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microstructure characterization and moisture permeation barrier properties

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Microstructure characterization and moisture permeation barrier properties

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Abstract

High-end devices developed on flexible polymer substrates, such as organic photovoltaics and organic light emitting diodes, demand moisture permeation barrier layers exhibiting a water vapor transmission rate (WVTR) in the order of $10^{-6} \text{ g m}^{-2} \text{ day}^{-1}$. Typically, a barrier film is a thin ceramic oxide or nitride film, such as SiO$_2$, Si$_3$N$_4$ and Al$_2$O$_3$. The bulk of these layers shows excellent barrier properties, however, due to the presence of defects at the nano- and macro-scale the barrier performance of a single thin layer is limited, typically exhibiting a WVTR in the range $10^{-2} - 10^{-3} \text{ g m}^{-2} \text{ day}^{-1}$.

The improvement in barrier performance of the layers requires the control of both the local permeation through pinholes/macropores as well as the permeation through the matrix of the barrier layer. The goal of this thesis work is to learn which factor controls the barrier performance of the matrix of the layer, excluding the local permeation through the pinholes/macropores. Several layers have therefore been investigated, namely SiO$_2$ and Al$_2$O$_3$ films deposited by means of plasma enhanced chemical vapor deposition and plasma enhanced atomic layer deposition. The techniques of spectroscopic ellipsometry, Fourier transform infrared spectroscopy and Rutherford backscattering spectroscopy/elastic recoil detection were applied to determine the optical properties, chemical composition and mass density of the deposited layers. Furthermore, the layers were characterized in terms of nanoporosity content by means of ellipsometric porosimetry which combines spectroscopic ellipsometry and isothermal adsorption/desorption studies. The obtained results in terms of residual nanoporosity in the layer were correlated with the results of the Calcium test, applied to determine the intrinsic moisture permeation barrier performance. It was found that the matrix barrier performance of the SiO$_2$ and Al$_2$O$_3$ layers is controlled by the residual nanoporosity in the films. Furthermore, an approach was investigated towards the control of the residual nanoporosity in barrier layers, namely the engineering of nano-laminates. In particular, the poor barrier performance of a SiO$_2$ layer was dramatically improved by applying a 2 nm-thick Al$_2$O$_3$ layer on top of the SiO$_2$ film. The characterization of the interface region of the SiO$_2$/Al$_2$O$_3$ nano-laminate by means of XPS has pointed out to the filling of the SiO$_2$ residual nanoporosity by means of Al$_2$O$_3$. 

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Chapter 1

Introduction

1.1 Moisture and vapor permeation barrier films

Polymers play an important role in many fields of applications. Over the years several materials in various industries have been replaced by polymers because of their flexibility, transparency, light weight, and compatibility with roll-to-roll processing [1, 2]. These beneficial characteristics make polymers useful for various applications, i.e. as packaging material in the food and pharmaceutical industry or as substrates for organic solar cells or OLED displays [3, 4].

The main drawback of a polymer, however, is that it suffers from high permeability of oxygen and moisture present in the atmosphere. This oxygen and moisture will reduce the shelf-life of food or lead to degradation of electronic devices. In figure 1.1 the barrier requirements for various applications are given together with the permeation rates of polymers 1. As can be seen in the figure the various technologies require different barrier properties and the transmission rates of polymers is orders of magnitude higher.

A way to decrease the permeation of moisture and oxygen through polymers is to protect them with inorganic thin films (< 100 nm) characterized by gas and vapor permeation barrier properties, so-called barrier layers. Typically, a barrier layer consists of a ceramic oxide or nitride film like SiO$_2$, Si$_3$N$_4$ and Al$_2$O$_3$. Various deposition techniques have been used to deposit these layers, e.g. evaporation [5], sputtering [6], or plasma-based techniques [2, 7, 8, 9].

The bulk of these layers shows excellent barrier properties, however, the barrier performance of a single thin film is limited, typically having a WVTR in the range $10^{-2} - 10^{-3}$ g m$^{-2}$ day$^{-1}$. The limited performance is due to

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1 The oxygen permeation rate is defined as Oxygen Transmission Rate (OTR) and generally reported in cm$^3$ m$^{-2}$ day$^{-1}$. The moisture permeation rate is referred to as Water Vapor Transmission Rate (WVTR) and generally reported in g m$^{-2}$ day$^{-1}$
Chapter 1 Introduction

Figure 1.1 The barrier requirements for various applications in terms of water vapor transmission rate and oxygen transmission rate.

defects present in the layers, giving rise to local permeation paths in the barrier layer. As can be seen in figure 1.1, the performance of these single layers is sufficient for packaging but high-end devices, like OLEDs, require better barrier properties. In the next section a short review is given of previous studies on permeation through single inorganic barrier layers in order to understand the limits of this technology.

1.2 Background on barrier layer technology

In a detailed review Chatham studied various single barrier layers by evaluating them in terms of oxygen transmission rate (OTR) as function of the layer thickness [10]. It was found that, in general, the OTR decreases with increasing layer thickness until a critical thickness is reached above which no further decrease is observed.
1.2 Background on barrier layer technology

The data was compared with a permeation model based on bulk diffusion via the solubility-diffusion mechanism\(^2\) and a model based on diffusion through macro-defects/pinholes. According to the pinhole model the permeation is independent of the layer thickness as is the case for the OTR data above the critical thickness. Therefore, the author concluded that the permeation through a single barrier layer is dominated by flow through macro-defects (ranging from hundreds of nm up to a few \(\mu\)m in size). These defects (or pores) mainly result from dust on the polymer, high surface roughness of the polymer or the presence of anti-static particles [10]. Da Silva Sobrinho et al. also found the same dependence of the OTR on the coating thickness for SiO\(_2\) and Si\(_3\)N\(_4\) films [7]. Moreover, macro-defects were visualized by etching the polymer underneath the defects using an O\(_2\) plasma. The OTR values for various coating thicknesses correlated well with the defect density as shown in figure 1.2, supporting the hypothesis that the flow through single layers is dominated by defects [12].

Later on, Erlat argued that permeation through smaller defects down to the nm scale (nano-defects) can be as large as permeation through macro-defects [9]. The SiO\(_2\) barrier layers studied were macro-defect free but did not show considerably better barrier properties than barriers containing macro-defects. The important role that nano-defects can play was shown by Affinito who made an estimation of the density of pores and pinholes in barrier layers using a mathematical model and permeation measurements from literature [11]. It was estimated that the nanopore density can be more than 4 orders of magnitude larger than the macropore/pinhole density. This higher density translates into a 15-20 times larger area density of nanopores compared to macropores and thus 15-20 times more permeation through nanopores. To

\(^2\)Transport through a solid takes place via the so-called solubility-diffusion mechanism [10, 11]. Permeability of molecules is defined as the product of diffusivity (cm\(^2\) s\(^{-1}\)) and solubility (cm\(^3\) cm\(^{-3}\) atm\(^{-1}\)), \(P = D \cdot S\), with \(D\) and \(S\) being characteristic properties of a material. In steady-state conditions and in the case the upstream partial pressure \(p_0\) is much larger than the downstream partial pressure \(p_f\) (\(p_0 \gg p_f\)), the permeation through a material can be expressed as [11]:

\[
Permeation = P \cdot \frac{p_0}{d}. \tag{1.1}
\]

According to the ideal laminate theory the steady state transport through a layered system (such as a polymer/barrier layer) is given by the following equation (providing that the mechanism is bulk diffusion):

\[
\frac{d_{\text{polymer/barrier}}}{P_{\text{polymer/barrier}}} = \frac{d_{\text{polymer}}}{P_{\text{polymer}}} + \frac{d_{\text{barrier}}}{P_{\text{barrier}}}, \tag{1.2}
\]

where \(P_{\text{polymer}}\) and \(P_{\text{barrier}}\) are the polymer substrate and barrier permeabilities, \(d_{\text{polymer}}\) and \(d_{\text{barrier}}\) are the polymer and barrier layer thicknesses, \(P_{\text{polymer/barrier}}\) and \(d_{\text{polymer/barrier}}\) are the permeability and the thickness of the polymer/barrier layer system, respectively [11]. This theory indicates that the permeability of the layered system decreases as the thickness of any layer increases.
Figure 1.2 Oxygen transmission rate (OTR) (■) and defect density, n (△), as a function of the SiO$_2$ barrier layer thickness. The graph shows a critical thickness of about 12 - 15 nm. Below the critical thickness, the higher permeability is attributed to incomplete coverage of the polymer by the barrier layer [12].

be able to interpret experimental results that could neither be explained by the ideal laminate theory nor by a model assuming only permeation through macro-pores, Roberts et al. proposed a quantitative permeation model taking into account the diffusion through the barrier film lattice (< 0.3 nm), nano-defects (0.3-1 nm) and macro-defects (> 1 nm) (see figure 1.3):

$$P_b = C_{md}P_p + \left( \frac{\phi_p}{P_p} + \frac{\phi_g}{P_{la} + P_{nd}} \right)^{-1},$$  

(1.3)

with $P_b$, $P_p$, $P_{la}$, and $P_{nd}$ the permeability of the barrier layer, the polymer substrate, the oxide lattice and nano-defects, respectively, $C_{md}$ a dimensionless constant depending on the number and size of macro-defects in the layer, and $\phi_p = d_p/d$ and $\phi_g = d_g/d$ the polymer and barrier layer volume fraction (and $d_p$, $d_g$ and $d$ the polymer thickness, barrier layer thickness and total thickness, respectively) [13].

From these studies it is learned that not only the local permeation through pinholes should be controlled but also the permeation through nanopores present in the barrier layer. A distinction can be made between the extrinsic barrier properties, taking into account the permeation through pores of all sizes, and the intrinsic barrier properties, considering only the permeation through the nanoscale porosity. Analysis of the intrinsic barrier properties is important on the way towards a better control of the nanoscale porosity.

\footnote{In the remaining part of this thesis, defects/pores will be named pores. In section 2.1.1 a classification of pores according to their size will be introduced as adopted by the IUPAC.}
1.3 Barrier layers by CVD and ALD

Figure 1.3 A schematic overview of the proposed permeation pathways through a barrier layer. The relative importance of each path depends on the permeant molecule diameter [13].

and improvement of the barrier performance. These intrinsic properties can be measured by means of the Calcium test, a diagnostic tool capable to discern between the permeation through macropores and nanopores. This technique was adopted in this work for the measurement of intrinsic barrier properties and will be introduced in more detail later on.

Hereafter, a short literature review of barrier layers deposited by plasma enhanced chemical vapor deposition and atomic layer deposition is given since these barrier layers were characterized in this work.

1.3 Barrier layers by CVD and ALD

Single (transparent) layers with very good barrier properties can be deposited by plasma enhanced chemical vapor deposition (PECVD) [4]. An advantage of a plasma based deposition technique is that, due to the high reactivity of plasma species, a low thermal budget is sufficient for the deposition of layers with good barrier properties; a desirable condition for deposition on polymers as their glass transition temperature limits the processing temperature. These PECVD layers are typically SiO$_2$ or Si$_3$N$_4$ films providing an improvement in barrier performance of two to three orders with respect to the bare polymer substrates which exhibit a WVTR of $10 - 20 \, \text{g m}^{-2} \, \text{day}^{-1}$ [2, 7, 8]. Da Silva Sobrinho et al. deposited SiO$_2$ layers by PECVD on PET substrates. For a thickness of 100 nm these layers showed a WVTR of $0.1 \, \text{g m}^{-2} \, \text{day}^{-1}$ (at T= 33 °C and R.H. = 100%) [7]. A WVTR of $0.15 \, \text{g m}^{-2} \, \text{day}^{-1}$ (at T= 25 °C and R.H. = 100%) was obtained by Schaepkens et al. for Si$_3$N$_4$ films deposited by PECVD at a substrate temperature of 50 °C. 225 nm thick SiO$_2$ layers, deposited on PEN substrates by atmospheric pressure-PECVD, even showed a WVTR...
Recently, atomic layer deposition (ALD) has also been introduced as deposition technique for barrier layers. Because of its potential of delivering virtually pinhole-free, dense and ultra-thin films [15], ALD appears to be a suitable technique for the deposition of good quality barrier layers. Most barrier layers deposited by ALD were Al$_2$O$_3$ films and these layers were grown either on polymers [16, 17, 18] or directly on OLED [19, 20] or PV [21, 22] devices. Groner et al. deposited a 26 nm thick Al$_2$O$_3$ layer by ALD on various polymer substrates at a substrate temperature of 120 °C and obtained a WVTR of $1 \cdot 10^{-3}$ g m$^{-2}$ day$^{-1}$ (at T= 25 °C and R.H. = 100%) [17]. A WVTR of $1.7 \cdot 10^{-5}$ g m$^{-2}$ day$^{-1}$ (at T= 38 °C and R.H. = 85%) was reported by Carcia et al., also for an ALD Al$_2$O$_3$ layer of 25 nm grown at 120 °C on a PEN substrate [16]. Langereis et al. deposited Al$_2$O$_3$ films on PEN by means of plasma enhanced ALD (PEALD) [18]. He found a WVTR of $5 \cdot 10^{-3}$ g m$^{-2}$ day$^{-1}$ (at T= 21 °C and R.H. = 60%) for a 20 nm thick film deposited at room temperature. Care should be taken when comparing these results as the layers were tested using different methods and conditions. The results are all extrinsic WVTR values. For a single 20-40 nm thick Al$_2$O$_3$ layer, deposited by PEALD at room temperature, an intrinsic WVTR value of $1.5 \cdot 10^{-6}$ g m$^{-2}$ day$^{-1}$ (at T= 20 °C and R.H. = 50%) was measured [19].

Despite the good results, the permeation mechanism of these virtually defect-free ALD layers is still defect-driven as the WVTR values of these layers were shown to decrease with increasing layer thickness until a thickness of 20-25 nm was reached [17, 18]. Moreover, OLEDs encapsulated with a single PEALD Al$_2$O$_3$ barrier still show the development of black spots also indicating the presence of defects. Figure 1.4 (a) shows the average number of black spots found on OLEDs covered with PEALD Al$_2$O$_3$ layers and a PECVD SiN$_x$ layer. Figure 1.4 (b) shows black spots on an OLED covered with Al$_2$O$_3$ during electroluminescence measurements. The lower density of black spots on OLEDs encapsulated with a PEALD layer compared to a device covered with a PECVD layer points out a better conformality around macropores on the surface [19]. This is also confirmed by the superior extrinsic barrier properties of the ALD layers with respect to the PECVD layers [16, 17, 18]. Both the PEALD Al$_2$O$_3$ layers and the PECVD SiN$_x$ layer on the OLED showed the same intrinsic WVTR value. However, the ALD technique allows for a better control at nano-scale level for a much lower thickness range compared to PECVD.

Based on these results, ALD appears to be the preferred technique for the

---

*Water vapor permeating through defects in a barrier layer on top of an OLED device induces local oxidation of the cathode layer. At these oxidized spots charge injection at the cathode/organic active matrix interface is prevented, resulting in non-emissive (black) spots [19].*
1.4 Characterization of film microstructure

Figure 1.4 (a) The average number of black spots on OLED samples encapsulated with 300 nm a-SiNx:H, 40 nm and 20 nm Al2O3 and a stack of a-SiNx:H (300 nm) and Al2O3 (40 nm). The barrier films were deposited on the cathode of the OLED and tested under 20°C/50% R.H. conditions. (b) Black spots on the OLED during electroluminescence measurements [19].

deposition of barrier layers. Nevertheless, further improvement of the barrier properties of these ALD layers is desirable for the engineering of high-end devices on polymer substrates. Better insight in the microstructure (e.g. film matrix density and porosity) is an essential step towards a better control of the porosity and improvement of the performance of the barrier layers.

1.4 Characterization of film microstructure

Typically, the characterization of barrier layers is discussed in terms of chemical composition and optical and structural properties. Mainly for SiO$_2$ films this information was obtained by widely-used techniques such as X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), Rutherford backscattering spectroscopy/elastic recoil detection (RBS/ERD) and spectroscopic ellipsometry (SE) [8, 23, 24]. From the film chemistry, structure and density already some qualitative information about the porosity in the layers can be inferred, as it will be shown in the discussion of the results. In table 1.1 an overview is given of the information obtained by the various techniques.

These diagnostic tools already give an indication about the presence of pores in the films, however, no quantitative information can be inferred in terms of pore content and size (distribution). To this purpose, in this thesis work, ellipsometric porosimetry (EP) has been introduced as a technique allowing
Chapter 1 Introduction

Table 1.1 The information obtained by various techniques used to characterize barrier layers.

<table>
<thead>
<tr>
<th>Technique</th>
<th>information obtained</th>
<th>Indication of porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>XPS</td>
<td>Elemental composition</td>
<td>stoichiometry, carbon content</td>
</tr>
<tr>
<td>FTIR</td>
<td>Chemical bonds</td>
<td>network structure, OH associated vibrational modes</td>
</tr>
<tr>
<td>RBS/ERD</td>
<td>Elemental concentration</td>
<td>stoichiometry, mass density</td>
</tr>
<tr>
<td>SE</td>
<td>Refractive index (n)</td>
<td>in situ and ex situ evaluation (i.e. upon exposure to ambient)</td>
</tr>
</tbody>
</table>

for the analysis of the open porosity at nanoscale level [25, 26]. EP combines SE measurements with equilibrium adsorption/desorption isotherms [27, 28, 29]. This technique was used for the characterization of the microstructure of barrier films in this work and will be fully introduced in section 2.1.3.

1.5 Nano-laminates

A better insight in the microstructure of barrier layers will contribute to a better control of the nanoporosity, however, residual porosity will usually be present in the single layers limiting their performance. Combining single inorganic layers into nano-laminates can give rise to improved barrier properties. Dameron et al. deposited SiO$_2$/Al$_2$O$_3$ nano-laminates by ALD on polymer substrates with a WVTR of $1 \cdot 10^{-4}$ g m$^{-2}$ day$^{-1}$, whereas the single Al$_2$O$_3$ layer displayed a WVTR of only $1 \cdot 10^{-3}$ g m$^{-2}$ day$^{-1}$ [30]. Carcia et al. examined SiN/Al$_2$O$_3$ nano-laminates [31]. The single 100 nm thick SiN film had a WVTR of $7 \cdot 10^{-3}$ g m$^{-2}$ day$^{-1}$. By depositing a 5 nm thick Al$_2$O$_3$ on top, the WVTR decreased to $\leq 5 \cdot 10^{-5}$ g m$^{-2}$ day$^{-1}$. To reach this WVTR with a single Al$_2$O$_3$ layer, a minimal thickness of 10 nm was required. As these results could not be explained by the ideal laminate theory, it was suggested that the reduction in WVTR was either due to improved nucleation of the barrier layer on top, or due to the filling of pores in the first barrier layer by the second layer. In this thesis the barrier properties of SiO$_2$/Al$_2$O$_3$ nano-laminates have also been analysed.

$^5$Pores connected to the surface of the solid are called open pores, whereas pores not communicating with the surface are called closed pores.
1.6 Goal and approach

SiO₂ and Al₂O₃ barrier layers deposited by PEALD were analyzed in terms of chemical composition, optical properties and density and these characteristics were related to the microstructure of the layers. Subsequently, the intrinsic barrier properties of the SiO₂ and Al₂O₃ films were measured to learn how the barrier performance is controlled by the layer chemistry, properties and microstructure. A comparison was made with SiO₂ and Al₂O₃ layers deposited by PECVD to determine the influence of the deposition process/technique on the microstructure of the layer.

First, two PEALD SiO₂ layers, deposited at different substrate temperatures, were studied. A comparison was made with a dense and a porous PECVD SiO₂ layer. Subsequently two Al₂O₃ films deposited by PEALD using different substrate temperatures were analyzed and compared to a dense and porous Al₂O₃ layer deposited by expanding thermal plasma chemical vapor deposition (ETP-CVD).

In particular, the following research question has been addressed:

• What is the factor controlling the ultimate (intrinsic) barrier performance of barrier layers?

The barrier layers were analysed by means of SE, FTIR and RBS/ERD measurements and the microstructure of the films was characterized by performing EP measurements. For the measurement of the intrinsic barrier properties, the calcium test was used. The principles of these diagnostic tools are further explained in chapter 3. From this study it was concluded that the intrinsic barrier properties of the barrier layers are controlled by the open (nano-)porosity of the layers. Residual porosity, however, will usually be present in a single barrier layer limiting its performance. This issue gives rise to a second research question:

• How can the residual (open) porosity in an inorganic barrier layer be controlled?

In cooperation with Fujifilm, SiO₂/Al₂O₃ nano-laminates were analyzed to learn if this is a useful approach for controlling the residual porosity in single barrier layers and leads to an improvement of barrier properties. SiO₂ films were deposited by Fujifilm on PEN substrates by making use of an atmospheric pressure glow discharge (APG). PEALD Al₂O₃ layers of various thickness were deposited on top of two different SiO₂ films, a dense and a porous film. These nano-laminates were evaluated in terms of extrinsic barrier properties and the SiO₂/Al₂O₃ interface was studied by means of XPS to see if pores in the SiO₂ film were filled by Al₂O₃.
Chapter 1 Introduction

1.7 Outline of the thesis

The outline of this master thesis is as follows: In chapter 2 the general concepts of porosimetry are treated and the basics of ellipsometric porosimetry are introduced. In chapter 3 a description is given of the deposition setups, processes and conditions used to deposit the SiO$_2$ and Al$_2$O$_3$ barrier layers which were examined in this work. Also the deposition process of the SiO$_2$/Al$_2$O$_3$ nano-laminates is explained. This chapter ends with an overview of complementary diagnostics used for the characterization of the barrier films. In chapter 4 the experimental results are reported and discussed. First, the results obtained from the SiO$_2$ layers are discussed, followed by the results of the Al$_2$O$_3$ layers. The last section presents the outcomes of the experimental work on the SiO$_2$/Al$_2$O$_3$ nano-laminates. Finally, in chapter 5 the conclusions are reported and recommendations for future work are given.
Chapter 2

Basics on porosimetry

2.1 Porosimetry

2.1.1 Adsorption

Porosimetry is a technique used to determine the size and density of (open) pores of a porous material by means of adsorption and desorption studies. Pores connected to the surface of the solid are called open pores, whereas pores not communicating with the surface are called closed pores. The adsorption and desorption studies involve the adsorption and desorption of a vapor or a gas in the pores of a solid and therefore, only open porosity can be determined.

The gas or vapor, also called the adsorptive, is adsorbed by the solid (the adsorbent), defined as the enrichment of the adsorptive at the interface between solid and vapor. Once adsorption has occurred the adsorptive is called adsorbate.

The forces between solid and gas molecules involved in adsorption can give rise to physisorption as well as chemisorption. Ideally, for porosimetry only physisorption is involved, which means no new chemical compounds are formed and therefore, the adsorption is a reversible process. The physical forces which bring about adsorption are the so-called Van der Waals forces [28]. Dependent on the polar nature of both adsorbent and adsorptive also electrostatic forces can be involved. The total potential energy \( \phi(z) \) of a molecule as function of its distance \( z \) from the surface of the adsorbent is given by a Lennard-Jones-like potential as shown in figure 2.1. A state of minimum energy is obtained at distance \( z_0 \) from the surface.

For a specific gas, and a solid maintained at a fixed temperature \( T \), the amount of gas adsorbed by the solid is only a function of the partial gas
Chapter 2 Basics on porosimetry

\[ \phi_i(n, P_{g}) = f\left(\frac{P_{g}}{P_{sat}}\right)_{T, gas, solid} \]

where \( n \) is the quantity of gas adsorbed (e.g., mol/gram) and \( P_{sat} \) the saturation vapor pressure of the adsorptive. This expression is called an adsorption isotherm. The shape of the isotherm is related to the interaction between the gas molecules and the surface. In the case of a porous solid this interaction depends on the type of pores. Pores are usually classified according to their size [27]:

- micropores: pores with widths less than 2 nm;
- mesopores: pores of widths between 2 nm and 50 nm;
- macropores: pores with widths exceeding 50 nm.

In micropores the mechanism of adsorption is volume filling rather than layer-by-layer coverage on a plane surface. In the narrow pores the potential fields of the walls overlap, resulting in an enhanced adsorbent-adsorbate interaction energy [28, 29]. The increased interaction potential depends on the ratio of the pore width \( w \) to the adsorbate molecule diameter \( d \), as well as on the pore shape. Figure 2.2 shows the enhanced adsorption energy in a slit-shaped micropore, \( \phi \), compared to the adsorption energy on an open surface, \( \phi_0 \), for various pore widths \( w \).

This enhanced adsorption energy leads to complete pore filling at very low relative pressure for micropores that can accommodate a maximum of 2 layers of molecules. This process is called primary micropore filling. For wider micropores the enhanced interaction energy decreases and complete pore filling takes place at somewhat higher relative pressures. Once a monolayer has adsorbed on the walls of these wider micropores, molecules opposite
2.1 Porosimetry

Figure 2.2 Enhancement of the adsorption energy $\phi$ of a molecule with diameter $d$ in slit-shaped pores of various widths $w$ with respect to the adsorption energy on an open surface, $\phi_0$ [29].

one another will induce adsorbate-adsorbate interaction which promotes the adsorption of further molecules. This is called secondary micropore filling.

In meso- and macro pores first a monolayer will adsorb on the walls at low relative pressure. At a certain pressure, monolayer formation is completed and further molecules will be attracted for increasing pressure resulting in the formation of a multilayer. Dependent on the nature of the adsorbent and adsorptive, multilayer formation can already start before the surface coverage is completed.

2.1.2 Isotherms

The majority of the experimental adsorption isotherms can be grouped into 6 types of the IUPAC classification [27]. These types are related to solids with a specific pore structure and are shown in figure 2.3. Often, the experimental isotherms can not easily be assigned to one type but show features of 2 or 3 different types. As will be shown in chapter 4 the isotherms obtained in this work are related to the type I, II, and III isotherms which are shortly explained hereafter.

The type I isotherm shows a steep rise at low relative pressure which is associated with micropore filling. The plateau reached at high relative pressure indicates limited multilayer adsorption. This isotherm is usually characteristic for a microporous solid with a small external surface in comparison with the internal pore surface [27].
Figure 2.3 The 6 isotherm types according to the IUPAC classification [27].

The type II isotherm indicates unrestricted monolayer-multilayer adsorption and is obtained with non-porous or macroporous adsorbents [27]. Point B is often taken to represent the completion of monolayer coverage and the starting of multilayer adsorption.

The type III isotherm is indicative of weak adsorbent-adsorbate interactions and is given by non-porous or macroporous materials [29]. Due to this weak interaction the uptake at low relative pressure is small but once some molecules have adsorbed, the adsorption of further molecules is promoted by the adsorbate-adsorbate forces [28].

2.1.3 Ellipsometric porosimetry

In this work the technique of ellipsometric porosimetry (EP) was used for porosimetry measurements on the SiO$_2$ and Al$_2$O$_3$ barrier layers. EP combines the use of spectroscopic ellipsometry (SE) and equilibrium adsorption/desorption isotherms to determine the open porosity of a solid. The adsorption of a gas or vapor in the pores of a solid induces a change in refractive index. Once all pores are filled and the adsorption process continues by means of multilayer adsorption, this will result in an increase in layer thickness. Both changes in refractive index and thickness are measured by SE (introduced in section 3.2.1) as function of relative vapor pressure. From these measurements isotherms are obtained and these isotherms allow the
characterization of the microstructure of the layers in terms of pore type, pore relative content and pore size.

EP has several advantages over other porosimetry techniques like volumetric or gravimetric methods. The volumetric method measures a change in pressure of a constant volume around a porous sample upon uptake, while the gravimetric method measures the change in mass of the porous sample. First of all, SE has a sensitivity down to the monolayer level and is therefore suitable for the accurate determination of isotherms of thin barrier layers with a very small pore volume. The uptake of very small volumes will never be detected by using a conventional volumetric or gravimetric method. For these thin layers, gravimetric or volumetric methods require the use of extremely sensitive devices like a quartz crystal microbalance for example. A drawback when using a microbalance is that the layer has to be deposited on the device itself instead of on a wafer or polymer substrate which can lead to different film properties [26]. Another advantage of EP is that structural changes, like swelling of the layer, can also be analyzed during the adsorption and desorption processes [25].

2.1.4 Porosity

During the EP measurements the changes in the layer refractive index upon adsorption/desorption of a vapor in the pores as function of the relative pressure were monitored. The porosity of the layers can be extracted from the refractive index values by making use of the Lorentz-Lorenz equation which describes the relation between the optical constants and material properties of a multi-component system:

\[
B_{\text{eff}} = \frac{3}{4\pi} \frac{n_{\text{eff}}^2 - 1}{n_{\text{eff}}^2 + 2} = \sum N_i \alpha_i, \quad \text{(2.2)}
\]

with \( B_{\text{eff}} \) the effective polarizability of a unit of volume, \( n_{\text{eff}} \) the effective refractive index of the multi-component system, and \( \alpha_i \) and \( N_i \) the molecular polarizability and the number of molecules per unit volume of each component \( i \), respectively.

The porous films analyzed in this work consist of two components: matrix and pores. By introducing the porosity \( P \) as the relative amount of pores, equation 2.2 can be expressed as:

\[
B_{\text{eff}} = P \cdot B_p + (1 - P) \cdot B_m, \quad \text{(2.3)}
\]

with \( B_p \) and \( B_m \) the volume polarizability of the pores and matrix, respectively.

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Chapter 2 Basics on porosimetry

When the partial vapor pressure is zero, all pores are empty with a refractive index $n_p=1$. This means that the volume polarizability of the pores is zero and equation 2.3 reduces to:

$$B_0 = (1 - P) \cdot B_m,$$  \hspace{1cm} (2.4)

where $B_0$ is the the effective polarizability of the film at zero partial vapor pressure.

When, at a certain vapor pressure, all pores are filled with vapor molecules equation 2.3 can be written as:

$$B_{fill} = P \cdot B_{vapor} + (1 - P) \cdot B_m,$$  \hspace{1cm} (2.5)

where $B_{fill}$ is the the effective polarizability of the film at the vapor pressure for which the pores are filled and $B_{vapor}$ the volume polarizability of the vapor. An expression for the porosity $P$ is obtained by combining equation 2.4 and 2.5:

$$P = \frac{B_{fill} - B_0}{B_{vapor}}.$$  \hspace{1cm} (2.6)

Using the relation between the volume polarizability and the refractive index (equation 2.2) the equation is written as:

$$P = \frac{n_{fill}^2 - n_p^2}{n_{fill}^2 + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \cdot \frac{n_{vapor}^2 - 1}{n_{vapor}^2 + 2}.$$  \hspace{1cm} (2.7)

This equation was used to calculate the open porosity of the barrier layers.
Chapter 3

Experimental

3.1 Deposition set-ups, processes, and conditions

In this section the set-ups, deposition processes and deposition conditions for SiO$_2$ and Al$_2$O$_3$ barrier layers are described. The basics of the deposition techniques used are given in appendix A. First, the plasma enhanced atomic layer deposition (PEALD) processes of the SiO$_2$ and Al$_2$O$_3$ layers are explained together with the reactor and deposition conditions. The PEALD SiO$_2$ films were compared with two SiO$_2$ films deposited by plasma enhanced chemical vapor deposition (PECVD) and for the PEALD Al$_2$O$_3$ films a comparison was made with two Al$_2$O$_3$ films deposited using expanding thermal plasma chemical vapor deposition (ETP-CVD). Both the PECVD and the ETP-CVD process and the deposition conditions are also reported in this section. All layers were deposited on crystalline silicon wafers. The section ends with a description of the deposition process of the SiO$_2$/Al$_2$O$_3$ nano-laminates.

3.1.1 Plasma enhanced atomic layer deposition

The PEALD processes of both SiO$_2$ and Al$_2$O$_3$ were carried out in a remote plasma reactor, the Oxford Instruments FlexAL, which is also suited for thermal ALD (figure 3.1). The main parts of the reactor are a loadlock, a deposition chamber, and an inductively coupled plasma source controlled by an automated matching network. The plasma is generated remotely from the substrate, a so-called remote plasma set-up and this configuration allows for a good (independent) control of the plasma and substrate conditions. Optical viewports located at 70° with the normal on the substrate stage were used for in situ spectroscopic ellipsometry measurements.
Before every deposition, the chamber was purged with O\(_2\) (\(\Phi_{O_2} = 100 \text{ sccm}\)) and Ar (\(\Phi_{Ar} = 100 \text{ sccm}\)) for at least 5 minutes to have uniform starting conditions for each deposition and to heat the sample for depositions above room temperature.

For Al\(_2\)O\(_3\) films, Al(CH\(_3\))\(_3\) (trimethylaluminum, TMA) was used as a precursor and for SiO\(_2\) films, the precursor H\(_2\)Si[N(C\(_2\)H\(_5\))\(_2\)]\(_2\) (SAM.24) was used. TMA and SAM.24 were vaporized at 30 °C and 70 °C, respectively, for vapor drawn delivery into the deposition chamber. The delivery line was constantly purged with Ar which also acted as a carrier gas to deliver the precursors into the deposition chamber. To prevent condensation of the precursor in the delivery lines, the temperature of these lines was set 20 °C higher than the precursor pots. The precursors are injected in the deposition chamber above the substrate a few cm from the center.

In the second half reaction a 200 W O\(_2\) plasma was used for the oxidation step. During the plasma step, the argon purge of the precursor line was diverted to the exhaust line to ensure a pure O\(_2\) plasma. Because O\(_2\) does not react with TMA [32] and SAM.24 [33] under the used operating conditions, a constant O\(_2\) flow of 100 sccm was used during the entire ALD cycle and served as a purge gas. After each deposition, the chamber was pumped down for 1 minute to remove all species (precursor and byproducts). The Al\(_2\)O\(_3\) and SiO\(_2\) films were deposited at substrate temperatures of 25 °C and 100 °C.
3.1 Deposition set-ups, processes, and conditions

Optimization of PEALD processes

A limitation of (PE)ALD compared to other deposition techniques is that the process is relatively slow \(^1\). Therefore, it is desirable to optimize the PEALD process time, which means finding the minimum times for the precursor dose, plasma exposure and purge steps for which the PEALD process is truly saturated. If the precursor dose or the plasma exposure is not sufficient not all surface groups will react which means that the process is not saturated. The non-saturated process results in a lower growth per cycle (GPC) and worse material properties. Too short purge steps can lead to a direct reaction between the precursor and the plasma species in the gas phase, causing a CVD-like growth. These CVD processes result in a higher GPC.

For the optimization of the PEALD processes, series of depositions were performed for both Al\(_2\)O\(_3\) and SiO\(_2\). For each material four deposition series were performed for the optimization of the four steps in the PEALD process. For each series, the duration of one of the four steps in the process was varied whereas the duration of the other steps was taken sufficiently long to guarantee saturation. The film growth was monitored using spectroscopic ellipsometry (SE, introduced in section 3.2.1). For each time step the GPC was determined after 50 ALD cycles from the thickness of the films as measured by SE. The thickness was fitted and the optical constants were kept constant in the SE model since the thickness and optical constants are correlated for thin layers (5-10 nm). The GPC was plotted as function of step time, a so-called saturation curve. From the four saturation curves obtained, the optimum time for each step could be determined. The depositions for the Al\(_2\)O\(_3\) and SiO\(_2\) saturation curves were done at 25 °C.

3.1.2 Plasma enhanced chemical vapor deposition

SiO\(_2\) layers

In this work the PEALD SiO\(_2\) layers were compared to two SiO\(_2\) films deposited by RF PECVD. The layers were deposited in a homebuilt capacitively-coupled plasma reactor (Polymobas, figure 3.2). The main parts of the reactor are a deposition chamber and two parallel electrodes. The top electrode is connected to a RF power generator and a matching network, the bottom electrode is grounded and serves as substrate holder. Optical viewports located at \(\sim 71.5^\circ\) with the normal on the substrate stage were used for in situ spectroscopic ellipsometry measurements.

\(^1\)Faster ALD processes are being developed, for example spatial ALD. In this process the time separation of the precursors is replaced by space separation of the precursors [34].
Chapter 3 Experimental

Figure 3.2 Schematic of the parallel plate PECVD set-up used for the deposition of SiO$_2$ layers.

Before the depositions an Ar plasma was generated ($\Phi_{Ar} = 30$ sccm, $P = 150$ W) for ten minutes to remove adsorbed water since the set-up has no loadlock. During the Ar plasma a shutter was placed above the substrate to avoid any plasma-substrate interaction.

As a precursor a cyclic siloxane monomer, 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane ($V_3D_3$) was used. The monomer was evaporated in a stainless steel bubbler kept at a constant temperature of 100 °C and the flow rate was metered through a vapor source controllers. The temperature of the delivery line was set to 120 °C to avoid $V_3D_3$ condensation. The walls of the reaction chamber were heated to a temperature of 80 °C also to avoid condensation of the monomer. The monomer was injected into the chamber through a ring above the substrate holder at a constant flow rate of 0.7 sccm in a continuously running Ar ( $\Phi_{Ar} = 70$ sccm) and O$_2$ ( $\Phi_{O_2} = 35$ sccm) plasma. The layers were deposited at a substrate temperature of 100 °C and a plasma power of 150 W and 250 W [35].

In table 3.1 a short overview of the deposition conditions is given for the four SiO$_2$ layers which were analyzed, hereafter referred to as SiO$_2$ PEALD, 25 °C, SiO$_2$ PEALD, 100 °C, SiO$_2$ PECVD, 150 W, and SiO$_2$ PECVD, 250 W.

<table>
<thead>
<tr>
<th>Layer Description</th>
<th>$T_{sub}$ (°C)</th>
<th>$P_{plasma}$ (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ PEALD, 25 °C</td>
<td>25</td>
<td>200</td>
</tr>
<tr>
<td>SiO$_2$ PEALD, 100 °C</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>SiO$_2$ PECVD, 150 W</td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td>SiO$_2$ PECVD, 250 W</td>
<td>100</td>
<td>250</td>
</tr>
</tbody>
</table>

Table 3.1 Deposition conditions SiO$_2$ layers.
3.1 Deposition set-ups, processes, and conditions

Al₂O₃ layers

For the PEALD Al₂O₃ layers, a comparison was made with two Al₂O₃ layers deposited by the ETP-CVD technique. The layers were deposited in a homebuilt remote plasma set-up in which an Ar plasma is generated in a high pressure plasma source (cascaded arc, 30 A arc current), emanates through a nozzle and expands supersonically in a low pressure reaction chamber towards the substrate (figure 3.3). Samples were loaded via a loadlock.

The precursor used was TMA which is the same precursor as for the PEALD Al₂O₃ process. O₂ and TMA were injected in the Ar plasma in the low pressure reaction chamber. From a bubbler at room temperature TMA was injected via short pulses (30 ms) in the argon-oxygen plasma running in the reaction chamber. The time between the TMA pulses was different for the two layers analyzed, namely, 1.1 s and 7.5 s, hereafter referred to as the TMA off time. The substrate temperature for these depositions was 80 °C [36].

![Figure 3.3 Schematic of the ETP-PECVD set-up used for the deposition of Al₂O₃ layers.](image)
Chapter 3 Experimental

In table 3.2 a short overview of the deposition conditions is given for the Al$_2$O$_3$ layers analyzed, hereafter referred to as Al$_2$O$_3$ PEALD, 25°C, Al$_2$O$_3$ PEALD, 100°C, 2s, Al$_2$O$_3$ PEALD, 100°C, 10s, Al$_2$O$_3$ ETP, 1.1s, and Al$_2$O$_3$ ETP, 7.5s.

<table>
<thead>
<tr>
<th>Deposition Conditions</th>
<th>$T_{\text{sub}}$ (°C)</th>
<th>$P_{\text{plasma}}$ (W)</th>
<th>Extra Info</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$ PEALD, 25°C</td>
<td>25</td>
<td>200</td>
<td>2 s plasma time</td>
</tr>
<tr>
<td>Al$_2$O$_3$ PEALD, 100°C, 2s</td>
<td>100</td>
<td>200</td>
<td>2 s plasma time</td>
</tr>
<tr>
<td>Al$_2$O$_3$ PEALD, 100°C, 10s</td>
<td>100</td>
<td>200</td>
<td>10 s plasma time</td>
</tr>
<tr>
<td>Al$_2$O$_3$ ETP, 1.1s</td>
<td>80</td>
<td></td>
<td>1.1 s TMA off time</td>
</tr>
<tr>
<td>Al$_2$O$_3$ ETP, 7.5s</td>
<td>80</td>
<td></td>
<td>7.5 s TMA off time</td>
</tr>
</tbody>
</table>

3.1.3 Nano-laminate depositions

SiO$_2$ layers were deposited by Fujifilm on polyethylene naphthalate (PEN) substrates. These depositions were performed by PECVD by making use of an atmospheric pressure glow discharge (APG). As a precursor O[Si(CH$_3$)$_3$]$_2$ (hexamethyldisiloxane, HMDSO) was used in a N$_2$/Ar/O$_2$ plasma. The films were grown in a roll-to-roll process and the thickness and quality of the films depend on the dynamic deposition rate as determined by the web speed of the foil during the roll-to-roll process [38]. Two sets of SiO$_2$ layers were deposited: a set deposited at high dynamic deposition rate (HDDR, 33 nm · m/min) resulting in 70 nm thick films, and a set deposited at low dynamic deposition rate (LDDR, 10 nm · m/min) resulting in a film thickness of 100 nm. The layers were deposited at a temperature of 80 °C. A schematic picture of the deposition set-up is given in figure 3.4.

Subsequently, Al$_2$O$_3$ PEALD layers with a thickness varying between 0.5 nm and 20 nm were deposited on top of these SiO$_2$ layers. Besides, Al$_2$O$_3$ PEALD layers of 2 nm, 5 nm, and 20 nm were also deposited directly on PEN substrates. The number of ALD cycles required for the various film thicknesses were determined from thickness measurements on silicon wafers. The deposition process of these Al$_2$O$_3$ layers is described in section 3.1.1. The layers were deposited at a substrate temperature of 80 °C, consistent with the process temperature during the SiO$_2$ depositions.

As will be shown in section 4.3.1, the PEALD layers contain a substantial amount of carbon compared to the Al$_2$O$_3$ ETP, 7.5s layer. To learn more about the relation between these carbon impurities and the porosity of the layers, a PEALD Al$_2$O$_3$ layer deposited at 100 °C with 10 seconds plasma exposure (instead of 2 seconds) was also analyzed. It is known from literature that a longer plasma exposure time results in a reduced carbon content for the PEALD layer [37]. Therefore, a comparison with the PEALD layer deposited using a longer plasma time should give better insight in the effect of the carbon content on the porosity.

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3.2 Diagnostic tools

Figure 3.4 A schematic representation of the roll-to-roll deposition set-up for the deposition of SiO$_2$ layers on PEN substrates. Depositions were performed by PECVD by making use of an atmospheric pressure glow discharge, a uniform mode of atmospheric dielectric barrier discharge (DBD). The PEN substrate served as dielectric barrier for the DBD [38].

In table 3.3 a short overview of the deposition conditions is given for the nano-laminates analyzed, hereafter referred to as SiO$_2$ APG, HDDR/Al$_2$O$_3$ PEALD, 80°C and SiO$_2$ APG, LDDR/Al$_2$O$_3$ PEALD, 80°C.

<table>
<thead>
<tr>
<th>T$_{\text{sub}}$ (°C)</th>
<th>extra info</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ APG, HDDR/Al$_2$O$_3$ PEALD, 80°C</td>
<td>80 High dyn. dep. rate SiO$_2$</td>
</tr>
<tr>
<td>SiO$_2$ APG, LDDR/Al$_2$O$_3$ PEALD, 80°C</td>
<td>80 Low dyn. dep. rate SiO$_2$</td>
</tr>
</tbody>
</table>

3.2 Diagnostic tools

In this section complementary diagnostics are described which were used to obtain information about the optical properties, microstructure, chemical composition, density and barrier performance of the SiO$_2$ and Al$_2$O$_3$ barrier layers.

3.2.1 Spectroscopic ellipsometry

Spectroscopic ellipsometry (SE) is an optical method for the analysis of surfaces which involves the use of polarized light. It is mostly used to determine optical constants and thin film thickness [39, 40].
The polarization of light is characterized by its electric field vector. The type of polarization (linear, circular, or elliptic) is determined by the relative amplitude and phase difference of the s-component (perpendicular to the plane of incidence) and the p-component (parallel to the plane of incidence) of the electric field vector.

An ellipsometer launches a beam with a known polarization state onto a sample under an angle $\varphi$, and then measures the polarization state of the reflected beam (figure 3.5). It measures the complex ellipsometric parameter $\rho \equiv \frac{R_p}{R_s}$, with $R_p$ and $R_s$ the complex total reflection coefficients for the p- and s-component of the polarized light. $\rho$ can also be expressed in terms of the angles $\Psi$ and $\Delta$:

$$\rho \equiv \frac{R_p}{R_s} \equiv \tan \Psi e^{i\Delta},$$

where $\tan \Psi$ is the magnitude of the ratio of the p- and s- reflection coefficients, which is a measure for the relative amplitude of the p- and s-components, and $\Delta$ is the shift in phase difference between the p- and s-wave, induced by reflection.

Because SE measures the ratio of two values and does not depend on absolute values, it can be highly accurate and very reproducible. Since the ratio is a complex number it also contains phase information which makes the method very sensitive and it allows SE to study ultra-thin films on a sub-monolayer level [39].

The spectroscopic ellipsometers used were a J.A. Woollam Co., Inc. M2000D (193-1000 nm) for ex-situ measurements and a J.A. Woollam Co., Inc. M2000U (245-1000 nm) for in-situ measurements.

Figure 3.5 A schematic representation of the principle of SE: a linear polarized light beam, launched on a sample, changes into an elliptically polarized beam upon reflection on the surface.
3.2 Diagnostic tools

Optical model

To obtain physical parameters of interest from the measured data, a model has to be constructed from which the parameters of interest can be calculated. The desired parameters are the film thickness and refractive index. The refractive index can be defined as

\[ \tilde{n} = n + i\kappa, \]  

(3.2)

where \( n \) is the refractive index, indicating the phase velocity of light in the material, and \( \kappa \) is the extinction coefficient, which is a measure of the absorption losses when the light propagates through the material.

The barrier layers were deposited on crystalline silicon wafers which have a thin film of native oxide on their surface due to contact with the ambient. All bare wafers were measured before deposition to determine the thickness of this native oxide film, by using a model comprised of a semi-infinite silicon layer and a native oxide layer on top. Since SiO\(_2\) and Al\(_2\)O\(_3\) are both transparent (\( \kappa \approx 0 \)) in the spectral range covered by the ellipsometers used (193 to 1000 nm) a Cauchy function has been applied to model these films, an empirical dispersion relation for transparent materials (figure 3.6):

\[ n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}, \]  

(3.3)

where \( n \) is the refractive index, \( \lambda \) the wavelength, and A, B, and C the Cauchy dispersion coefficients. The fit parameters were the layer thickness and the coefficients A, B and C (C was only included as it improved the fit).

<table>
<thead>
<tr>
<th>Cauchy</th>
<th>Native oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.6 A schematic of the SE model used to calculate the thickness and refractive index of the deposited films: a semi-infinite silicon layer, a native oxide layer, and a Cauchy layer on top representing the deposited film.

The modeling of the Al\(_2\)O\(_3\) \text{ETP,1.14} layer was different from the other films. First of all, this layer has a high carbon content (as will be shown in section 4.3.1) which gives rise to absorption in the low wavelength range. Because the cauchy model used is only valid for transparent layers, the data was fitted
in a restricted wavelength range of 400-1000 nm. Since the data in the low
wavelength range might contain extra information affecting the thickness or
refractive index values, a comparison was made with another model, the B-
spline model, which takes into account the absorption in the low wavelength
range. The B-spline model makes use of control points (nodes) to describe
the complex dielectric function $\epsilon = \epsilon_1 + i\epsilon_2 = (n + i\kappa)^2$. Basis splines (B-
splines), a basis set for polynomial splines, are used to interpolate between
the control points. Furthermore, the Al$_2$O$_3$ ETP$_{1.1s}$ layer has a high surface
roughness compared to the other films which had to be taken into account
for a correct fit of the SE data. This high roughness was confirmed by
atomic force microscopy measurements as will be shown in section 3.2.6.
This roughness was modeled adding a mixed layer of the bulk film (Al$_2$O$_3$,
50%) and voids (50%) on top of the Al$_2$O$_3$ layer. The Bruggeman Effective
Medium Approximation (EMA) was used to calculate the optical constants
of this mixed layer, hereafter referred to as the EMA layer. The expression
used is:

$$\sum_i f_i \frac{\epsilon_i - <\epsilon>}{\epsilon_i + 2 <\epsilon>} = 0,$$

(3.4)

where $f_i$ and $\epsilon_i$ are the volume fraction and optical constant of each con-
stituent $i$, respectively. $<\epsilon>$ is the optical constant of the mixed layer.

### 3.2.2 Ellipsometric porosimetry

Porosimetry measurements were carried out to characterize the microstruc-
ture of the SiO$_2$ and Al$_2$O$_3$ barrier layers. For these measurements the
technique of ellipsometric porosimetry (EP) was used which provides infor-
mation about the open porosity by combining SE measurements with equilib-
rium adsorption/desorption isotherms. The set-up and conditions for
the EP measurements are described followed by the fitting procedures of the
SE data.

The EP measurements were carried out in the same set-up used for the
PECVD depositions of the SiO$_2$ layers (section 3.1.2). The adsorptive used
during the measurements was V$_3$D$_3$, the precursor for the PECVD SiO$_2$
process, which is supposed not to react with the surface groups of the SiO$_2$
and Al$_2$O$_3$ layers $^3$. He was used as a carrier gas. The walls of the reaction
chamber were heated to a temperature of 80 °C to avoid condensation of
the adsorptive. The substrate temperature was set to 25 °C. Table 3.4 gives
an overview of the experimental conditions for the EP measurements.

$^3$V$_3$D$_3$ is used as these measurements are a follow-up of earlier studies. In the set-up
inorganic/organic multilayers were grown, using V$_3$D$_3$ as monomer for both the inorganic
and organic layers. Studies were done on the way V$_3$D$_3$ would adsorb on the surface/open
porosity of SiO$_2$ layers and give rise then to the organic layer growth [35, 41].
Table 3.4 Experimental conditions for the EP measurements.

<table>
<thead>
<tr>
<th>V$_3$D$_3$ (sccm)</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>He (sccm)</td>
<td>2</td>
</tr>
<tr>
<td>T$_{sub}$ (K)</td>
<td>298</td>
</tr>
<tr>
<td>P (mbar)</td>
<td>$10^{-5}$ - 0.78</td>
</tr>
<tr>
<td>P$<em>M$/P$</em>{sat}$</td>
<td>0 - 1</td>
</tr>
</tbody>
</table>

Before the measurement, samples were outgassed overnight in the reaction chamber at base pressure ($10^{-6}$ mbar). The outgassing process was monitored by measuring the change in refractive index of the sample. The refractive index value after outgassing was taken as the starting value for the adsorption/desorption measurements (i.e. $n_0$). V$_3$D$_3$ and He were injected into the chamber at the base pressure at a flow rate of 5 sccm and 2 sccm, respectively. The pressure was increased stepwise from $2.5 \cdot 10^{-2}$ mbar to 0.78 mbar during the adsorption path and decreased again stepwise for the desorption path. At the substrate temperature of 25 °C, this allows for the measurement of the relative pressure over the range $0 < P_M/P_{sat} < 1$ as the monomer saturation vapor pressure, $P_{sat}$, is 0.571 mbar at this temperature [42]. $P_M$ is the partial monomer pressure. The monomer adsorption and desorption was monitored continuously by means of in-situ SE measurements (fig 3.7). After the measurement, the sample was left in the chamber overnight at base pressure and a final measurement was done the next day. The reproducibility of these porosity measurements was confirmed by repeating a measurement on the same sample.

3.2.3 Fitting procedures isotherms

SiO$_2$ layers

As will be shown in chapter 4, from the shape of the isotherms it was concluded that for all SiO$_2$ layers micropore filling occurred at low relative pressure and monomer multilayer adsorption took place at higher relative pressure. These processes are schematically shown in figure 3.8.

To represent both the processes of micropore filling and multilayer adsorption, the isotherms have been reported in terms of optical thickness. In the range $0 < P_M/P_{sat} \leq 0.2$ the optical thickness is defined as follows:

$$n \cdot d = n_{SiO_2(fill)} \cdot d_{SiO_2},$$

with $n_{SiO_2(fill)}$ the SiO$_2$ refractive index due to the micropore filling and $d_{SiO_2}$ the constant SiO$_2$ layer thickness.
Chapter 3 Experimental

Figure 3.7 The typical change in the $\Psi$-signal during an EP measurement after an increase in pressure. At $t=0$ the initial pressure is increased and at $t=5$ the new value is reached.

![Figure 3.7](image)

Figure 3.8 The adsorption of $V_3D_3$ on the SiO$_2$ layer at (a) $P_M/P_{sat} = 0$, (b) $P_M/P_{sat} = 0.2$ (micropore filling) and (c) $P_M/P_{sat} = 1$ (multilayer adsorption).

![Figure 3.8](image)

For $0.2 < P_M/P_{sat} < 1$ the optical thickness is given by:

$$n \cdot d = n_{SiO_2(P_M/P_{sat}=0.2)} \cdot d_{SiO_2} + n_{V_3D_3} \cdot d_{V_3D_3},$$

(3.6)

where $n_{V_3D_3}$ is the monomer refractive index and $d_{V_3D_3}$ the monomer multilayer thickness. For the desorption path, starting at $P_M/P_{sat} = 1$, the optical thickness is given by equation 3.6 until the relative pressure at which the monomer thickness becomes zero again. From that point on, which is not the same for each layer, the optical thickness is given by equation 3.5.

For $0 < P_M/P_{sat} \leq 0.2$ the SE data was fitted using the optical model given in equation 3.3 as the monomer $V_3D_3$ is transparent in the wavelength range covered by the ellipsometer. For the multilayer adsorption in the range $0.2 < P_M/P_{sat} < 1$ the SE model was extended with a second Cauchy layer. The thickness and dispersion coefficients of the first Cauchy layer
were kept constant. For the second Cauchy layer, representing the monomer multilayer, the dispersion coefficients were kept constant ($n_{V_3D_3}=1.422$ at $\lambda=589$ nm and $T=293$ K [43]) and only the thickness of this layer was fitted.

**Al$_2$O$_3$ layers**

As will be shown in chapter 4, the Al$_2$O$_3$ PEALD layers and the Al$_2$O$_3$ ETP, 7.5 s layer contain no pores that can be probed by V$_3$D$_3$ molecules and therefore, the process of monomer multilayer adsorption took place over the full relative pressure range. The optical model used to fit the SE data was the same as for the multilayer adsorption on the SiO$_2$ layers. The isotherms have been reported in terms of monomer thickness over the full relative pressure range.

For the Al$_2$O$_3$ ETP, 1.1 s layer, the fitting procedure was different due to its high roughness and the presence of micropores. As will be shown in chapter 4, during monomer adsorption two processes started simultaneously at low relative pressure: the filling of micropores in the Al$_2$O$_3$ film and surface modification in terms of roughness decrease. The filling of the pores was modeled by fitting the refractive index of the Al$_2$O$_3$ layer. To model the roughness decrease a third component was added to the EMA layer (50% Al$_2$O$_3$ and 50% voids) which was used to model the roughness. This third component represents the monomer. At $P_M/P_{sat}=0$ the amount of monomer was set to 0%. Subsequently, the percentage of voids and monomer were fitted as function of the relative pressure, keeping the Al$_2$O$_3$ component fixed at 50%. As the monomer adsorbs in the valleys of the roughness, the percentage of voids will decrease, starting at 50%, and the percentage of monomer will increase, starting at 0%. A schematic of this process is shown in figure 3.9.

![Figure 3.9](image)

**Figure 3.9** The adsorption of V$_3$D$_3$ on the Al$_2$O$_3$ ETP, 1.1 s layer at (a) $P_M/P_{sat}=0$ and (b) $P_M/P_{sat}=1$.

### 3.2.4 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is an optical technique used to obtain information about the chemical composition of a film. FTIR involves the interaction between infrared light and vibrational modes of
molecules. The atoms in a molecule are in periodic motion and vibrate at the so-called vibration frequency. These vibration frequencies correspond with discrete energy levels characteristic for specific vibrational bonds and hence are used to identify them. When a sample is placed in front of the detector, infrared light from a broadband source is absorbed if the frequency matches the frequency of the vibrational modes of the molecules. An interferogram is obtained from a Michelson interferometer (figure 3.10) and shows the light intensity as function of the optical path difference. The interferogram is then fourier transformed into an intensity spectrum as function of frequency. The measured transmission spectrum can be transformed into an absorption spectrum via equation 3.7 (The Beer-Lambert law):

\[ A = -\log(T) = -\log\left(\frac{I}{I_0}\right), \]  

(3.7)

where \( A \) is the absorbance, \( T \) the transmittance, \( I \) the transmitted intensity of the substrate with the deposited layer, and \( I_0 \) the transmitted intensity of the bare substrate.

For the FTIR measurements a Bruker Tensor 27 was used at a resolution of 4 cm\(^{-1}\) and the region of interest of the spectra is 400-4000 cm\(^{-1}\), the mid-infrared. Before every measurement the spectrometer was purged with nitrogen for 5 minutes to minimize absorption peaks by CO\(_2\) and H\(_2\)O, which can be present in the spectrometer or adsorbed by the layer in the ambient air. Since the bare substrate and the substrate with a deposited layer were measured at different times, also a reference measurement, without a sample in front of the detector, was done each time to compensate for different amounts of CO\(_2\) and H\(_2\)O in the spectrometer. All spectra were baseline corrected and normalized by the thickness of the layers.
3.2 Diagnostic tools

In order to obtain extra information from the spectra, besides the chemical composition of the film, specific regions were fitted. For the SiO$_2$ spectra the Si-O-Si asymmetric stretch peak was fitted using three Gaussian functions to calculate the ratio of the area of the peak and the adjacent shoulder. This ratio gives information about the difference in porosity between the layers as will be explained in section 4.2.1.

3.2.5 Rutherford backscattering spectroscopy and elastic recoil detection

Rutherford backscattering spectroscopy (RBS) is an ion beam analysis technique used to determine the composition, density, and concentration depth profiles of thin films [44]. A beam of high energy ions (1-2 MeV, usually He ions) is directed at a sample. These ions are backscattered and detected under a specific angle. The detector counts the number of ions as function of their energy which depends on the mass of the target atom as well as the depth of this atom (figure 3.11 (a)).

Hydrogen atoms can not be detected by RBS since these light atoms are recoiled (in a forward direction) by the incident energetic ions. Therefore, a complementary technique can be used called elastic recoil detection (ERD). In ERD the ion beam hits the surface at a grazing angle and the recoiled H atoms are detected. A stopper foil in front of the detector prevents the detection of scattered ions (figure 3.11 (b)).

**Figure 3.11** (a) Schematic of the RBS set-up. An ion beam is directed at a sample and the backscattered ions are detected under a specific angle. (b) Schematic of the ERD set-up. The ion beam hits the surface at a grazing angle and the recoiled H atoms are detected. A stopper foil in front of the detector prevents the detection of scattered ions. [44]

RBS/ERD measurements were done using a 2 MeV He$^+$ beam. First, the beam was directed perpendicular on the sample surface and the backscattered ions were measured under a scattering angle of 170°. Then a measurement was performed using a beam impinging under a grazing angle with a scattering angle of 115°.
3.2.6 Atomic force microscopy

Atomic force microscopy (AFM) was used to characterize the surface topography of the samples. The surface of the samples are scanned with a tip attached to a cantilever. When the tip approaches the surface, atomic force interactions between tip and surface cause a deflection of the cantilever, measured using a laser and photodiode detector. A constant force is maintained between tip and sample by moving the sample in the vertical direction. The sample is scanned by moving it in the lateral direction, monitoring the changes in vertical position. A topographic map is created from which the root mean square (RMS) surface roughness of the sample is obtained. A Solver Pro Scanning Probe microscope was used and tips with a radius of curvature of 20 nm to measure the surface of the Al$_2$O$_3$ layers. The RMS surface roughness of the Al$_2$O$_3$ layers is given in table 3.5. These measurements confirm the higher roughness of the Al$_2$O$_3$ ETP,1.1 s film as was already suggested by the SE data since roughness had to be included for a good fit. (section 3.2.1) The other Al$_2$O$_3$ layers are assumed to have a flat surface as their roughness is close to the roughness of a bare silicon wafer ($\approx 0.3$ nm).

Table 3.5 RMS surface roughness of the Al$_2$O$_3$ layers.

<table>
<thead>
<tr>
<th>Layer Description</th>
<th>RMS Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$ PEALD, 25°C</td>
<td>0.32 ± 0.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$ PEALD, 100°C, 2 s</td>
<td>0.35 ± 0.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$ PEALD, 100°C, 10 s</td>
<td>0.38 ± 0.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$ ETP, 1.1 s</td>
<td>2.22 ± 0.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$ ETP, 7.5 s</td>
<td>0.26 ± 0.2</td>
</tr>
</tbody>
</table>

3.2.7 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface analysis technique for analyzing the relative concentrations of elements on surfaces. A sample is placed in an ultra high vacuum chamber and irradiated with soft X-rays of energy $h\nu$. The X-ray photons will eject electrons from a core level and the energy of these photoelectrons is analyzed. The spectrum is obtained as a plot of photoelectron flux against binding energy. The spectrometer measures the kinetic energy ($E_k$) of the photoelectrons from which the binding energy $E_B$ can be calculated using:

$$E_B = h\nu - E_k - W,$$

(3.8)
with $W$ the spectrometer work function, a measure of the energy loss of the electrons caused by the spectrometer. The binding energy identifies the electron in terms of its parent element and atomic energy level. The measuring depth depends on the mean free path of the electrons and is in the order of a few nanometers. The measuring depth can be reduced by increasing the angle of incidence of the incoming X-ray beam. In this way the measurement is more surface sensitive. Performing multiple measurements using various angles of incidence, so-called angle resolved measurements, allows the characterization of a surface or interface between two layers without modifying the layer. To obtain information from larger depths, material can be removed by sputtering surface atoms. A Thermo Scientific K-Alpha KA1066 spectrometer was used with an Al Kα X-ray source ($h\nu = 1486.6$ eV). The position of the hydrocarbon component of the C1s peak was used to charge correct the spectra.

XPS measurements were carried out on SiO$_2$ and Al$_2$O$_3$ layers after the porosity measurements to find out if V$_3$D$_3$ was present on the surface of the samples. A depth profile was made for one of the Al$_2$O$_3$ samples, using sputtering with argon ions, to see if monomer had diffused into the layer. Angle resolved XPS measurements were carried out on SiO$_2$/Al$_2$O$_3$ nanolaminates to study the interface region of these layers. Three different SiO$_2$ layers were analyzed with a 5 nm Al$_2$O$_3$ on top: a SiO$_2$ APG_HDDR layer, a SiO$_2$ APG_LDDR layer and a SiO$_2$ layer grown by thermal oxidation. This thermal SiO$_2$ layer is nonporous which means there should be a discrete interface between SiO$_2$ and Al$_2$O$_3$. From these measurements the atomic concentrations as function of the depth were obtained for Al, Si, O, and C. Using the density and stoichiometry of the SiO$_2$ and Al$_2$O$_3$ layers, the data was modeled to obtain a depth profile of the chemical compounds.

### 3.2.8 Calcium test (intrinsic WVTR)

Water vapor transmission rate (WVTR) measurements were performed at Holst Centre, by means of the calcium test for both Al$_2$O$_3$ and SiO$_2$ layers [45] to test the intrinsic barrier properties of these layers. Initially, calcium has almost no transmission but due to reaction with water and oxygen, metallic calcium evolves to a transparent calcium oxide layer according to the following reactions:

\[
Ca + H_2O \rightarrow CaO + H_2 \quad (3.9)
\]

\[
CaO + H_2O \rightarrow Ca(OH)_2 \quad (3.10)
\]

\[
2Ca + O_2 \rightarrow 2CaO \quad (3.11)
\]
Chapter 3 Experimental

The WVTR of a barrier layer can be obtained by following the changes of the optical properties of a Ca layer underneath the barrier film when H₂O and O₂ permeate through this film. The WVTR values obtained are upper limits as no distinction can be made between the oxidation due to water and due to oxygen. However, from RBS measurements of Ca oxidation by using the ¹⁸O₂ isotope, it was shown that Ca does not react with O₂ at room temperature [46]. The WVTR values obtained in our working conditions are therefore attributed solely to oxidation by H₂O. The detection limit of this test is 3 \cdot 10^{-7} \text{g/m}²/\text{day} [4]. Pinholes present in the barrier layer, which become visible as white spots in the Ca layer, can be excluded from the considered measurement area. This allows the measurement of the intrinsic WVTR (the transmission through the matrix of the layer, excluding the diffusion through pinholes and defects).

For the calcium test a structure of 4 Ca samples of 40 nm, each one divided in 9 pads, was deposited on a glass plate. By using this structure, white spots generated in one pad due to pinholes can not develop across the whole Ca area. The Ca samples were encapsulated with a temporary transparent SiO₂ layer to avoid oxidation of the calcium when the samples were loaded in the barrier layer deposition set-ups through air. The WVTR of this layer is in the order of 10^{-2} \text{g/m}²/\text{day}. Subsequently, barrier layers were deposited on top of these samples. An example of a calcium sample is given in figure 3.12.

![Figure 3.12](image)

**Figure 3.12** Pictures of a Ca sample consisting of 9 pads at different exposure times in a climate chamber. Oxidation of the calcium layer is clearly visible after 7.9 days. On the left of the samples the nontransparent black reference is visible.

Testing conditions for the samples were 20 °C and 50 % relative humidity. The optical transmission of the samples was measured as function of time by using a lamp and a CCD camera. The optical transmission was determined by following the gray tint of the calcium sample. The gray scale was set by a nontransparent black reference and a white reference from the transparent part of the glass plate. An optical model was used to determine the calcium thickness distribution from these transmission measurements. By plotting
3.2 Diagnostic tools

the amount of water required to oxidize the residual calcium layer versus time, one can obtain the WVTR from the slope of this graph [45]. To obtain an accuracy of 10% of the measurement at least 1 nm of calcium must oxidize. The formation of calcium hydroxide is not taken into account because this requires the formation of CaO first and the determination of the WVTR is based on the oxidation of only 1 nm of calcium.

The testing time depends on the quality of the barrier layer, below a short calculation is given to estimate the barrier quality based on the testing time:

Assuming a Ca density of 1.55 g/cm$^3$, a Ca plate of 1x1x10$^{-9}$ m$^3$ contains 1.55 · 10$^{-3}$ g Ca which is equal to 3.87 · 10$^{-5}$ mol Ca. To oxidize this amount of carbon, 3.87 · 10$^{-5}$ mol H$_2$O is required according to equation 3.9, which is equal to 6.96 · 10$^{-4}$ g H$_2$O. The time required for this amount of H$_2$O to diffuse through a barrier layer with an area of 1x1 m$^2$ can be calculated as function of the barrier quality and is given in figure 3.13.

![Figure 3.13 An estimation of the time required for the Ca test as function of the quality of the barrier layer.](image)

3.2.9 Deltaperm Permeation Tester (extrinsic WVTR)

The extrinsic WVTR of the SiO$_2$/Al$_2$O$_3$ nano-laminates deposited on PEN substrates was measured by Fujifilm using a Deltaperm Permeation Tester made by Technolox. Extrinsic means that the permeation through pinholes is taken into account as is not the case for the WVTR measurements by the Ca test. Figure 3.14 shows a schematic of the Deltaperm Permeation
Chapter 3 Experimental

Tester [47, 48]. A sample is fixed in a chamber dividing the chamber in two parts. The upstream and downstream side are both evacuated and water vapor is supplied on the upstream side at a certain relative humidity and temperature. The water vapor diffusing through the sample causes a pressure change on the downstream side. Once steady-state conditions are reached, the WVTR can be calculated from the change in pressure as function of time. The sensitivity of this system is $> 2 \times 10^{-4}$ g/m²/day [47]. The testing conditions were 40 °C and 90 % relative humidity.

![Diagram of Deltaperm setup](image)

**Figure 3.14** The principle of the Deltaperm set-up. Water vapor is supplied on the upstream side and permeates through the sample. From the pressure change on the downstream side the WVTR can be determined. [48]
Chapter 4

Results

In this chapter, the results are reported and discussed as far as the measurements performed on SiO$_2$ and Al$_2$O$_3$ barrier layers are concerned. In section 4.1 the characterization of the PEALD processes of SiO$_2$ and Al$_2$O$_3$ at 25 °C is given. In section 4.2 and 4.3 results are reported for the measurements performed on the SiO$_2$ and Al$_2$O$_3$ barrier layers, respectively. The optical properties, chemical composition, and the density of the layers were evaluated by SE, FTIR, and RBS/ERD measurements. Subsequently the microstructure of the layers was characterized by EP and the intrinsic barrier performance of the layers was determined by the Ca test. Finally, in section 4.4 the extrinsic barrier properties of the SiO$_2$/Al$_2$O$_3$ nano-laminates measured using a Deltaperm Permeation Tester are discussed. Also the results of the SiO$_2$/Al$_2$O$_3$ interface study by XPS are given and related to the barrier properties of the bilayer system. An overview of the barrier layers discussed in this chapter is given in table 4.1. Details on the deposition conditions of these layer are given in section 3.1.

<table>
<thead>
<tr>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Nano-laminates</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ PEALD, 25°C</td>
<td>Al$_2$O$_3$ PEALD, 25°C</td>
<td>SiO$_2$ APG, HDDR/Al$_2$O$_3$ PEALD, 80°C</td>
</tr>
<tr>
<td>SiO$_2$ PEALD, 100°C</td>
<td>Al$_2$O$_3$ PEALD, 100°C, 2s</td>
<td>SiO$_2$ APG, LDDR/Al$_2$O$_3$ PEALD, 80°C</td>
</tr>
<tr>
<td>SiO$_2$ PECVD, 150 W</td>
<td>Al$_2$O$_3$ PEALD, 100°C, 10 s</td>
<td>SiO$_2$ ETP, 1.1 s</td>
</tr>
<tr>
<td>SiO$_2$ PECVD, 250 W</td>
<td>Al$_2$O$_3$ ETP, 1.1 s</td>
<td>Al$_2$O$_3$ ETP, 7.5 s</td>
</tr>
</tbody>
</table>

Table 4.1 Overview of the SiO$_2$ and Al$_2$O$_3$ barrier layers.
4.1 PEALD process characterization

As explained in section 3.1.1, the PEALD processes of SiO$_2$ and Al$_2$O$_3$ were optimized with respect to the exposure times of the precursors. Saturation curves of the SiO$_2$ and Al$_2$O$_3$ processes were obtained at 25 °C and are shown in figure 4.1 and 4.2, respectively. These curves show the growth per cycle (GPC) as function of the time for the four steps in the PEALD process. For too short precursor dosing or plasma exposure times the process is not saturated resulting in a lower GPC. The GPC increases for too short purge steps due to reactions between precursor and plasma species in the gas phase.

The optimum exposure length for every step, as determined from these saturation curves, is given in table 4.2 for the SiO$_2$ and Al$_2$O$_3$ processes. When depositing at higher temperature, more thermal energy is provided to enhance the reactions and it was generally observed that the exposure times determined at low processing temperature are sufficient also in the case of higher processing temperature. Therefore, these times have been used for the depositions at 25 °C as well as at 100 °C.

![Figure 4.1 Saturation curves for the SiO$_2$ PEALD process at 25 °C, showing the GPC as function of step time for the four steps in the PEALD process. The red lines serve as a guide to the eye.](image1)

![Figure 4.2 Saturation curves for the Al$_2$O$_3$ PEALD process at 25 °C, showing the GPC as function of step time for the four steps in the PEALD process. The red lines serve as a guide to the eye.](image2)
4.2 SiO₂ barrier layers

Table 4.2 The optimum cycle time for the SiO₂ and Al₂O₃ PEALD processes at 25 °C.

<table>
<thead>
<tr>
<th>Step</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor dose (s)</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>Purge after precursor dose (s)</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Plasma exposure (s)</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Purge after plasma exposure (s)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Total cycle time (s)</td>
<td>7.55</td>
<td>4.52</td>
</tr>
</tbody>
</table>

4.2.1 Optical properties, density and chemical composition

The refractive index and density of a film can provide information on the porosity of the layer, i.e. the higher the degree of porosity, the lower the refractive index and density. In figure 4.3 the in-situ and ex-situ refractive index values as determined from SE are provided for the PEALD and PECVD SiO₂ layers together with the density of the layers from RBS/ERD measurements. The in-situ values are all below the refractive index value of fused silica (1.465 at 633 nm) which indicates the presence of porosity in the films. The ex-situ measurements show that exposure to ambient atmosphere results in a higher refractive index value with respect to the in-situ value for all layers. This increase in refractive index is due to uptake of water in the open pores (so-called ageing), inducing an increase in refractive index of the pores from 1.00 (under vacuum) to 1.33 (water) [23]. The ageing is most pronounced for the SiO₂ PEALD, 25 °C layer, the less dense film, suggesting that this layer has the highest degree of porosity. The SiO₂ PECVD, 150 W layer has the highest density and refractive index, indicating that this layer has the lowest degree of porosity.

More insight into the porosity can be obtained from the film chemistry. The chemical composition of the SiO₂ layers was determined by FTIR and the absorption spectra are reported in figure 4.4. Typical absorption features for a Si-O-Si unit shown by all spectra are: a rocking mode at 450 cm⁻¹, a bending mode at 810 cm⁻¹, and asymmetric stretching in the range 1050-1070 cm⁻¹. The peak at 3650 cm⁻¹ indicates OH stretching in isolated SiOH groups and the peak at 3450 cm⁻¹ represents OH stretching in hydrogen bonded SiOH. The spectra of the SiO₂ PEALD, 25 °C and the SiO₂ PECVD, 150 W layer show an extra peak at 920 cm⁻¹, representing the bending mode of SiOH. From the spectra it can be concluded that the layers have the same chemical composition. The peaks corresponding to the silanol (SiOH) groups confirm the presence of porosity in the layers as the OH groups terminate the silica chains resulting in pores [49]. Peaks related to carbon are not observed.
Chapter 4 Results

Figure 4.3 The in-situ and ex-situ refractive index values as determined from SE and the volume mass density as determined from the area mass density by RBS/ERD and the thickness from SE for the PEALD and PECVD SiO$_2$ layers. No RBS/ERD data is available for the PECVD$_{SiO_2,150W}$ layer.

and this result was confirmed by RBS analysis as the carbon content is below the detection limit of 1 at.%. The results obtained from RBS/ERD measurements are given in table 4.3. All three layers have good material properties, they are stoichiometric within the error (O/Si ratio = 2.1 ± 0.4) and the hydrogen content varies between 5 and 9 at.%. The density of the layers increases with decreasing hydrogen content confirming that the hydrogen is related to the porosity in the layers.

Table 4.3 Data on the SiO$_2$ layers as determined by RBS/ERD measurements.

<table>
<thead>
<tr>
<th>Layer</th>
<th>[Si] (at.%)</th>
<th>[O] (at.%)</th>
<th>[H] (at.%)</th>
<th>O/Si ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ PEALD, 25°C</td>
<td>29 ± 3</td>
<td>62 ± 7</td>
<td>9 ± 1</td>
<td>2.1 ± 0.4</td>
</tr>
<tr>
<td>SiO$_2$ PEALD, 100°C</td>
<td>30 ± 3</td>
<td>63 ± 7</td>
<td>7 ± 1</td>
<td>2.1 ± 0.4</td>
</tr>
<tr>
<td>SiO$_2$ PECVD, 250W</td>
<td>31 ± 3</td>
<td>65 ± 7</td>
<td>5 ± 1</td>
<td>2.1 ± 0.4</td>
</tr>
</tbody>
</table>

From the asymmetric stretching signal in the FTIR spectra information about the difference in porosity of the layers can be obtained. The peak in the range 1050-1070 cm$^{-1}$ and the high energy shoulder ($\approx 1140$ cm$^{-1}$) refer to adjacent oxygen atoms performing the asymmetric stretching in phase and 180° out of phase, respectively [50]. The asymmetric stretching in phase is called the AS$_1$ mode and the asymmetric stretching out of phase is referred to as the AS$_2$ mode. The AS$_2$ mode is associated with film porosity and a higher peak intensity with respect to the AS$_1$ mode indicates a higher degree of porosity [51]. The ratio of the area of the AS$_1$ and AS$_2$
4.2 SiO₂ barrier layers

![Absorption FTIR spectra for the PEALD and the PECVD SiO₂ layers.](image)

Figure 4.4 Absorption FTIR spectra for the PEALD and the PECVD SiO₂ layers. The spectra are baseline corrected and normalized by the thickness.

The absorption mode is plotted in figure 4.5 as function of the in-situ refractive index for the four SiO₂ layers. The AS₁-to-AS₂ peak ratio increases with increasing refractive index indicating a decrease in porosity.

The differences in chemical composition, optical properties and density of the layers can be explained by the different deposition conditions used. For the two PECVD layers the plasma power was varied and the two PEALD layers were deposited at a different substrate temperature.

- Effect of the plasma power.

Increasing the plasma power from 150 W to 250 W in the PECVD process is expected to result in a larger ion flux and a higher energy of the ions impinging on the surface. The enhanced ion bombardment of the surface gives rise to increased surface diffusion, breakage of chemical bonds and heating. These effects promote the condensation of vicinal silanol groups to form Si-O-Si bonds with loss of water [8] which explains the decrease in hydrogen content with increasing power. The formation of more Si-O-Si bonds results in better cross-linking of the SiO₂ network [9]. Less hydrogen and better crosslinking lead to a densification of the SiO₂ layer which is confirmed by the mass density values in figure 4.3.
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Figure 4.5 The AS$_1$-to-AS$_2$ peak ratio as function of the in-situ refractive index value for the four SiO$_2$ layers.

- Effect of the substrate temperature.
  
  Increasing the substrate temperature from 25 °C to 100 °C in the PEALD process has the same qualitative effect on the hydrogen content and density as the increase in power in the PECVD process. These effects can also be attributed to the condensation of silanol groups and improved cross-linking as the extra thermal energy enhances the surface diffusion of the precursor molecules and promotes the formation of Si-O-Si bonds [9, 52].

The SiO$_2$ PECVD, 250 W and SiO$_2$ PEALD, 100 °C layer were both deposited at 100 °C but the SiO$_2$ PECVD, 250 W film shows a higher density and lower hydrogen content according to RBS/ERD. First of all, different precursors were used in the PEALD and PECVD process which can give rise to differences in the chemical structure and density. The better film properties of the PECVD layer can also be a result of less steric hindrance at the surface during film growth. In the PEALD process the precursor molecules reach the surface without undergoing any prior fragmentation, whereas in the PECVD process fragments of precursor molecules arrive at the surface since the precursor is dissociated in the plasma medium. Therefore, steric hindrance will play a larger role in the PEALD process and can result in a higher porosity and thus a lower density of the film. Another factor that can cause a difference in layer properties is the ion bombardment. To compare the effect of the ion bombardment in the two processes, the ion energy per depositing particle, $E_p$, is calculated for the PEALD and the PECVD
4.2 SiO$_2$ barrier layers

process. Details on the calculations can be found in appendix B. For the PEALD processes the $E_p$ values were calculated from the ion energies and fluxes measured in the reactor and turn out to be 2.1 eV and 1.6 eV during deposition of the SiO$_2$ PEALD$_{100^\circ C}$ layer and the SiO$_2$ PEALD$_{25^\circ C}$ layer, respectively. For SiO$_2$ films it was shown that the porosity is affected by ion bombardment for $E_p$ values between 30 – 100 eV [53]. As the $E_p$ values in the PEALD processes are 1 order lower, it is reasonable to assume that the effect of the ion bombardment on the densification of the films is negligible. A rough estimation was made for the ion energy per depositing particle in the PECVD process. $E_p$ was estimated to be in the same order as in the PEALD process. This low value seems to be in contradiction with the improved film properties observed for a higher plasma power which was attributed to enhanced ion bombardment. Therefore, it is hypothesized that the ion energy in the PECVD process is higher than the estimated value. For example, the electron density can be up to one order higher than the value used for the estimation and the average speed of the ions used, as determined from the Bohm criterion, is a minimum velocity the ions should have for the formation of a plasma sheath. Based on these considerations, it is plausible to assume that the ion bombardment can not be neglected in the PECVD process and contributes to the better film properties of the SiO$_2$ PECVD$_{250\,\text{W}}$ film when compared to the SiO$_2$ PEALD$_{100^\circ C}$ layer.

To summarize, the SE, FTIR and RBS/ERD measurements are in good agreement for the SiO$_2$ layers. The refractive index values being lower than that of fused silica and the ageing of the samples indicate the presence of porosity in all layers. This is confirmed by the FTIR and ERD measurements showing the presence of hydrogen in the layers, mainly in the form of silanol groups, which is associated with porosity. Increasing the substrate temperature in the PEALD process or the plasma power in the PECVD process results in denser layers.

4.2.2 Porosity and intrinsic WVTR

As explained in the Introduction, the control of the nanoscale porosity in barrier layers is expected to play a major role on the improvement of the moisture permeation barrier performance. In order to achieve a better control on the residual porosity, the characterization of the film microstructure is essential. Porosity measurements by means of ellipsometric porosimetry (EP) were carried out on the SiO$_2$ layers which provide details on the microstructure of the layers in terms of pore size and relative content and allow for a good comparison of the nanoporosity of these layers.

The four isotherms as obtained from the EP measurements are characterized by a combination of a type I (microporous film) and a type II (non-porous film) isotherm, which is interpreted as follows: micropore filling occurs and
Chapter 4 Results

once the pores are filled, multilayer adsorption takes place. Based on the literature [28] and on the shape of the isotherms, it is assumed that the filling of micropores was completed at $P_M/P_{sat} = 0.2$ (the inflection point) after which multilayer adsorption started. The increase in the mean square error of the fit, when fitting the refractive index of the SiO$_2$ layer instead of the multilayer thickness for $P_M/P_{sat} > 0.2$, confirms this assumption. To represent both the processes of micropore filling and multilayer adsorption, the isotherms are reported in terms of optical thickness (defined as the refractive index multiplied by the layer thickness) as function of relative pressure (see section 3.2.3 for more details). The isotherms are given in figure 4.6.

![Figure 4.6](image.png)

**Figure 4.6** The adsorption/desorption isotherms for the SiO$_2$ layers as obtained from ellipsometric porosimetry measurements using V$_3$D$_3$ as adsorptive.

All isotherms show an increase at very low relative pressure ($P_M/P_{sat} \leq 0.03$) indicating primary micropore filling (section 2.1.1). The process of secondary micropore filling gives rise to the rounded knee for $0.03 < P_M/P_{sat} < 0.2$. For higher relative pressure no plateau is reached, as for a true type I isotherm, but the isotherms show an increase in terms of optical thickness indicating monomer multilayer adsorption on top of the SiO$_2$ layers.
This multilayer adsorption implies that the layers have a low micropore density and therefore an appreciable external surface \(^1\) on which multilayer adsorption can take place [29].

The isotherms of the SiO\(_2\) PEALD, 25 °C and SiO\(_2\) PECVD, 150 W layers show hysteresis over the complete relative pressure range. The isotherm of the SiO\(_2\) PEALD, 100 °C layer shows limited hysteresis while no hysteresis is observed for the SiO\(_2\) PECVD, 250 W film. A plausible explanation for the hysteresis is chemisorption [28] as H-bonding can occur between the silanol groups in the SiO\(_2\) layers and the oxygen of the siloxane ring of the monomer molecules [35]. Since the SiO\(_2\) PEALD, 25 °C and SiO\(_2\) PECVD, 150 W layers are characterized by the largest concentration of silanol groups, their isothermal curves exhibit also the largest hysteresis.

After desorption at \(P_M/P_{\text{sat}} = 0\), the PEALD layers show an increase in optical thickness, whereas the optical thickness of the PECVD layers is reversible upon evacuation. XPS measurements demonstrated the presence of the siloxane monomer in the PEALD layers after the porosity measurements. The SiO\(_2\) PECVD layers showed no signature of the monomer after porosity measurements. It is hypothesized that some monomer molecules were trapped in pores in the SiO\(_2\) PEALD layers during desorption causing an increase in (optical) thickness. The results of the XPS measurements can be found in appendix C.

In figure 4.7 the adsorption isotherms from figure 4.6 have been separated into two regions for a more detailed characterization and comparison of the layers. The process of micropore filling is given in figure 4.7 (a) by means of the change in refractive index of the layers as function of the relative pressure. The refractive index values have been scaled to the \(n_0\) values (the starting value at \(P_M/P_{\text{sat}} = 0\)) according to:

\[
n(\text{normalized}) = \frac{n_x^2 - 1}{n_x^2 + 2} - \frac{n_0^2 - 1}{n_0^2 + 2},
\]

with \(n_x\) being the refractive index at a relative pressure \(x\) [53]. In figure 4.7 (b) the process of monomer multilayer adsorption is shown by means of the multilayer thickness adsorbed on the SiO\(_2\) films as function of the relative pressure.

In figure 4.7 (a) clear differences in adsorption are observed for the four SiO\(_2\) layers indicating various degrees of porosity. The open porosity of the SiO\(_2\) films was determined at \(P_M/P_{\text{sat}} = 0.2\) (i.e. when the micropore filling is complete). This porosity was calculated using formula 2.7, with \(n_{\text{fill}}\) the refractive index of the layers at \(P_M/P_{\text{sat}} = 0.2\). The porosity was also

\(^1\)The external surface is defined as the area of surface outside pores and the walls of pores which are wider than they are deep. The internal surface comprises the walls of pores which are deeper than they are wide [28].
Figure 4.7 The adsorption isotherms of the SiO$_2$ layers. (a) Micropore filling in the range $0 < P_M/P_{sat} \leq 0.2$ represented by means of the change in refractive index of the layers as function of the relative pressure. The refractive index values have been scaled to the $n_0$ values (the starting value at $P_M/P_{sat} = 0$). (b) Multilayer adsorption for $0.2 < P_M/P_{sat} < 1$ shown by means of the multilayer thickness adsorbed on the SiO$_2$ films as function of the relative pressure.

calculated from the adsorption of H$_2$O during exposure to the ambient using the same formula with $n_0$ the in-situ refractive index value and $n_{fill}$ the ex-situ refractive index value of the layers. These porosity values are given in table 4.4 and confirm that the SiO$_2$ PEALD, 25$^\circ$C layer has the highest degree of porosity and the SiO$_2$ PECVD, 250 W layer the lowest degree of porosity.

The size of the micropores that are filled during the EP measurements can be determined from the size of the V$_3$D$_3$ molecule which was estimated to have a diameter of $\sim 0.5 \text{ nm}$ $^2$ [35, 54]. Since primary micropore filling occurs in pores twice the diameter of the probing molecule and micropores are classified as pores with width less than 2 nm, it is concluded that pores with a diameter between 1 and 2 nm are filled by the monomer. As shown in table 4.4 the open porosity as determined from the adsorption of V$_3$D$_3$ results lower than the porosity calculated from the H$_2$O adsorption. Since the diameter of a water molecule ($\sim 0.27 \text{ nm}$) is smaller than the diameter of a V$_3$D$_3$ molecule ($\sim 0.5 \text{ nm}$), it is reasonable to assume that a large amount of pores is present with a diameter below 1 nm, inaccessible to V$_3$D$_3$, but large enough to be filled by H$_2$O molecules, explaining the difference in porosity.

Analysis of the variation in primary and secondary micropore filling in the
4.2 SiO₂ barrier layers

Table 4.4 The open porosity as determined from the adsorption of V₃D₃ during the porosity measurements and from the adsorption of H₂O during exposure to the ambient, and intrinsic WVTR values of the SiO₂ layers from the Ca test at 20 °C / 50% RH.

<table>
<thead>
<tr>
<th>SiO₂ layer</th>
<th>Open porosity (%) (V₃D₃)</th>
<th>Open porosity (%) (H₂O)</th>
<th>WVTR (g/m²/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ PEALD, 25°C</td>
<td>1.1 ± 0.1</td>
<td>8.4 ± 0.1</td>
<td>&gt; 10⁻²</td>
</tr>
<tr>
<td>SiO₂ PEALD, 100°C</td>
<td>0.7 ± 0.1</td>
<td>6.4 ± 0.1</td>
<td>(9 ± 1) · 10⁻³</td>
</tr>
<tr>
<td>SiO₂ PECVD, 150 W</td>
<td>0.7 ± 0.1</td>
<td>7.4 ± 0.1</td>
<td>(3 ± 1) · 10⁻³</td>
</tr>
<tr>
<td>SiO₂ PECVD, 250 W</td>
<td>0.5 ± 0.1</td>
<td>4.3 ± 0.1</td>
<td>(2 ± 1) · 10⁻⁵</td>
</tr>
</tbody>
</table>

SiO₂ layers allows to obtain more insight in the differences in the structure of the layers. The primary micropore filling occurs in the smallest micropores accessible to V₃D₃ molecules (≈ 1 nm) and during secondary micropore filling larger micropores are filled (1 - 2 nm). In figure 4.7 (a) it is seen that the adsorption at Pₘ/Pₕₐₜ = 0.03 (primary micropore filling) is comparable for the PECVD layers, whereas the adsorption in the PEALD layers is much higher. This higher adsorption indicates a higher relative content of small micropores in the PEALD layers. This higher relative micropore content can be a result of the different precursor used but can also be due to steric hindrance which plays a larger role in the PEALD process, as explained in the previous section. From the isotherms in figure 4.7 (a) it can also be argued that the reduction in SiOH groups in the PEALD layers following upon the increase in substrate temperature results in a decrease in small as well as large micropores. The increase in plasma power in the PECVD process only affects the larger micropores as the PECVD layers have a comparable density of small micropores.

After the completion of the secondary micropore filling the process continued by means of monomer multilayer adsorption starting at Pₘ/Pₕₐₜ = 0.2. The thickness of the multilayer adsorbed on the SiO₂ layers as function of the relative pressure is given in figure 4.7 (b). At saturation pressure the thickness of the multilayer adsorbed on the SiO₂ PEALD, 25°C, SiO₂ PEALD, 100°C, and SiO₂ PECVD, 250 W layers, was 0.96 nm, 0.82 nm, and 0.65 nm, respectively. Since hydrogen bonding between the silanol groups and the siloxane monomer can promote the monomer adsorption and because the variation in thickness correlates with the variation in hydrogen content in the layers (table 4.3), it is hypothesized that the difference in multilayer thickness is caused by the difference in hydrogen content. The SiO₂ PECVD, 150 W layer shows the largest multilayer thickness of 1.34 nm. The amount of hydrogen in the SiO₂ PECVD, 150 W layer is approximately equal to the hydrogen content in the SiO₂ PEALD, 25°C layer (figure 4.4) but it has a lower relative
Chapter 4 Results

micropore content and therefore the SiO$_2$ \textsubscript{PECVD,150W} layer has a larger external surface which can explain the higher multilayer adsorption.

The porosity measurements revealed the microstructure of the SiO$_2$ layers and it is learned how the microporosity is affected by the deposition technique and deposition conditions like temperature and plasma power. The intrinsic WVTR of these films was measured by the Ca test to see how the barrier properties relate to the porosity of the films. The WVTR values of the layers are given in table 4.4 and correlate with the open porosity of the layers. The SiO$_2$ \textsubscript{PEALD,25°C} has the highest porosity and also the highest WVTR\textsuperscript{3} and the most dense film, the SiO$_2$ \textsubscript{PECVD,250W} layer, turns out to be the best barrier. The barrier properties thus improve for decreasing relative pore content from which it can be concluded that the intrinsic barrier properties are controlled by the open microporosity in the barrier layers.

The importance of the EP measurements for understanding the difference in barrier performance is emphasized by the results of the SiO$_2$ \textsubscript{PEALD,25°C} and SiO$_2$ \textsubscript{PECVD,150W} layers. These layers have a comparable refractive index (figure 4.3) and a similar concentration of silanol groups (figure 4.4) suggesting similar barrier performances. However, the open porosity is significantly different as shown by the EP measurements, which explains the difference in barrier performance.

Besides the amount of open pores, the pore size distribution and interconnectivity of pores in a barrier layer will influence the barrier performance as well. The SiO$_2$ \textsubscript{PECVD,150W} and SiO$_2$ \textsubscript{PEALD,100°C} layers have the same porosity but a different pore size distribution as can be seen in figure 4.7 (a). The SiO$_2$ \textsubscript{PEALD,100°C} layer has a higher relative content of small micropores. It is therefore also presumable to assume a higher content of smaller pores, not detected by V$_3$D$_3$, but still accessible to H$_2$O which can explain the higher WVTR value of the SiO$_2$ \textsubscript{PEALD,100°C} with respect to the SiO$_2$ \textsubscript{PECVD,150W} film. From literature it is also known that the permeation mechanism of H$_2$O molecules through pores in a SiO$_2$ barrier layer is influenced by the interaction between the H$_2$O molecules and SiO$_2$ [12, 55]. H$_2$O molecules can bind via H-bonding to OH groups on the internal surface of the pores resulting in a delay of the permeation. As the SiO$_2$ \textsubscript{PECVD,150W} layer contains more SiOH groups compared to the SiO$_2$ \textsubscript{PEALD,100°C} layer (figure 4.4), the permeation delay is likely to be more pronounced in the SiO$_2$ \textsubscript{PECVD,150W} layer which can tentatively explain its somewhat lower WVTR. From the high WVTR value of the SiO$_2$ \textsubscript{PEALD,25°C} layer it is likely to assume that the porosity in this layer is too high and the delay by OH groups is not

\textsuperscript{3}The calcium underneath the SiO$_2$ \textsubscript{PEALD,25°C} layer was almost fully oxidized already after 1 day of ageing at 20 °C / 50% RH and this testing period was too short to obtain the WVTR of this layer. Therefore, only a lower limit could be determined. It should be noted that the film had a rather large defect density compared to the other layers which probably also affected the barrier properties.
4.3 Al₂O₃ barrier layers

sufficient to obtain a low WVTR.

To summarize, from the porosity measurements it was learned that all SiO₂ layers are microporous with pores smaller than 2 nm. The films have a considerable external surface as pointed out by the monomer multilayer adsorption for higher relative pressure. The porosity values estimated by the isothermal studies correlate with the intrinsic barrier properties.

4.3 Al₂O₃ barrier layers

In this section the results are reported of the measurements performed on the PEALD and ETP-CVD Al₂O₃ barrier layers. The deposition conditions of these layers are given in section 3.1 and are summarized in table 3.2.

4.3.1 Optical properties, density and chemical composition

The in-situ and ex-situ refractive index values of the PEALD and ETP-PECVD Al₂O₃ layers as determined from SE are given in figure 4.8 together with the density of the layers from RBS/ERD measurements. The different in-situ refractive index values, all being lower than the refractive index of a bulk amorphous Al₂O₃ layer (1.65), indicate various degrees of porosity in the layers. The ex-situ refractive index value of the Al₂O₃ ETP,1.1 s layer is higher with respect to the in-situ value indicating the uptake of water in open pores (ageing). However, the PEALD layers and the Al₂O₃ ETP,7.5 s film do not age upon exposure to the ambient atmosphere, i.e. the refractive index does not increase from in-situ to ex-situ. This stable refractive index suggests that pores are either not connected with the surface (i.e. closed porosity) or too small to be infiltrated by H₂O molecules. In the last case this means that the open pores have a diameter smaller than twice the diameter of a H₂O molecule (∼ 0.54 nm).

The chemical composition of the films was determined by FTIR as the film chemistry can give more insight in the porosity present in the films. In figure 4.9 the FTIR absorption spectra for the Al₂O₃ films are given. The spectra show an O-Al-O bending mode around 650-700 cm⁻¹ and a Al-O stretching mode in the range 750-850 cm⁻¹. The peaks in the region 1200-1800 cm⁻¹ are attributed to C=O vibrations. It is not straightforward to assign the closely spaced peaks individually but in literature the features around 1600, 1550, and 1480 cm⁻¹ are assigned to C=O, COO-, and the asymmetric deformation of CH₃, respectively [56, 57]. The peak at 3650 cm⁻¹ indicates OH stretching in isolated AlOH groups and the tail towards lower wavenumbers is due to OH stretching in hydrogen bonded AlOH. The peak near 2945 cm⁻¹ in the spectrum of the Al₂O₃ ETP,1.1 s layer shows the C-H stretching mode of CHₓ groups originating from the TMA precursor.
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**Figure 4.8** The in-situ and ex-situ refractive index values as determined from SE and the volume mass density as determined from the area mass density by RBS/ERD and the thickness from SE for the PEALD and ETP-PECVD Al\(_2\)O\(_3\) layers.

**Figure 4.9** Absorption FTIR spectra for the PEALD and ETP-PECVD Al\(_2\)O\(_3\) layers. The spectra were baseline corrected and normalized by the thickness.
The area of the O-Al-O and Al-O peaks is related to the density of the layers, the denser the layer, the higher this peak area. The absorption band associated with Al-O (750-850 cm$^{-1}$) was attributed to the presence of large Al-O-Al rings which were associated with porosity, similar to the SiO$_2$ layers [58]. When the density increases this peak decreases and the O-Al-O band (650-700 cm$^{-1}$) increases. This was related to the predominance of shorter O-Al-O chains and a denser network. The C=O vibrations point out to non-quantitative combustion of carbon-containing ligands from the TMA precursor during the plasma exposure step as the C=O and COO- bonds are intermediate reaction states in the oxidation reactions during the plasma exposure [59]. The peaks related to Al-OH and Al–CH$_3$ groups indicate the presence of porosity as the OH- and CH$_3$-containing groups terminate the alumina chains resulting in pores [58]. RBS/ERD measurements also confirm the presence of hydrogen and carbon in these layers. The RBS/ERD results are given in table 4.5. The density and refractive index of the Al$_2$O$_3$ layers decreases with increasing amount of hydrogen, present as OH groups, confirming that hydrogen is related to porosity just as for the SiO$_2$ films.

The layers are over-stoichiometric which can be attributed to the high amounts of hydrogen. Whereas the stoichiometry of the SiO$_2$ PEALD layers was not affected by the deposition temperature, the Al$_2$O$_3$ PEALD layers deposited at 25 °C and 100 °C show some difference in stoichiometry which can be explained by the higher hydrogen content in the Al$_2$O$_3$ layers with respect to the SiO$_2$ layers.

**Table 4.5** Data on the Al$_2$O$_3$ layers as determined by RBS/ERD measurements.

<table>
<thead>
<tr>
<th>Layer</th>
<th>[Al] (at.%)</th>
<th>[O] (at.%)</th>
<th>[C] (at.%)</th>
<th>[H] (at.%)</th>
<th>AlC$_x$O$_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$ PEALD, 25°C</td>
<td>27 ± 4</td>
<td>53 ± 7</td>
<td>3 ± 1</td>
<td>17 ± 3</td>
<td>AlC$<em>{0.1}$O$</em>{2.0}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$ PEALD, 100°C, 2 s</td>
<td>34 ± 4</td>
<td>57 ± 7</td>
<td>3 ± 1</td>
<td>7 ± 1</td>
<td>AlC$<em>{0.1}$O$</em>{1.7}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$ PEALD, 100°C, 10 s</td>
<td>36 ± 4</td>
<td>59 ± 7</td>
<td>&lt; 1</td>
<td>5 ± 1</td>
<td>AlO$_{1.6}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$ ETP, 1.1 s</td>
<td>31 ± 4</td>
<td>50 ± 6</td>
<td>9 ± 2</td>
<td>10 ± 2</td>
<td>AlC$<em>{0.3}$O$</em>{1.6}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$ ETP, 7.5 s</td>
<td>37 ± 4</td>
<td>59 ± 6</td>
<td>&lt; 1</td>
<td>5± 1</td>
<td>AlO$_{1.6}$</td>
</tr>
</tbody>
</table>

Increasing the substrate temperature from 25 °C to 100 °C in the PEALD process results in a decrease in carbon and hydrogen content as seen by the FTIR spectra and RBS/ERD data. The decrease in carbon content is a result of more complete oxidation reactions as more thermal energy is provided. The hydrogen decrease can be attributed to improved condensation of OH groups and the formation of Al-O-Al bridges due to enhanced surface diffusion as was also seen for the SiO$_2$ layers. The formation of Al-O-Al bridges results in better cross-linking [57, 58]. The reduction in hydrogen and carbon content and the better cross-linking result in a higher density as confirmed by the mass density values in figure 4.8.

For the ETP layers a reduction of the carbon and hydrogen content and a
large increase in density is observed when the TMA off time, the time between the short precursor pulses, is increased from 1.1 to 7.5 seconds. The film growth mechanism is a two-stage process; first a porous Al$_2$O$_3$ film is deposited and subsequently densification of the film occurs [36, 60]. The densification takes place mainly via diffusion of oxygen-containing radicals into the film leading to combustion of hydroxyl and hydrocarbon groups. The low quality of the Al$_2$O$_3$ ETP,1.1s layer is explained by the higher frequency of the precursor pulsing (resulting in a higher deposition rate) and the insufficient flux of plasma species required for the densification of the film during the plasma exposure time of 1.1 s. Moreover, the residence time of TMA related fragments is in the range of 1.5-2 s [36]. The TMA off time of 1.1 s is therefore too short resulting in an accumulation of precursor and ongoing film deposition. With a plasma exposure time of 7.5 s, the precursor is fully depleted after 2 s and sufficient time is available for the combustion of most of the hydroxyl and hydrocarbon groups resulting in a denser film.

The same effect of the longer plasma treatment time on the film properties was observed for the PEALD layers. Figure 4.10 shows the FTIR spectra of PEALD layers deposited at 25 °C and 100 °C with various plasma exposure times. The peak related to C=O vibrations clearly decreases for increasing plasma time and also the amount of hydrogen is slightly reduced due to more complete oxidation of the hydrocarbon ligands. Increasing the plasma exposure time from 2 to 10 seconds for the Al$_2$O$_3$ PEALD,100°C layer also resulted in a slightly higher refractive index and a somewhat better stoichiometry, comparable to the Al$_2$O$_3$ ETP,7.5s layer as seen in figure 4.8 and table 4.5.

**Figure 4.10** Absorption FTIR spectra of PEALD Al$_2$O$_3$ layers deposited with various plasma exposure times at (a) 25 °C and (b) 100 °C.

To summarize, the results from SE, FTIR, RBS and ERD measurements correspond well for both the PEALD and the ETP Al$_2$O$_3$ layers. The re-
4.3 Al₂O₃ barrier layers

The refractive index values being lower than the bulk value of Al₂O₃ together with the hydrogen content in the layers point out the presence of porosity. However, the PEALD layers and the Al₂O₃ ETP, 7.5 s layer showed no ageing upon exposure to the atmosphere which suggests that there are either no open pores or open pores inaccessible to H₂O molecules. Nevertheless, the presence of pores accessible to H₂O molecules in the carbon containing Al₂O₃ PEALD, 25 °C and Al₂O₃ PEALD, 100 °C, 2 s layers can not be excluded as hydrophobic groups like CH₃ can repel H₂O molecules. Increasing the substrate temperature or the plasma exposure time results in denser layers with less hydrogen and carbon content.

4.3.2 Porosity and intrinsic WVTR

Porosity measurements by means of ellipsometric porosimetry (EP) were carried out on the Al₂O₃ layers to characterize the microstructure of the layers. In line with the results of the SiO₂ films, the porosity measurements carried out on the Al₂O₃ ETP, 1.1 s layer confirmed the presence of open micropores as was already suggested by the ageing of the sample in the ambient. The Al₂O₃ PEALD layers and the Al₂O₃ ETP, 7.5 s layer, however, showed no ageing upon exposure to the ambient, which suggests the absence of open pores accessible to H₂O molecules. Porosity measurements by EP using V₃D₃ as adsorptive showed that the V₃D₃ molecules were not able to probe pores in the non-ageing layers as multilayer adsorption started immediately at low relative pressure whereas the refractive index of these layers was constant. These measurements confirm the absence of open pores with a diameter between 1 nm and 2 nm which are accessible to V₃D₃ molecules. Hereafter, the isotherms of the Al₂O₃ layers are presented and discussed in more detail.

First, the results of the EP measurements on the Al₂O₃ ETP, 1.1 s layer are presented. As explained in section 3.2.1, for this layer, a Cauchy model and a B-spline model was used to model the SE data since the Cauchy model was only applicable in a restricted wavelength range due to adsorption. Both models resulted in similar isotherms which justifies the use of the Cauchy model in the restricted wavelength range without any loss of information affecting the isotherm shape. Therefore, only the isotherm obtained by using the Cauchy model is given here.

The EP measurements showed that monomer adsorbed inside pores. Besides, monomer adsorption gave rise to surface modification in terms of roughness decrease ⁴. The filling of the pores is represented by the change in refractive index of the layer as function of the relative pressure and is shown in figure 4.11 (a). This isotherm is a true type I isotherm indicat-

⁴AFM measurements showed that the Al₂O₃ ETP, 1.1 s has a high roughness compared to the other Al₂O₃ layers which are assumed to have a flat surface (section 3.2.6).
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ing that micropores are filled. To model the roughness decrease a third component (monomer) was added to the mixed layer of the bulk film and voids representing the roughness (section 3.9). The adsorption of monomer in the valleys of the roughness, which leads to roughness decrease, is represented in figure 4.11 (b) in terms of the percentage of voids filled by the monomer as function of the relative pressure. The isotherm is in between a type II (non-porous layer) and a type III (non-porous layer and a weak adsorbent-adsorbate interaction) isotherm indicating that monomer multilayer adsorption occurs in the valleys of the roughness and that there is a weak interaction between Al₂O₃ and V₃D₃. More details about this behavior will be given later on when the isotherms of the Al₂O₃ PEALD, 100 °C, 10 s and Al₂O₃ ETP, 7.5 s layer are discussed.

Figure 4.11 The adsorption/desorption isotherms for the Al₂O₃ ETP, 1.1 s layer as obtained from ellipsometric porosimetry measurements using V₃D₃ as adsorptive. (a) The change in refractive index due to filling of micropores and (b) the percentage of voids filled with monomer representing the roughness decrease.

The isotherm in figure 4.11 (a) shows an increase at very low relative pressure \( P_M/P_{\text{sat}} < 0.03 \) indicating the process of primary micropore filling. Secondary micropore filling gives rise to the rounded knee for \( 0.03 < P_M/P_{\text{sat}} < 0.4 \) as was also seen for the SiO₂ layers. During desorption the refractive index stays constant and drops at \( P_M/P_{\text{sat}} = 0 \) when also most of the monomer has desorbed again from the valleys of the roughness. The constant refractive index during desorption suggests that the emptying of the pores is hindered by the monomer adsorbed in the valleys of the roughness. In figure 4.11 (b) it is seen that monomer starts to adsorb in the valleys of the roughness already at low relative pressure indicating that the process of pore filling and the roughness decrease occurred simultaneously. At \( P_M/P_{\text{sat}} = 1 \), 70% of the voids is filled pointing out a considerable decrease in roughness.
4.3 Al₂O₃ barrier layers

In figure 4.12 a comparison is made with the micropore filling in the SiO₂ layers. The refractive index values have been scaled to the \( n_0 \) values (the starting value at \( P_M/P_{sat} = 0 \)) according to equation 4.1. As explained in section 4.2.2, micropores with a diameter between 1 nm and 2 nm are probed by the \( V_3D_3 \) molecules and the micropores in the SiO₂ layers are filled at \( P_M/P_{sat} = 0.2 \). The filling of pores in the Al₂O₃ ETP,1.1s layer continues until \( P_M/P_{sat} = 0.6 \). This comparison indicates that the Al₂O₃ ETP,1.1s layer has a broader pore size distribution and some small mesopores (> 2 nm) can be present. The relative pore content in the Al₂O₃ ETP,1.1s film is comparable to the relative pore content in the SiO₂ PEALD,100°C and SiO₂ PECVD,150W layer.

![Figure 4.12](image)

**Figure 4.12** A comparison of the micropore filling in the Al₂O₃ ETP,1.1s layer and the SiO₂ layers represented by means of the change in refractive index of the layers as function of the relative pressure. The refractive index values have been scaled to the \( n_0 \) values (the starting value at \( P_M/P_{sat} = 0 \)). The micropores in the SiO₂ layers are filled at \( P_M/P_{sat} = 0.2 \) whereas the filling of pores in the Al₂O₃ ETP,1.1s layer continues until \( P_M/P_{sat} = 0.6 \).

EP measurements on the other Al₂O₃ layers indicated that no open pores accessible to \( V_3D_3 \) molecules were present, in contrast with the Al₂O₃ ETP,1.1s film. The isotherms for the Al₂O₃ PEALD,100°C,10s and Al₂O₃ ETP,7.5s layer are given in figure 4.13. The isotherms are given in terms of \( V_3D_3 \) multilayer thickness as function of the relative pressure. When comparing these isotherms to the isotherm types given in section 2.1.2, they seem to be in between a type II (non-porous layer) and a type III (non-porous layer and a weak adsorbent-adsorbate interaction) isotherm pointing out multilayer adsorption. The shape is similar to the isotherm in figure 4.11 (b) showing the adsorption in the valleys of the roughness of the Al₂O₃ ETP,1.1s layer. The
shape of the isotherms at low relative pressure is not convex as for a type II isotherm but almost linear and the inflection point, often interpreted as the completion of a monolayer and the start of multilayer uptake, is not well defined. This ill-defined inflection point suggests that multilayer formation started before the monolayer coverage of the surface was completed. These characteristics indicate a weak interaction between Al$_2$O$_3$ and V$_3$D$_3$. Due to this weak interaction the adsorption at low relative pressure is limited but once some molecules have adsorbed, the adsorption of further molecules is promoted by the adsorbate-adsorbate forces [28]. The layers are comparable in terms of density and chemical composition and both show an uptake of 1.2 nm, comparable to the multilayer uptake of the SiO$_2$ layers.

During desorption hysteresis is observed. For the SiO$_2$ layers the hysteresis was attributed to H-bonding between OH-groups on the surface and the oxygen of the siloxane ring of the monomer molecules. It is hypothesized that also for the Al$_2$O$_3$ films H-bonding is the reason for the hysteresis.

The isotherms for the Al$_2$O$_3$ PEALD, 25°C and Al$_2$O$_3$ PEALD, 100°C, 2s layers are given in figure 4.14. The black curves represent the isotherms obtained on 100 nm thick films just like the other Al$_2$O$_3$ films. Again the isotherms are in between a type II and a type III isotherm. These layers show a V$_3$D$_3$ multilayer thickness of 9 nm at saturation pressure which is much larger than...
the multilayer thickness on the other layers in figure 4.13 and quite remarkable. Moreover, for these layers also a rather large hysteresis is seen and the desorption data suggests that at the end of the desorption 1 to 5 nm of adsorbed V$_3$D$_3$ is present in the Al$_2$O$_3$ PEALD, 25 $^\circ$C and Al$_2$O$_3$ PEALD, 100 $^\circ$C, 2s layers. Ex-situ SE measurements were performed after the porosity measurements. Assuming that the monomer is at the surface of the films, this results in a monomer thickness of 2.9 nm and 6.8 nm on the Al$_2$O$_3$ PEALD, 25 $^\circ$C and Al$_2$O$_3$ PEALD, 100 $^\circ$C, 2s, respectively.

The same porosity measurements were carried out on two layers of 30 nm, deposited at 25 $^\circ$C and 100 $^\circ$C, using the same deposition conditions as for the 100 nm thick layers. The isotherms are given by the red curves in figure 4.14. The adsorption on these layers, which are three times thinner, is about 3 nm. These results suggest that the adsorption on the surface depends on the thickness of the layers which is very unlikely. An effect that is thickness dependent is swelling of the Al$_2$O$_3$ films, however, the layers can only swell upon absorption of the siloxane monomer inside the layer.

To learn more about the interaction between the Al$_2$O$_3$ films and V$_3$D$_3$, XPS measurements were performed on the Al$_2$O$_3$ layers after the porosity measurements. For comparison, also a Al$_2$O$_3$ PEALD, 100 $^\circ$C, 2s layer on which no porosity measurements were done, was analyzed by XPS. The results can be found in appendix C. The XPS measurements show that monomer is present in the Al$_2$O$_3$ layers but only near the surface. Together with the constant refractive index of the layers and the absence of open pores this suggests that the monomer has adsorbed on top of the Al$_2$O$_3$ layers forming
Chapter 4 Results

a multilayer. However, for the Al₂O₃ PEALD, 25°C and Al₂O₃ PEALD, 100°C, 2 s layers the decrease in monomer multilayer thickness for a thinner Al₂O₃ film suggests that the adsorption on the surface depends on the thickness of the layers which can not be explained assuming the process of multilayer adsorption. Moreover, the multilayer thickness of 9 nm suggests a strong interaction between the V₃D₃ molecules which is not expected for a precursor. Another possibility could be swelling of the Al₂O₃ PEALD, 25°C and Al₂O₃ PEALD, 100°C, 2 s layers. From the XPS measurements it is assumed that V₃D₃ has chemisorbed on the surface of the Al₂O₃ layers rather than physisorbed since the monomer did not desorb from the samples in the ultra high vacuum chamber during the measurements. As a result of this chemical reaction V₃D₃ fragments can diffuse in the Al₂O₃ layers resulting in swelling and the amount of swelling is likely to depend on the thickness of the Al₂O₃ layer. However, swelling would induce a change in refractive index which is not observed. Moreover, most of the monomer desorbs again as shown by the desorption isotherms which is very unlikely if a chemical reaction took place between the monomer and Al₂O₃. Based on these arguments it must be concluded that the behavior of the isotherms for the Al₂O₃ PEALD, 25°C and Al₂O₃ PEALD, 100°C, 2 s layers can not be explained at the moment.

The suggested chemisorption of V₃D₃ at the Al₂O₃ surface is an unwanted interaction. As explained in section 2.1.1, porosimetry measurements should only involve physisorption of the adsorptive to make sure that the microstructure of the adsorbent is preserved and the adsorption is a reversible process. The chemisorption together with the weak interaction between V₃D₃ and Al₂O₃ at low relative pressure lead to conclude that V₃D₃ is not an ideal adsorptive for EP measurements on Al₂O₃ layers.

Despite V₃D₃ being not the ideal adsorptive, the EP measurements do confirm the absence of open pores accessible to V₃D₃ molecules in the Al₂O₃ PEALD layers and the Al₂O₃ ETP, 7.5 s layer. The absence of these open pores is an interesting characteristic regarding the barrier properties of the Al₂O₃ layers since the intrinsic barrier properties of the SiO₂ layers appeared to be controlled by the open microporosity. The intrinsic WVTR of the Al₂O₃ films was measured by the Ca test and the WVTR values are given in table 4.6. In the same table the open porosity of the Al₂O₃ ETP, 1.1 s layer is given as determined from the V₃D₃ porosity measurements at Pₘ/Pₜₐ₇ = 0.6 (i.e. when the micropore filling is complete). This porosity was calculated using formula 2.7 with nₖ = the refractive index of the layers at Pₘ/Pₜₐ₇ = 0.6. The porosity was also calculated from the adsorption of H₂O during exposure to the ambient using the same formula with n₀ the in-situ refractive index value and nₖ = the ex-situ refractive index value of the layers.

The Al₂O₃ ETP, 1.1 s layer has a porosity of 0.7% according to the porosity measurements with V₃D₃. The porosity calculated from the H₂O adsorp-
Table 4.6 The open porosity as determined from the adsorption of V$_3$D$_3$ during the porosity measurements and from the adsorption of H$_2$O during exposure to the ambient, and intrinsic WVTR values of the Al$_2$O$_3$ layers from the Ca test at 20 °C / 50% RH.

<table>
<thead>
<tr>
<th>Layer Description</th>
<th>Open Porosity (%) (V$_3$D$_3$)</th>
<th>Open Porosity (%) (H$_2$O)</th>
<th>WVTR (g/m$^2$/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$ ETP, 1.1 s</td>
<td>0.7 ± 0.1</td>
<td>6.1 ± 0.1</td>
<td>(3 ± 1) · 10$^{-3}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$ PEALD, 25 °C</td>
<td>-</td>
<td>-</td>
<td>&lt; 10$^{-5}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$ PEALD, 100 °C, 2 s</td>
<td>-</td>
<td>-</td>
<td>&lt; 10$^{-4}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$ PEALD, 100 °C, 10 s</td>
<td>-</td>
<td>-</td>
<td>&lt; 10$^{-4}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$ ETP, 7.5 s</td>
<td>-</td>
<td>-</td>
<td>5 · 10$^{-5}$</td>
</tr>
</tbody>
</table>

The exact WVTR of the PEALD Al$_2$O$_3$ films is not known yet as the layers are still in test at the moment of writing. This means that less than 1 nm of Ca has oxidized so far. The WVTR values reported are an upper limit obtained from figure 3.13. The upper limit of the Al$_2$O$_3$ PEALD, 25 °C layer is lower as this layer is in test for a longer time.
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the $\text{Al}_2\text{O}_3 \text{ETP}_{7.5s}$ layer as the former contains more OH groups.

### 4.4 $\text{SiO}_2/\text{Al}_2\text{O}_3$ nano-laminates

Since residual porosity will usually be present in single barrier layers limiting their performance, inorganic nano-laminates were analyzed to learn if they are a useful approach for controlling the residual porosity in single barrier layers and lead to an improvement of barrier properties. In this section the results are reported and discussed for the measurements on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ nano-laminates.

In figure 4.15 the extrinsic WVTR values of the barrier layers as function of the $\text{Al}_2\text{O}_3$ layer thickness are reported. Extrinsic means that the permeation through pinholes is taken into account as was not the case for WVTR measurements of the single barrier layers in the previous sections. The results for three different samples are given:

- $\text{Al}_2\text{O}_3 \text{PEALD, } 80^\circ\text{C}$ films on PEN substrates (black points);
- $\text{Al}_2\text{O}_3 \text{PEALD, } 80^\circ\text{C}$ films on PEN substrates coated with $\text{SiO}_2 \text{APG, HDDR}$ films (blue points);
- $\text{Al}_2\text{O}_3 \text{PEALD, } 80^\circ\text{C}$ films deposited on PEN substrates coated with $\text{SiO}_2 \text{APG, LDDR}$ films (red points);

Details on the deposition conditions of these layers can be found in section 3.1.3. The $\text{SiO}_2 \text{APG, HDDR}$ layer exhibits no barrier properties as the WVTR is similar to the WVTR of a bare PEN substrate. The $\text{SiO}_2 \text{APG, LDDR}$ layer on the other hand is a good barrier with a WVTR of $2 \cdot 10^{-3}$ g/m$^2$/day.

From figure 4.15 it is seen that the WVTR of the $\text{SiO}_2 \text{APG, HDDR}$ layer can be dramatically reduced by 3 orders of magnitude with a $\text{Al}_2\text{O}_3$ layer of only 2 nm. When $\text{Al}_2\text{O}_3$ is deposited directly on PEN a thickness of 5 nm is required to reach a WVTR in the same order. The steep reduction in WVTR observed at a thickness of 5 nm defines the critical thickness. The higher permeability below the critical thickness is attributed to incomplete coverage of the polymer by the barrier layer [12]. No improved barrier properties are observed when $\text{Al}_2\text{O}_3$ is deposited on top of the $\text{SiO}_2 \text{APG, LDDR}$ layer.

The limited WVTR value of $2 \cdot 10^{-3}$ g/m$^2$/day reached for all films suggests that the permeation through these layers is controlled by macro-defects which are not covered by the $\text{Al}_2\text{O}_3 \text{PEALD, } 80^\circ\text{C}$ film. The influence of defects also becomes clear when applying the ideal laminate theory. According to this theory, which assumes that the diffusion takes place only through the bulk, therefore excluding the role of macro-defects, the total permeation
4.4 SiO$_2$/Al$_2$O$_3$ nano-laminates

Figure 4.15 The extrinsic WVTR values of Al$_2$O$_3$ PEALD, 80°C layers of various thickness on PEN substrates and on PEN substrates coated with SiO$_2$ layers.

through the bilayer system would be given by:

$$
\frac{d_{\text{total}}}{P_{\text{total}}} = \frac{d_{\text{PEN}}}{P_{\text{PEN}}} + \frac{d_{\text{SiO}_2}}{P_{\text{SiO}_2}} + \frac{d_{\text{Al}_2\text{O}_3}}{P_{\text{Al}_2\text{O}_3}},
$$

(4.2)

with $P_{\text{PEN}}$, $P_{\text{SiO}_2}$, $P_{\text{Al}_2\text{O}_3}$ and $d_{\text{PEN}}$, $d_{\text{SiO}_2}$ and $d_{\text{Al}_2\text{O}_3}$, the permeabilities and thicknesses of the PEN substrate, the SiO$_2$ barrier and the Al$_2$O$_3$ barrier, respectively. $P_{\text{total}}$ and $d_{\text{total}}$ are the permeability and the thickness of the polymer/barrier layer system, respectively.

The permeability can be calculated from the WVTR values according to:

$$
P = \frac{p_0 \cdot \text{WVTR}}{d},
$$

(4.3)

with $p_0$ the water partial pressure at the top side of the barrier. The WVTR measurements were carried out under the conditions of 40 °C / 90% RH. At these conditions $p_0 = 0.066$ bar.

To make this calculation for the SiO$_2$ APG, HDDR/Al$_2$O$_3$ PEALD, 80°C nano-laminate with an Al$_2$O$_3$ film thickness of 2 nm, first, the $P_{\text{Al}_2\text{O}_3}$ and $P_{\text{SiO}_2}$
values have to be obtained using the following equations:

\[
\frac{d_{PEN/Al_2O_3}}{P_{PEN/Al_2O_3}} = \frac{d_{Al_2O_3}}{P_{Al_2O_3}} + \frac{d_{PEN}}{P_{PEN}}, \quad (4.4)
\]

\[
\frac{d_{PEN/SiO_2}}{P_{PEN/SiO_2}} = \frac{d_{SiO_2}}{P_{SiO_2}} + \frac{d_{PEN}}{P_{PEN}}, \quad (4.5)
\]

Using the data from figure 4.15 gives the values \( P_{Al_2O_3} = 5.36 \cdot 10^{-8} \text{ g/m/day/bar} \) and \( P_{SiO_2} = 4.57 \cdot 10^{-6} \text{ g/m/day/bar} \). Substituting these values in equation 4.2 gives a total permeability of \( P_{tot} = 1.17 \cdot 10^{-3} \text{ g/m/day/bar} \). The total WVTR is \( \text{WVTR}_{total} = 0.8 \text{ g/m}^2/\text{day} \) which is much higher than the measured value of \( 2 \cdot 10^{-3} \text{ g/m}^2/\text{day} \). This result confirms that the permeation in the nano-laminate is not occurring through the bulk of this bilayer system.

The good barrier properties of the SiO\(_2\) APG, HDDR/Al\(_2\)O\(_3\) PEALD, 80\(^\circ\)C nano-laminate can have several reasons. First of all, the lower critical thickness of Al\(_2\)O\(_3\) on the SiO\(_2\) APG, HDDR layer compared to the PEN substrate can be due to improved nucleation of Al\(_2\)O\(_3\) on SiO\(_2\). As the polymer surface is relatively porous, precursor molecules can penetrate the PEN and more ALD cycles would be required for a continuous Al\(_2\)O\(_3\) film on the surface [31]. Secondly, the enhancement in barrier performance can be due to the filling of pores in the SiO\(_2\) film by Al\(_2\)O\(_3\) [30, 31]. As the SiO\(_2\) APG, HDDR layer exhibits no barrier properties it is assumed that this layer has a high relative pore content. It is hypothesized that during the PEALD process TMA molecules penetrate into the pores. Subsequently, during the plasma exposure, Al\(_2\)O\(_3\) is formed inside the pores and the pores are sealed. The sealed pores are then no longer pathways for gas permeation resulting in increased barrier performance.

To prove the hypothesis of pore filling by Al\(_2\)O\(_3\), XPS measurements were carried out on SiO\(_2\) APG, HDDR and SiO\(_2\) APG, LDDR layers both covered with a 5 nm thick Al\(_2\)O\(_3\) layer to study the interface region of the nano-laminates. The interface of a 5 nm thick Al\(_2\)O\(_3\) layer deposited on top of a SiO\(_2\) layer grown by thermal oxidation on PEN was also analyzed for comparison. This SiO\(_2\) Thermal layer is nonporous which means there should be a discrete interface between SiO\(_2\) and Al\(_2\)O\(_3\). Figure 4.16 shows the surface coverage and pore filling of the SiO\(_2\) layers by Al\(_2\)O\(_3\) as hypothesized; no pores in the thermal layer, a low relative pore content in the SiO\(_2\) APG, LDDR layer and a high relative pore content in the SiO\(_2\) APG, HDDR layer.

Figure 4.17 shows the Si\(_2p\) peak obtained from XPS measurements on the SiO\(_2\) layers without Al\(_2\)O\(_3\) on top (Figure 4.17 (a)) and with 5 nm Al\(_2\)O\(_3\)
4.4 SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} nano-laminates

![Figure 4.16](image)

**Figure 4.16** Surface coverage and pore filling of the SiO\textsubscript{2} layers by Al\textsubscript{2}O\textsubscript{3} as hypothesized for the (a) SiO\textsubscript{2} Thermal layer, (b) SiO\textsubscript{2} APG, LDDR layer, and (c) SiO\textsubscript{2} APG, HDDR layer.

(Figure 4.17 (b)) on top. The peaks in figure 4.17 (a) are at binding energy 103.3 eV which is associated with a Si(−O)\textsubscript{4} environment [62]. In figure 4.17 (b) the peaks of the SiO\textsubscript{2} APG, LDDR and SiO\textsubscript{2} APG, HDDR films show an increase in binding energy with respect to the thermal layer. The peak shift is a result of Al\textsubscript{2}O\textsubscript{3} present inside pores at the interface and can be explained by comparing the Al-O and Si-O bonds. The electronegativity values of O, Si and Al are 3.4, 1.9 and 1.6, respectively. Because the electronegativity of Si is somewhat higher than for Al, an Al-O bond is slightly more polarized than the Si-O bond. The more polarized system allows for a stronger partial negative charge on the O atom in an Al-O-Si bond compared to a Si-O-Si bond. The stronger negative charge on the O atom in a Al-O-Si bond results in a shift of the Si2p peak to higher binding energy. As the Si2p peak of the SiO\textsubscript{2} APG, HDDR film is at the highest binding energy it is suggested that at the interface of this film the most aluminum is present from which it can be argued that this layer is more porous than the SiO\textsubscript{2} APG, LDDR layer. This is in agreement with the barrier performance of the SiO\textsubscript{2} APG, LDDR and SiO\textsubscript{2} APG, HDDR layers as was shown in figure 4.15.

![Figure 4.17](image)

**Figure 4.17** The Si2p peaks obtained from XPS measurements on (a) SiO\textsubscript{2} layers deposited on PEN substrates and (b) SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} nano-laminates deposited on PEN substrates.

Angle resolved XPS (ARXPS) measurements were performed to study the
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interface region of the nano-laminates. From these measurements the atomic concentrations as function of the depth were obtained for Al, Si, O, and C. Using the density and stoichiometry of the deposited SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} layers, the data were modeled to obtain a depth profile of the chemical compounds. The density and stoichiometry of the layers as determined from RBS/ERD measurements are given in table 4.7.

Table 4.7 The density and stoichiometry of the Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} layers used for the nano-laminates as obtained from RBS/ERD measurements.

<table>
<thead>
<tr>
<th></th>
<th>(\rho) (g/cm(^3))</th>
<th>Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2} APG, HDDR</td>
<td>2.1</td>
<td>O/Si = 2.4</td>
</tr>
<tr>
<td>SiO\textsubscript{2} APG, LDDR</td>
<td>2.2</td>
<td>O/Si = 2.2</td>
</tr>
<tr>
<td>SiO\textsubscript{2} Thermal</td>
<td>2.2</td>
<td>O/Si = 2</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3} PEALD, 80 (^\circ)C</td>
<td>2.9</td>
<td>O/Al = 1.7</td>
</tr>
</tbody>
</table>

The depth profiles as obtained from the ARXPS measurements are given in figure 4.18. The vertical black line is an indication of the interface between the Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} layers. The position of this black line is at 7.2 nm, 6.8 nm and 6.6 nm for the SiO\textsubscript{2} APG, HDDR, SiO\textsubscript{2} APG, LDDR and SiO\textsubscript{2} Thermal layers, respectively. Since the SiO\textsubscript{2} Thermal layer is nonporous it can be concluded that the interface being at larger depths for the SiO\textsubscript{2} APG layers is a result of the intermixing between Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2}, as Al\textsubscript{2}O\textsubscript{3} has penetrated inside pores in the SiO\textsubscript{2} layers. The effect is more pronounced for the SiO\textsubscript{2} APG, HDDR layer indicating a higher relative pore content, in agreement with the peak shift of the Si2p peak observed in figure 4.17. The relative intensity of Al\textsubscript{2}O\textsubscript{3} in the SiO\textsubscript{2} APG, LDDR layer is not reaching 0\% for larger depths which is assumed to be an artifact of the modeling of the data and needs to be further addressed.

On the basis of the XPS analysis, it is concluded that the improved barrier performance of the nano-laminate is due to the pore filling mechanism, earlier discussed.
Figure 4.18 The depth profiles obtained from ARXPS measurements showing the relative intensities of the chemical compounds in the three SiO$_2$/Al$_2$O$_3$ nano-laminates. (a) the SiO$_2$ APG, HDDR layer, (b) the SiO$_2$ APG, LDDR layer and (c) the SiO$_2$ Thermal layer.
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Chapter 5

Conclusions and recommendations

5.1 Conclusions

SiO$_2$ and Al$_2$O$_3$ barrier layers were analyzed to learn what factor controls the ultimate (intrinsic) barrier performance of barrier layers. The techniques of SE, FTIR and RBS/ERD were used to obtain information about the chemical composition, optical properties and density of the layers. These diagnostic tools already give an indication about the presence of pores in the films, however, no quantitative information can be inferred in terms of pore content and size (distribution). To this purpose, ellipsometric porosimetry (EP) was introduced as a technique allowing for the analysis of the open porosity of the layers. Ca test measurements were used to measure the intrinsic barrier properties of these layers.

- EP measurements turn out to be essential to understand and explain differences in barrier properties. The technique allows for the characterization of the microstructure of the layers in terms of pore relative content and pore size distribution.

The SiO$_2$ layers are characterized by a residual open porosity in the micropore range, i.e. pores smaller than 2 nm in diameter. The layers have a low relative pore content and an appreciable external surface.

The Al$_2$O$_3$ PEALD layers and the Al$_2$O$_3$ ETP, 7.5 s layer do not contain open pores accessible to V$_3$D$_3$ molecules nor to H$_2$O, since their refractive index values do not change upon exposure to the ambient. The Al$_2$O$_3$ ETP, 1.1 s layer is characterized by a residual open porosity including micropores and some small mesopores.

- The intrinsic barrier performance of both the SiO$_2$ and Al$_2$O$_3$ barrier
layers is controlled by the residual open porosity in the layers. The higher the degree of porosity, the larger the WVTR of the films. Regarding the SiO₂ films, the SiO₂ \textsubscript{PEALD, 25°C} has the highest porosity of 1.1% as determined from adsorption by V₃D₃. This layer has a WVTR > 10⁻² g/m²/day. The SiO₂ \textsubscript{PECVD, 250 W} layer has the lowest relative pore content (0.5%) and a WVTR of 2 · 10⁻⁵ g/m²/day. The SiO₂ \textsubscript{PECVD, 150 W} and SiO₂ \textsubscript{PEALD, 100°C} layers both have a porosity of 0.7 % and a WVTR in the order of 10⁻³ g/m²/day.

The porosity of 0.7 % and a WVTR in the order of 10⁻³ g/m²/day for the Al₂O₃ \textsubscript{ETP, 1.1 s} is in agreement with the results for SiO₂. The other Al₂O₃ films do not contain pores accessible to V₃D₃ molecules and their intrinsic barrier properties are found to reach values down to 10⁻⁶ g/m²/day.

The intrinsic barrier properties of the SiO₂ and Al₂O₃ barrier layers are controlled by the residual open porosity of the layers, however, residual porosity will usually be present in a single barrier layer therefore limiting its performance. SiO₂/Al₂O₃ nano-laminates were analyzed to learn if they are a useful approach for controlling the residual porosity in single barrier layers and lead to an improvement of barrier properties.

- The WVTR of a SiO₂ layer deposited by APG-PECVD, exhibiting no barrier properties, was dramatically reduced by 3 orders of magnitude with a Al₂O₃ PEALD layer of only 2 nm.
- The critical thickness of the Al₂O₃ PEALD layer can be reduced from 5 nm on a PEN substrate to 2 nm on a PEN substrate coated with a SiO₂ APG layer.
- Characterization of the interface region of the SiO₂/Al₂O₃ nano-laminates proved the filling of pores in the SiO₂ layers by Al₂O₃. The improved barrier performance of the nano-laminate is attributed to the pore filling mechanism.
5.2 Recommendations

In this section a few recommendations are given for future research. Since \( V_3D_3 \) molecules are only able to probe pores of 1 nm and larger, another solvent with smaller molecules should be used for the EP measurements in order to probe smaller micropores. Water is a good alternative as these measurements would immediately give an idea about the water permeation properties of the barrier layer. The use of smaller molecules can provide more insight in the differences in small micropores and specific arrangement of the network structure of the various \( SiO_2 \) and \( Al_2O_3 \) barrier layers.

The effect of the ion bombardment on the densification of the films in the PEALD process turned out to be negligible. For \( SiO_2 \) layers it has been shown that the increase of ion energy promotes the reduction of open porosity [53]. A non-porous film was obtained for \( E_p \) values around 100 eV. Therefore, an external substrate bias can be used during deposition of the \( SiO_2 \) films to enhance the film densification at low substrate temperature.

The characterization of the single barrier layers in this work has been carried out on layers deposited on a silicon substrate. Since barrier layers are applied to decrease the permeation of moisture and oxygen through polymers, the same characterization should be performed on layers deposited on polymer substrates. Characterization of the microstructure is important to learn what the effect is of the polymer substrate on the microstructure of the barrier layers. Most polymers have a rough surface and the transitions from a defective, rough substrate to a smooth, nonporous barrier layer is a challenge. In order to perform the microstructure characterization of barrier layers deposited on polymers, the ellipsometric porosimetry technique should be extended to allow for measurements on polymer substrates.
Chapter 5 Conclusions and recommendations
# List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>APG</td>
<td>Atmospheric pressure Glow Discharge</td>
</tr>
<tr>
<td>AR-XPS</td>
<td>Angle Resolved X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>EMA</td>
<td>Effective Medium Approximation</td>
</tr>
<tr>
<td>EP</td>
<td>Ellipsometric Porosimetry</td>
</tr>
<tr>
<td>ERD</td>
<td>Elastic Recoil Detection</td>
</tr>
<tr>
<td>ETP-CVD</td>
<td>Expanding Thermal Plasma Chemical Vapor Deposition</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GPC</td>
<td>Growth Per Cycle</td>
</tr>
<tr>
<td>HMDSO</td>
<td>Hexamethyldisiloxane</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
</tr>
<tr>
<td>OTR</td>
<td>Oxygen Transmission Rate</td>
</tr>
<tr>
<td>PEALD</td>
<td>Plasma Enhanced Atomic Layer Deposition</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma Enhanced Chemical Vapor Deposition</td>
</tr>
<tr>
<td>PEN</td>
<td>Polyethylene naphthalate</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaics</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford Backscattering Spectroscopy</td>
</tr>
<tr>
<td>RMS</td>
<td>Root Mean Square</td>
</tr>
<tr>
<td>SAM.24</td>
<td>$\text{H}_2\text{Si[N(C}_2\text{H}_5)_2]\text{]}_2$</td>
</tr>
<tr>
<td>SE</td>
<td>Spectroscopic Ellipsometry</td>
</tr>
</tbody>
</table>
List of abbreviations

TMA Trimethylaluminum, Al(CH$_3$)$_3$
WVTR Water Vapor Transmission Rate
XPS X-ray Photoelectron Spectroscopy
V$_3$D$_3$ 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane
Acknowledgements

I would like to thank the people who contributed to this work for their support, advice and effort throughout the last year. First of all thanks to Adriana Creatore, my direct supervisor, for her guidance and help, the valuable discussions during the meetings and the effort you put in reading my thesis. Many thanks to my daily supervisors, Gianfranco Aresta and Wytze Keuning. Gianfranco, you helped me improving my experimental and analytical skills, even during the stressful final stage of your PhD which I really appreciated. Wytze, thanks for the training in the lab, your great support during the experiments and the instructive discussions. I also would like to thank Anu Jagia and Zhengyu Fan, the other members of the barrier layer team, for the discussions and their new insights and ideas. The technicians Cristian van Helvoirt, Joris Meulendijks, Ries van de Sande and Janneke Zeebregts are gratefully acknowledged for their technical assistance. Many thanks to Tatiana Fernandez Landaluce for the XPS measurements and your support during the analysis of the data. I also would like to give my thanks to: Hindrik de Vries and Sergei Starostin for the SiO$_2$ depositions and WVTR measurements of the nano-laminates, Wim Arnold Bik for the RBS/ERD measurements, Peter van de Weijer for the Ca test measurements and Bart Macco and Vincent Vandalon for performing AFM measurements. Thanks to all the people in the student room, who contributed to a very pleasant working atmosphere. Finally, I would like to thank my family. Pap, mam en Inge, bedankt voor jullie steun en vertrouwen!
Bibliography


Bibliography


Bibliography


Bibliography


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Appendix A

Deposition techniques

For the deposition of the SiO$_2$ and Al$_2$O$_3$ barrier layers, three different deposition techniques were used, i.e. plasma enhanced atomic layer deposition, plasma enhanced chemical vapor deposition and expanding thermal plasma chemical vapor deposition. These techniques are shortly explained hereafter.

A.1 Atomic layer deposition

Atomic layer deposition (ALD) is a process based on saturative surface reactions. It is a cyclic process that consists of two self-limiting half reactions. During the first half cycle a precursor is pulsed into the reaction chamber which reacts with surface groups on the substrate. After the precursor exposure the chamber is purged to remove the volatile byproducts and the excess precursor. A second precursor is pulsed into the reaction chamber and this precursor reacts with the new surface functional groups, adding a new element and restoring the initial surface functional groups. The cycle ends again with a purge step. The purge steps prevent any direct reaction between the precursors in the gas phase. For sufficient precursor doses, the amount of material deposited during each cycle is not proportional to the precursor flux, but depends on the temperature and density of surface groups and is the same for each cycle. Ideally, one full monolayer is deposited per cycle, however, due to a limited number of reactive surface sites or steric hindrance between ligands, only a submonolayer may be deposited. This technique is the method of choice for depositing films with excellent conformality and uniformity with accurate growth control at the atomic level [15, 63].

The reactions in an ALD process are usually enhanced by thermal energy and they are called thermal ALD processes. For these thermal processes the reactant is typically a gas, like O$_2$, or a vapor, like H$_2$O. The two half
cycles of a thermal ALD process are shown in figure A.1. Since barrier layers are often deposited on temperature sensitive substrates the thermal energy that can be used in the ALD process is limited although better layer properties are usually obtained at a higher deposition temperature. A different way of enhancing the ALD process is by using a plasma, so-called plasma enhanced atomic layer deposition (PEALD). In a PEALD process a plasma is generated in a reactant gas during the second half reaction. The radicals in the plasma react with surface groups and energetic ions and electrons can provide extra energy to the substrate to enhance the reactions. Because of the high reactivity of the plasma species, less thermal energy is required to enhance the reactions at the surface. This means that layers with the same material properties can be deposited at lower temperature compared to thermal ALD [64].

![ALD cycle diagram](image)

**Figure A.1** A (thermal) ALD cycle consisting of two self-limiting half reactions enhanced by thermal energy. In each half reaction, a precursor is dosed which reacts with surface groups on the substrate, followed by a purge step.

### A.2 Chemical vapor deposition

Chemical vapor deposition (CVD) is a deposition technique based on chemical reactions of precursor species in the gas phase and on the substrate [65]. Multiple precursors are introduced in the reaction chamber at constant flow rate. The precursor molecules react in the gas phase and the reactants are then transported towards the substrate where they adsorb on the surface. Diffusion, nucleation and chemical reactions of the adsorbed species on the surface lead to film growth. The last step is the desorption of volatile reaction products from the substrate. A schematic overview of this process is given in figure A.2.

Usually, the reactions in a CVD process are initiated by thermal energy and
A.3 Expanding thermal plasma chemical vapor deposition

The growth rate mainly depends on the substrate temperature and the pressure in the reactor, so-called thermal CVD. Just as for the ALD process, the reactions can be enhanced by using a plasma. In a plasma enhanced CVD (PECVD) process a plasma is generated in a reactant gas and a precursor gas is injected at a constant flow rate in the continuously running plasma. The plasma species and precursor molecules will react in the gas phase and on the surface, in contrast to the PEALD process in which only surface reactions occur. Besides, energetic ions and electrons can provide extra energy to the substrate to enhance the reactions.

**Figure A.2** The basic physicochemical steps in an overall CVD reaction process [65].

The expanding thermal plasma chemical vapor deposition (ETP-CVD) technique is a PECVD-like process in which a plasma is generated in a high pressure plasma source, a cascaded arc, consisting of a housing with three cathodes, a plasma channel, and a grounded anode plate with a nozzle. The plasma emanates through the nozzle and expands supersonically in a low pressure reaction chamber, shocks, and flows at subsonic velocity towards the substrate. Precursors are injected in the low pressure reaction chamber into the expanding plasma. The precursor molecules react with the plasma species and the reactants are transported towards the substrate along with
A Deposition techniques

the plasma expansion. The expansion of the plasma in the low pressure reaction chamber results in a reduction of the electron temperature, $T_e$, to 0.1-0.3 eV. As a result of this low electron temperature, ions and electrons reaching the substrate have a low energy and the enhancement of the reactions by these ions and electrons is negligible.
Appendix B

Ion bombardment

To compare the effect of the ion bombardment in the different deposition processes used to deposit the SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} barrier layers, the ion energy per depositing particle, \( E_p \), is calculated. \( E_p \) is given by equation B.1:

\[
E_p = E_i \frac{\Gamma_{ions}}{\Gamma_{growth}}, \tag{B.1}
\]

with \( E_i \) the mean kinetic energy of the ions, which is the maximum value in the ion energy distribution (IED), \( \Gamma_{ions} \) the ion flux, and \( \Gamma_{growth} \) the particle flux during deposition.

The PEALD depositions were carried out in a remote plasma reactor (Oxford Instruments FlexAL) in which the plasma is generated remotely from the substrate. Measurements of the ion energies and fluxes in an O\textsubscript{2} plasma in this reactor were performed by Profijt et al. [66]. For the conditions used during deposition (\( p = 25 \) mTorr, \( P = 200 \) W), \( E_i = 13 \pm 1 \) eV and \( \Gamma_{ions} = 2 \cdot 10^{13} \) cm\(^{-2}\) cycle\(^{-1}\). The particle fluxes are determined from RBS/ERD measurements. The ion energy per atom during deposition of the SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} PEALD layers can now be calculated from equation B.1. The values are given in table B.1.

Table B.1 The ion flux, particle flux and the ion energy per depositing particle during deposition of the PEALD SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} layers.

<table>
<thead>
<tr>
<th>Layer Type</th>
<th>Temperature (°C)</th>
<th>( E_i ) (eV)</th>
<th>( \Gamma_{ions} ) (cm(^{-2}) cycle(^{-1}))</th>
<th>( \Gamma_{growth} ) (cm(^{-2}) cycle(^{-1}))</th>
<th>( E_p ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2} PEALD, 25°C</td>
<td>13</td>
<td>1 \cdot 10^{14}</td>
<td>7.9 \cdot 10^{14}</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>SiO\textsubscript{2} PEALD, 100°C</td>
<td>13</td>
<td>1 \cdot 10^{14}</td>
<td>6.2 \cdot 10^{14}</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3} PEALD, 25°C</td>
<td>13</td>
<td>4 \cdot 10^{13}</td>
<td>1.4 \cdot 10^{15}</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3} PEALD, 100°C, 2 s</td>
<td>13</td>
<td>4 \cdot 10^{13}</td>
<td>1.1 \cdot 10^{15}</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3} PEALD, 100°C, 10 s</td>
<td>13</td>
<td>4 \cdot 10^{13}</td>
<td>1.2 \cdot 10^{15}</td>
<td>0.4</td>
<td></td>
</tr>
</tbody>
</table>
Ion bombardment

It was shown for SiO$_2$ films that the porosity is affected by ion bombardment for $E_p$ values between 30 – 100 eV [53]. As the $E_p$ values for the PEALD layers are 1 to 2 orders lower, it is reasonable to assume that the effect of the ion bombardment on the densification of the films is negligible.

The PECVD process was carried out in a direct capacitively-coupled plasma (CCP) reactor in which the substrate is directly placed on one of the electrodes. The ion energies and fluxes have not been measured in this reactor and values are estimated. The pressure during deposition was 225 mTorr, ten times higher than for the PEALD process. Because of this high pressure the plasma sheath is collisional, resulting in a broad IED and lower energies of ions arriving at the substrate. At these high pressures, the ion energies at the grounded substrate are typically several tens of eV at maximum [67]. Typical values for the electron temperature, $T_e$, and the electron density, $n_e$, in a CCP reactor are 1-5 eV and $10^9 – 10^{10}$ cm$^{-3}$, respectively [67].

The ion flux is estimated from the definition of the random particle flux, that is the number of particles hitting a surface per unit time and unit area, from one side only. For an isotropic velocity distribution function this flux is given by:

$$\Gamma_i = \frac{n_e u_i}{4}, \quad (B.2)$$

with $u_i$ the average speed of the ions.

$u_i$ is determined using the Bohm criterion:

$$u_i > \left(\frac{kT_e}{m_i}\right)^{1/2}, \quad (B.3)$$

with $m_i$ the mass of an oxygen ion (16 u). This condition must be satisfied for the formation of a plasma sheath [68].

Using $T_e = 3$ eV and $n_e = 10^9$ cm$^{-3}$, the ion flux reaching the plasma sheath is estimated to be $\Gamma_{ions} = 1.1 \cdot 10^{14}$ cm$^{-2}$s$^{-1}$.

The ion energy can be estimated from the self-bias potential. During the sheath formation the substrate charges up negatively until the ion flux equals the electron flux:

$$\frac{n_i u_i}{4} = \frac{n_e u_e}{4} = \frac{u_e}{4} n_i exp\left(-\frac{e(V_p - V_f)}{kT_e}\right), \quad (B.4)$$

with $u_e$ the average speed of the electrons, $V_p$ the plasma potential and $V_f$ the floating potential. The self-bias potential is then given by:

$$eV_s = e(V_p - V_f) = kT_e ln(u_e/u_i). \quad (B.5)$$

Since the substrate during the depositions was grounded, $V_f$ is equal to zero. Assuming a Maxwell-Boltzmann velocity distribution and using equation

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B.3, equation B.5 is written as:

$$eV_p = kT_e ln \left( \frac{m_i}{2\pi m_e} \right)^{1/2}. \quad (B.6)$$

Using the mass of an oxygen atom \(2.7 \cdot 10^{-26} \text{ kg}\) and \(T_e = 3 \text{ eV}\), results in a plasma potential of 13 eV, a measure of the kinetic energy obtained by the ions in the plasma sheath.

Assuming a stoichiometric film, which is a reasonable assumption given the RBS/ERD values in table 4.3, the particle flux has been estimated from the deposition rate using formula B.7:

$$\Gamma_{\text{growth}} = \frac{\rho_{\text{SiO}_2} \cdot N_A}{m_{\text{SiO}_2}} R_d, \quad (B.7)$$

with \(\rho_{\text{SiO}_2}\) the density of the film \((2.2 \text{ g cm}^{-3})\), \(N_A\) the Avogadro's number and \(m_{\text{SiO}_2}\) the molecular weight of SiO

The ion bombardment during deposition of the ETP Al\(_2\)O\(_3\) films is negligible due to the low electron temperature in the low pressure reaction chamber \((0.2-0.3 \text{ eV})\) resulting in an ion energy of \(E_i \approx 2 - 3 \text{ eV}\).
B Ion bombardment
Appendix C

XPS results

C.1 SiO$_2$ layers

During the EP measurements, after desorption of the monomer at $P_M/P_{sat} = 0$, the SiO$_2$ PEALD layers showed an increase in optical thickness, whereas the optical thickness of the SiO$_2$ PECVD layers was reversible upon evacuation as can be seen in figure 4.6. XPS measurements were performed to learn more about this behavior of the PEALD layers.

Figure C.1 (a) shows the Si2p peak obtained from XPS measurements on a SiO$_2$ PEALD, 25$^\circ$C layer on which no porosity measurements were done. This peak was fitted using one component positioned at binding energy 103.4 eV which is associated with a Si(−O)$_4$ environment [62]. In figure C.1 (b) the Si2p peak is shown for a SiO$_2$ PEALD, 25$^\circ$C layer after porosity measurements. To fit this peak a second component was required positioned at 101.8 eV which can be associated with a Si(−O)$_2$ environment [62]. Moreover, the carbon concentration in the layer on which porosity measurements were performed was twice as large compared to the pristine layer. The same results were obtained for the SiO$_2$ PEALD, 100$^\circ$C layer as shown in figure C.1 (c) and (d). These results confirm the presence of the siloxane monomer in the PEALD layers after the porosity measurements. It is hypothesized that some monomer molecules were trapped in pores in the SiO$_2$ layers during desorption causing an increase in (optical) thickness. XPS measurements on the SiO$_2$ PECVD layers after porosity measurements showed no signature of the monomer.

C.2 Al$_2$O$_3$ layers

To learn more about the interaction between the Al$_2$O$_3$ films and V$_3$D$_3$ during the EP measurements, XPS measurements were performed on the
C XPS results

![Figure C.1](image)

**Figure C.1** The Si2p peak obtained from XPS measurements for (a) a SiO$_2$ PEALD, 25°C layer, (b) a SiO$_2$ PEALD, 25°C layer on which porosity measurements were done, (c) a SiO$_2$ PEALD, 100°C layer and (d) a SiO$_2$ PEALD, 100°C layer on which porosity measurements were done.

Al$_2$O$_3$ layers after the porosity measurements. For comparison, also a Al$_2$O$_3$ PEALD, 100°C, 2 s layer on which no porosity measurements were done, was analyzed by XPS.

Table C.1 reports the atomic concentrations of a Al$_2$O$_3$ PEALD, 100°C, 2 s layer which has not been in contact with V$_3$D$_3$. According to these measurements Al, O and C are present in the layer. In table C.2 the atomic concentrations are given for the Al$_2$O$_3$ films on which porosity measurements were performed. In these layers Si is also present besides Al, O and C. The Al$_2$O$_3$ PEALD, 100°C, 2 s film also has a higher carbon content after the porosity measurements as compared to the Al$_2$O$_3$ PEALD, 100°C, 2 s layer on which no porosity measurements were carried out. Moreover, this film showed the highest V$_3$D$_3$ thickness after desorption of the monomer (5 nm, figure 4.14 (b)) and also contains the highest amount of silicon as given in table C.2. These results confirm that monomer is present in the Al$_2$O$_3$ samples after the porosity measurements as the Si content can only originate from the siloxane monomer.

The XPS measurements were performed in an ultra high vacuum (UHV) chamber. As the monomer did not desorb from the samples under UHV, it is
Table C.1 Atomic concentrations derived from the XPS Al2p, O1s, Si2p and C1s peak intensities for a PEALD Al2O3, 100 °C, 2 s film.

<table>
<thead>
<tr>
<th>Layer</th>
<th>[Al] (at.%)</th>
<th>[O] (at.%)</th>
<th>[Si] (at.%)</th>
<th>[C] (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3 PEALD, 100 °C, 2 s</td>
<td>31.5</td>
<td>50.6</td>
<td>0</td>
<td>17.9</td>
</tr>
</tbody>
</table>

Table C.2 Atomic concentrations derived from the XPS Al2p, O1s, Si2p and C1s peak intensities for the Al2O3 films after porosity measurements.

<table>
<thead>
<tr>
<th>Layer</th>
<th>[Al] (at.%)</th>
<th>[O] (at.%)</th>
<th>[Si] (at.%)</th>
<th>[C] (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3 PEALD, 25 °C</td>
<td>22.5</td>
<td>50.0</td>
<td>4.3</td>
<td>23.2</td>
</tr>
<tr>
<td>Al2O3 PEALD, 100 °C, 2 s</td>
<td>18.1</td>
<td>43.2</td>
<td>8.3</td>
<td>30.4</td>
</tr>
<tr>
<td>Al2O3 PEALD, 100 °C, 10 s</td>
<td>28.5</td>
<td>48.3</td>
<td>3.5</td>
<td>19.6</td>
</tr>
<tr>
<td>Al2O3 ETP, 1.1 s</td>
<td>12.2</td>
<td>40.0</td>
<td>3.3</td>
<td>44.5</td>
</tr>
</tbody>
</table>

assumed that the monomer has chemisorbed to the Al2O3 layer, rather than physisorbed. The XPS measuring depth is in the order of a few nanometers and to find out if monomer is also present at larger depths in the film, a depth profile of the Al2O3 PEALD, 100 °C, 2 s film after porosity measurements was obtained by making use of ion sputtering. The depth profile is given in figure C.2 showing the atomic concentrations as function of the layer depth. From this profile it is observed that Si is only present near the surface of the layer. From the sputter rate the thickness of the Si layer was estimated to be 1.8 nm.

![Figure C.2](https://example.com/image.png)

**Figure C.2** XPS depth profile of the PEALD Al2O3, 100 °C, 2 s layer after porosity measurement showing the atomic concentrations as function of the depth.