometer roughness was measured for samples grown with the plasma power of 100, 180 and 300 W. In addition, the XRR measurements also revealed the presence of a ~1.3 nm interfacial layer of silicon oxide in all measured Al₂O₃ thin films except for the thin films grown with a power of 300 W, for which the silicon oxide layer
had a thickness of ~0.7 nm. This reduction of SiO₂ interface layer could be caused by the ion bombardment due to the use of the high plasma power.

Figure 24. Plasma power effect on the film density and surface roughness of PEALD Al₂O₃. The plasma exposure time and O₂ concentration were fixed at 1 s and 20%, respectively.

The effect of plasma power on the chemical composition of Al₂O₃ thin films is shown in Figure 25. The Al-O bond band fingerprint [100,101] of amorphous Al₂O₃ films was found between 525 and 1000 cm⁻¹ for all samples. The broad-band features in the 3200-3800 cm⁻¹ region can be assigned to the -OH groups. [100,102] Additionally, all spectra showed a strong Si-O mode band at 1107 cm⁻¹, [101] which hints to the presence of an interfacial silicon oxide layer. The spectrum of Al₂O₃ thin films grown with a power of 50 W was unique as it showed that,

i. There was a more pronounced intensity of the -OH band compared to other samples;
ii. There was the band overlapping of bending overtone, symmetric and asymmetric stretching vibrations of the C-H groups in the 2870-2980 cm⁻¹ range; [102]
iii. A band of 1239 cm⁻¹ was assigned to deformation vibrations of methyl [102,103] and supported the significant presence of -CH₃ species;
iv. The pronounced band in the region of 1350-1800 cm⁻¹ assigned to symmetric and asymmetric stretching modes of OCO molecule structures. [101]

In fact, the strong signals of C-H, O-C-O and -OH groups shown in the thin films grown at 50 W indicate the incomplete gas-solid interactions which can result in high impurities. Consequently, these high-level impurities inhibited the film growth and thus resulted in a low GPC and low refractive index. Unlike to 50 W, the higher power of 100-300 W led to the highest GPC of 1.57 Å/cycle and the better film properties, such as higher refractive index, higher film density and lower impurity levels. Taking into account the highest GPC and improved film quality, the growth saturation of Al₂O₃ thin films could occur when the plasma power of 100 W or more and plasma exposure time of 1 s were applied.
Figure 25. ATR-FTIR transmission spectra with chemical bond assignments of Al₂O₃ thin films prepared by different plasma powers. The plasma exposure time was fixed at 1 s.

For process condition with 1 s plasma exposure, both unsaturated and saturated growth were observed. Compared to 1 s, for a longer exposure time of 3 and 6 s GPC was found to decrease with an increase of power while the refractive index increased. This observation could be correlated to the film densification which is credited by the long-time plasma interaction.

As stated above, there are three specific stages during the PEALD of Al₂O₃ thin films. The first stage, in which the film growth is unsaturated, results in a low GPC and a low refractive index; the second stage, in which the growth saturation of the films occurs, leads to an increase of the GPC and the refractive index; Finally, the third stage, in which densification of the films dominates, leads to decreased GPC while the refractive index remains high.

In general, so-called saturated growth of a thin film is targeted in the ALD process. As shown in Fig. 23 (a), with 1 s plasma exposure, the growth saturation of Al₂O₃ thin films was observed in the samples prepared by higher plasma powers (≥100 W). Such conditions have a higher potential to lead to a good moisture permeation barrier performance.

4.2.2 Moisture permeation barrier

Moisture permeation barrier properties of 4-nm thick Al₂O₃ films grown on PEN substrates with varied plasma power and exposure time were investigated. In Figure 26, the uncoated PEN has an initial WVTR of 1.4 gm⁻²day⁻¹. The barrier performance was improved over 250 times upon the growth of 4-nm thick Al₂O₃ films. Power of 50W and exposure time of 1 and 3 s led to WVTR of 4.4 × 10⁻² and 1.1 × 10⁻² gm⁻²day⁻¹, respectively. An improvement was observed with the further increase of the plasma power to 100 and 180 W. This improvement can be attributed to the contribution of growth saturation or film densification. With a further increase of the exposure time to 6 s, the barrier performance of the Al₂O₃ thin films prepared with a power of 50 W was further improved. However, samples grown with 100 and 180 W showed a degradation, which is possibly
related to the ion bombardment during the long-time plasma exposure and thus results in the PEN substrate damage as observed for the Si substrate coated sample grown with a power of 300 W.

As shown above, the plasma parameters have a significant influence on the film properties of Al₂O₃ thin films prepared by O₂-based PEALD. By choosing an appropriate plasma power and exposure time, comparable properties (e.g. WVTR is of the order of 10⁻³ gm⁻²day⁻¹) for encapsulation applications are reachable below the critical film thickness of 5 nm. Thus, such thin films could potentially be used as moisture barriers in flexible devices.

![Figure 26. WVTR dependence of 4-nm thick Al₂O₃ coated PEN substrates on plasma power and exposure time. These values are compared to the WVTR of an uncoated PEN substrate.](image)

4.3 Al₂O₃ for encapsulation: combined H₂O thermal ALD with \textit{in-situ} N₂ plasma treatment process

This section shows the results of \textit{Publication 4}, where an alternative for preparing Al₂O₃ thin films was introduced. This particular approach is a combined H₂O thermal ALD with \textit{in-situ} N₂ plasma treatment which was used for the encapsulation application. Furthermore, the growth behavior, density, surface roughness, elemental composition and residual stress of 50-nm thick Al₂O₃ thin films on Si wafers were investigated. Figure 27 (a)-(c) show three different process configurations (process-I, process-II and process-III) with a fixed TMA pulse/purge time of 0.2 s/3 s and H₂O purge time of 7 s.

- **Process-I**: a standard thermal ALD process for the optimization of H₂O pulse time.
- **Process-II**: a combined H₂O thermal ALD with \textit{in-situ} N₂ plasma treatment process. Here, the H₂O pulse was immediately followed by the exposure of N₂ plasma for 1 to 6 s before the purge.
- **Process-III**: similar to the process-II with 6 s N₂ plasma treatment but involved a waiting step ($t$=0.5-2 s) between the H₂O pulse and the N₂ plasma exposure.

During process-I, the plasma generator was kept in the off-mode whereas in the process-II and -III a plasma power of 180 W was used.

4.3.1 Film growth and material properties

To optimize the H₂O dose, the dependence of the pulse time on the GPC and refractive index of the Al₂O₃ thin films was investigated for process-I and the results are shown in Figure 28 (a). The lowest GPC was obtained with an H₂O pulse time of 0.05 s, indicating the shortage of H₂O dose which leads to an unsaturated growth. When the pulse was set to 0.15 s or more, the self-limiting growth with a GPC of 0.84 Å/cycle was achieved. Surprisingly, there was no clear influence of H₂O pulse time on the refractive index despite the H₂O pulse of 0.05 s. The values of the refractive index were found to remain in the range of 1.58-1.6. Based on the trend seen in Fig. 28 (a), the H₂O pulse time was fixed to 0.15 s for the process-II and -III.
Results and Discussion

Figure 28. GPC and refractive index of the Al2O3 thin films as a function of (a) H2O pulse time in process-I, (b) plasma exposure time in process-II and (c) waiting step in process-III with 6 s plasma exposure. The plasma power of 180 W was used in the combined processes, while the generator was kept in the off-mode during process-I.

The influence of plasma exposure time on the GPC and refractive index of the Al2O3 thin films was also studied and is shown in Figure 28 (b). For process-II, the values of GPC and refractive index were higher than the ones (0.84 Å/cycle and 1.59) measured for samples grown by process-I. It can be attributed to the contributions of plasma interaction that the concentration of surface -OH groups could be increased favoring thereby the absorption of aluminum atoms. In this case, the increase in the amount of -OH groups involved in the surface reactions could result in a higher GPC. When plasma exposure time increased from 1 to 6 s, the GPC decreased from 1.44 to 1.28 Å/cycle while the refractive index increased from 1.6 to 1.63, indicating the film densification. For process-III, the effect of the waiting step ($t = 0.5-2$ s) between the H2O pulse and the N2 plasma exposure on the GPC and refractive index of the Al2O3 thin films was studied. As shown in Figure 28 (c), when the plasma was ignited right after the H2O pulse ($t = 0$ s), the GPC and refractive index of the Al2O3 thin films were 1.28 Å/cycle and 1.63, respectively. However, when the samples were exposed to N2 plasma 0.5 s after the H2O pulse, the GPC slightly decreased whereas the refractive index remained the same as in the case of $t = 0$ s. There were clear changes when the waiting step $\geq 1$ s. Both the GPC and refractive index dropped to the same level as the ones obtained from the process-I. This implies that plasma assistance was only efficient when H2O was involved in the reaction. In this case, the reactions in the process-II would then occur in the following sequences: (1) thermal ALD, and then (2) a hybrid reaction between thermal ALD and H2O-based PEALD using the residual water from (1). If the residual water is removed by the sufficient purge step (in the case of process-III), there will be a lack of
Results and Discussion

Indeed, the effect of plasma interaction can be ignored, and no hybrid reaction will be involved during the process.

The film properties of the Al₂O₃ thin films grown with the process-I and -II, such as density, surface roughness, elemental composition and residual stress, are shown in Table 7. The tensile residual stress was found in all measured samples. The highest value of 475±19 MPa was obtained for the process-I. The value was reduced by adding additional plasma assistance. With 1 s plasma exposure, the residual stress of 380±18 MPa was achieved. The value of residual stress further decreased to 160±13 MPa when the plasma exposure time was increased to 6 s.

Table 7. Results of density, roughness, elemental composition and residual stress for 50-nm thick Al₂O₃ films coated on Si wafer.

<table>
<thead>
<tr>
<th>Film properties</th>
<th>Process-I</th>
<th>Process-II (1 s)</th>
<th>Process-II (6 s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile residual stress (MPa)</td>
<td>475±19</td>
<td>381±18</td>
<td>160±13</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.7</td>
<td>2.7</td>
<td>3.1</td>
</tr>
<tr>
<td>Roughness (nm)</td>
<td>0.7</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Element (at.%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>33.4±0.5</td>
<td>32.2±0.5</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>55.4±0.7</td>
<td>54.1±0.7</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>10.0±1.0</td>
<td>10.1±1.0</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.20±0.10</td>
<td>1.60±0.10</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0²</td>
<td>0.51±0.06</td>
</tr>
<tr>
<td>O/Al ratio</td>
<td>1.7</td>
<td>1.7</td>
<td>1.6</td>
</tr>
</tbody>
</table>

During the density modelling, unlike the films grown with thermal ALD, the ones grown by process-II were found to have a structure requiring a bilayer model for simulation. This could be a consequence of the contribution of both H₂O and OH radicals [104] in the oxidation reactions. The process-II with a plasma exposure time of 1 s gave a film density of 2.7 g/cm³, which was in the same range as for films grown with process-I. When plasma exposure time was increased to 6 s, the film density increased to 3.1 g/cm³. This density improvement reflects the film densification and is in good agreement with the trend of the refractive index shown in Fig. 28 (b). Moreover, there was no clear roughness difference among measured samples and the values were in the range of 0.6-0.8 nm.

The elemental composition of the films was carried out using TOF-ERDA. Al, O, H and C were detected in all samples from process-I and -II, while nitrogen was only observed in the films grown with the process-II. The presence of N can be attributed to the formation of unstable surface N-species during plasma exposure in a N₂ environment. [105] This “N-contamination” effect could be simply avoided by using argon as a carrier gas. Except for the N impurity, H and C impurities were nearly the same for process-I and process-II with 1 s plasma exposure. Compared to the process-II with 1 s plasma exposure, the Al₂O₃ thin films grown with a plasma exposure time of 6 s had much lower concentrations of H, C and N, indicating the effective impurity removal of long-time plasma

² Below the detection limit of TOF-ERDA
Results and Discussion

The reduction of H contents in process-II with 6 s plasma exposure also reveals that the amount of unreacted -OH groups in the film was relatively low. Indeed, this low presence of -OH groups led to O/Al ratio closer to the stochiometric value of 1.5.

4.3.2 Moisture permeation barrier

Figure 29 shows the comparative study of the WVTR for H$_2$O thermal ALD (process-I), combined H$_2$O thermal ALD with \textit{in-situ} N$_2$ plasma treatment (process-II) and O$_2$ plasma-enhanced ALD (presented earlier in Section 4.2.2). Compared to uncoated PEN, there was no clear improvement of moisture barrier properties for 4-nm thick Al$_2$O$_3$ coated substrates, which were prepared by process-I. For process-II with a plasma exposure time of 1 s, the film showed a WVTR of 0.08 g m$^{-2}$ day$^{-1}$, which was more than fifteen-times lower than the one obtained from the sample prepared with the thermal ALD. With further increase of the plasma exposure time to 6 s, the barrier performance of the sample was improved significantly, leading to a WVTR of 2.9×10^{-3} g m$^{-2}$ day$^{-1}$. While for a plasma exposure time of 1 s, the WVTR of samples grown with process-II was higher than the one reported for O$_2$-based PEALD (7.1×10^{-3} g m$^{-2}$ day$^{-1}$), the best barrier performance was achieved with the process-II using a plasma exposure time of 6 s. This suggests that the substrate damage by ion bombardment during the combined H$_2$O thermal ALD with \textit{in-situ} N$_2$ plasma treatment process is negligible, which makes the process gentler and more suitable for sensitive substrates.

**Figure 29.** Comparative study of the WVTR for H$_2$O thermal ALD (process-I), combined H$_2$O thermal ALD with \textit{in-situ} N$_2$ plasma treatment (process-II) and O$_2$-based PEALD. Reproduced with permission from Z. Zhu, S. Merdes, O.M.E. Ylivaara, K. Mizohata, M.J. Heikkilä and H. Savin, Phys. Status Solidi A. (2019) 1900237. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
In this thesis, material properties of low-temperature PEALD SiO₂ and Al₂O₃ thin films were studied and related process optimization was carried out. A special emphasis was placed on the effect of plasma parameters, such as power and exposure time, on film growth as well as resulting structural, compositional, mechanical and moisture permeation barrier properties of the films.

Firstly, O₂-based PEALD SiO₂ processes, which focused on the plasma power effect on the elemental composition of SiO₂ thin films, were demonstrated. GDOES measurements were used as a primary analysis method. This technique provides the possibility to measure the elemental composition along the film depth with the high-enough resolution. The results indicated that the concentration of C and N impurities decreased with increasing plasma power. In addition to elemental composition, the GDOES was used to evaluate the film density. The sputtering rate implied that the film density increased with the increase of plasma power. The results thus suggest that if high quality film is needed, the plasma power should be set to as high as possible within the limits of plasma damage toleration of the substrate.

Secondly, the study of low-temperature PEALD SiO₂ process using CO₂ as an oxidant was presented in this thesis. To the best of the author’s knowledge, this is the first demonstration of SiO₂ thin films grown by CO₂-based PEALD at 90°. The variation of GPC was observed when plasma exposure time increased from 1 to 6 s. However, a relatively high film quality, such as high density and low impurity levels, was obtained with a longer exposure time. More specifically, it was shown that the film densification appeared with 6 s plasma exposure. In addition to the effect of plasma exposure time, the effect of process temperature on film growth was investigated as well. Due to the dehydroxylation reaction, the GPC of SiO₂ thin films decreased with increasing process temperature.

Thirdly, the studies of PEALD Al₂O₃ growth based on O₂ plasma were carried out. In addition to the film growth of Al₂O₃, the effect of both plasma power and exposure time on film properties were studied. As the highlight of this study, three specific stages during PEALD Al₂O₃ growth were found: i) the film growth is unsaturated, which results in a low GPC and a low refractive index; ii) the growth saturation, which leads to an increase of the GPC and the refractive index; and iii) densification of the film dominates, which leads to decreased GPC while the refractive index remains high. In addition, a WVRT of $5 \times 10^{-3}$ gm⁻²day⁻¹ was obtained for PEN substrates coated with 4-nm thick Al₂O₃ films.
Nevertheless, due to the ion bombardment, a degradation of barrier performance was found in the samples which were prepared using a long-time plasma exposure.

To retain the good barrier performance and minimize or eliminate the degradation, the other alternative for preparing Al₂O₃ thin films was finally introduced and a combined H₂O thermal ALD with in-situ N₂ plasma treatment process was investigated. WVTR measurements of PEN substrates coated with 4-nm thick Al₂O₃ films showed that the proposed combined process is likely to be gentler than the O₂-based PEALD and therefore is more suitable for sensitive substrates. The best WVRT result of $2.9 \times 10^{-3}$ g m⁻² day⁻¹ was obtained in the combined H₂O thermal ALD with a 6 s in-situ N₂ plasma treatment process. Moreover, with the contribution of plasma assistance, the Al₂O₃ thin films achieved a high density of ~3.1 g/cm³, a low tensile residual stress of ~160 MPa and low impurity levels of ~3.8, ~0.17 and ~0.51 at.% for hydrogen, carbon and nitrogen, respectively.

To conclude, the research on low-temperature PEALD of SiO₂ and Al₂O₃ processes indicates that the plasma parameters play a key role in fine-tuning and finding the optimal thin film properties. While the thesis has increased basic understanding of the plasma processes in ALD, the results are also directly applicable to the applications that use thermally sensitive materials. Therefore, in the next step, it will be interesting to apply the developed processes into device fabrication.
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