Plasma-enhanced atomic layer deposition
of binary metal oxides
as gas barrier layers on polymers

PhD Thesis

submitted by
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Faculty of Chemistry and Biochemistry
Ruhr-University Bochum
This thesis was written as publication based dissertation, comprising the details and results of the research carried out between October 2013 - July 2017 in the group *Inorganic Materials Chemistry* at Ruhr-University Bochum.

Supervisor: **Prof. Dr. Anjana Devi**

Co-supervisor: **Prof. Dr. Peter Awakowicz**

I hereby declare that the submitted thesis is my own unaided work. All direct or indirect sources used are acknowledged as references. I further declare that I have not submitted this thesis in this or in a similar form to any other university or college.

Bochum, October 2017

Maximilian Gebhard
From the warning signs at the 3-Mile-Resthouse at the Grand Canyon National Park, Arizona, USA, July 27th 2017:

*Down is obligatory, up is mandatory*
Acknowledgments

The following acknowledgments are written in German on purpose, as this is the best way to express my sincere gratitude to all the people who supported me during the last years.

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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>AC/DC</td>
<td>Alternating current/Direct current</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>ALE</td>
<td>Atomic layer etching (also atomic layer epitaxy)</td>
</tr>
<tr>
<td>BOPP</td>
<td>Biaxial oriented polypropylene</td>
</tr>
<tr>
<td>CCP</td>
<td>Capacitively coupled plasma</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary metal-oxide-semiconductor</td>
</tr>
<tr>
<td>EA</td>
<td>Elemental analysis</td>
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<tr>
<td>ECWR</td>
<td>Electron cyclotron resonance wave</td>
</tr>
<tr>
<td>FET</td>
<td>Field-effect transistor</td>
</tr>
<tr>
<td>FEBID</td>
<td>Focused electron beam induced deposition</td>
</tr>
<tr>
<td>GBL</td>
<td>Gas barrier layer</td>
</tr>
<tr>
<td>(GI)-XRD</td>
<td>(Grazing incidence) X-ray diffraction</td>
</tr>
<tr>
<td>GIZO</td>
<td>Gallium-indium-zinc-oxide</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>GPC</td>
<td>Growth per cycle</td>
</tr>
<tr>
<td>HiPIMS or HPPMS</td>
<td>High power Impulse magnetron sputtering or High power pulsed magnetron sputtering</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>---------</td>
<td>------------------------------------------------</td>
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<tr>
<td>MEMS</td>
<td>Microelectromechanical systems</td>
</tr>
<tr>
<td>MGPC</td>
<td>Mass gain per cycle</td>
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<tr>
<td>MuGFET</td>
<td>Multiple-gate-FET</td>
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<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>NRA</td>
<td>Nuclear reaction analysis</td>
</tr>
<tr>
<td>OTR</td>
<td>Oxygen transmission rate</td>
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<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>PLA</td>
<td>Polylactic acid</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
</tr>
<tr>
<td>RAM</td>
<td>Random access memory</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive ion etching</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford backscattering</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SLD</td>
<td>Solution layer deposition</td>
</tr>
<tr>
<td>SSP</td>
<td>Single source precursor</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conducting oxide</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<tr>
<td>TFEL</td>
<td>Thin film electroluminescent</td>
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<tr>
<td>TFT</td>
<td>Thin film transistor</td>
</tr>
<tr>
<td>TMI</td>
<td>Trimethylindium</td>
</tr>
<tr>
<td>TMD or TMDC</td>
<td>Transition metal dichalcogenide</td>
</tr>
<tr>
<td>TTFT</td>
<td>Transparent thin film transistor</td>
</tr>
<tr>
<td>VUV</td>
<td>Vacuum ultraviolet</td>
</tr>
<tr>
<td>WVTR</td>
<td>Water vapor transmission rate</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
1. Introduction

Nearly every aspect in our life is connected in one way or the other to thin films, which are considered in this thesis to be of a thickness on the nanometer-scale. Whether it is the touchscreen of our smartphone we use\textsuperscript{11} the central processing unit (CPU) of the computer\textsuperscript{8} used to write this thesis or solar cells for energy harvesting,\textsuperscript{5} thin films of various materials are the essential components allowing the design and technical feasibility of modern devices. These are just simple examples, but they count for nearly everybody and can be supplemented by many other examples in terms of more advanced devices and applications: Each component in computers and semiconductor-based devices like random access memory (RAM) units and micro-electro-mechanical-systems (MEMSs),\textsuperscript{6} transistors like the metal-oxide-semiconductor-field-effect transistor (MOSFET) and all its recent enhancements like the multiple-gate-FET (MuGFET, FinFET),\textsuperscript{10} optical applications such as IR reflectors and broadband filters,\textsuperscript{11,12} sensing of harmful or toxic gases,\textsuperscript{13,15} catalysis in water splitting\textsuperscript{16,19} and the protective coatings of tools to increase their wear-resistance are,\textsuperscript{20,21} again, just a few addings to this list. As the spectrum of thin film application covers virtually an infinite amount of examples, it is for the sake of convenience and clarity that this thesis will not discuss all of them in detail.

One example of thin film application is their usage as gas barrier layers (GBLs) to improve the barrier performance of packaging materials. Sensitive goods, such as foods, beverages, pharmaceuticals and electrical devices are often degraded by
CHAPTER 1. INTRODUCTION

oxygen gas or water vapor and standard packaging materials, like polymers, do not meet the requirements for protection in many cases. By adding a coating to these packaging materials, the barrier performance can be increased significantly.

In the following, this thesis will focus on the application of thin films as gas barrier layers (GBLs) on polymers, in particular discussing the materials aluminum oxide (Al\(_2\)O\(_3\), alumina), silicon oxide (SiO\(_2\), silica) and titanium oxide (TiO\(_2\), titania) and their deposition by means of plasma-enhanced atomic layer deposition (PEALD).

While this topic will be discussed in the chapters 2, 3 and 4, one has to consider the fact that the synthesis of thin films is not trivial and a huge scientific community works on both the fundamentals and applications of thin film deposition, the development of new materials and novel applications. Furthermore, a countless number of industries rely on the fabrication of these materials, indicating the necessity of further research carried out in this fascinating field of science. Therefore, different thin film deposition methods will be discussed in section 1.1 with a special focus on atomic layer deposition (ALD) and plasma-Enhanced atomic layer deposition (PEALD), with the latter one being the central deposition technique for the studies carried out in this thesis. In due turn, the term plasma is of high importance for the carried out research projects, which is why it is discussed in more detail in section 1.5. Finally, the introduction will conclude with an overview of the state of the art on GBLs on polymers and the most recent developments, in particular on those GBLs deposited by means of PEALD.
1.1. Thin film deposition methods

Thin films can be fabricated by several techniques and the most common ones are listed in Table 1.1, separated by their classification, and will be discussed in the following.

<table>
<thead>
<tr>
<th>CSD related</th>
<th>PVD related</th>
<th>CVD related</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin coating</td>
<td>Molecular beam epitaxy (MBE)</td>
<td>Metal-organic CVD (MOCVD)</td>
</tr>
<tr>
<td>Dip coating</td>
<td>Sputtering</td>
<td>Atomic layer deposition (ALD)</td>
</tr>
<tr>
<td>Spray coating</td>
<td>Evaporation</td>
<td>Plasma-enhanced ALD (PEALD)</td>
</tr>
<tr>
<td>Solution layer deposition (SLD)</td>
<td>High power pulsed magnetron sputtering (HPPMS)</td>
<td>Focused electron beam induced deposition (FEBID)</td>
</tr>
<tr>
<td></td>
<td>Pulsed laser deposition (PLD)</td>
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</table>

1.1.1. Chemical solution deposition

Owing to the simple setups and necessary equipment, chemical solution deposition (CSD) is known in particular for its low costs of the fabrication process, which is of high importance for the industry. With CSD, a broad variety of materials (e.g. ZnO, In$_2$O$_3$, SnO$_2$, ZnO–In$_2$O$_3$ (ZIO), In$_2$O$_3$–SnO$_2$ (ITO), ZnO–SnO$_2$ (ZTO) and In$_2$O$_3$–ZnO–SnO$_2$ (IZTO)) can be deposited, and also the fabrication of advanced electrical devices like transistors is possible. In CSD approaches, a precursor is dissolved in a solvent before it is applied to a substrate surface, either by dipping the substrate into the solution (dip coating) or by dispensing the precursor-solution on the substrate (spray coating and spin coating). In spin-coating, the substrate is
rotated, causing the solution to spread out evenly over the whole surface and thereby producing a homogeneous coating. In most cases, a heating and/or annealing step is performed to get rid of the solvent and to enable a chemical reaction, forming the desired material. By CSD, nearly every metal oxide and also carbon-nanotubes (CNTs) and solution-processed thin film solar cells can be produced. Recently, solution layer deposition (SLD) was reported as a new deposition method. In principle, this technique follows the dip-coating approach, with the difference that the formation of a metal oxide layer is repeated as often as desired.

1.1.2. Exfoliation

Mechanical exfoliation is a fabrication method especially feasible for 2D-materials like graphene and the transition-metal dichalcogenids (TMD or TMDCs) like WS$_2$, WSe$_2$, WTe$_2$, MoS$_2$, MoSe$_2$ and MoTe$_2$. These materials have attracted a lot of interest during the last years, owing to their fascinating electrical and optical properties, making them promising candidates to substitute established materials, like transparent conductive oxides (TCO) such as In$_2$O$_3$ or ZnO, in opto-electrical devices. For crystalline graphene, a zero-band-gap semiconductor with remarkable high transparency, the related properties arise from its unique electronic structure, based on a single-layer array of sp$^2$-hybridized orbitals. On the other hand, the TMDC materials and their properties are based on a different but highly interesting bonding situation. While strong covalent bonds are present within the sheets, for example having a molybdenum-atom with a sixfold coordination geometry toward sulfur atoms and a threefold coordination of the respective sulfur atoms in MoS$_2$, the bonding situation between two sheets is different, as only weak van-der-Waals attraction forces are formed. These weak attraction forces are also the reason for the possibility to produce highly pure monolayer or low-level multilayer sheets, i.e. thin films, of graphene or TMDCs by mechanical exfoliation, using a simple scotch-
tape. Using chemical exfoliation, the fabrication of graphene oxide (GO) is possible. This material must be considered as a complete different one than graphene, as the surface consists of a heterogeneous mixture of both sp$^2$ (graphene, C=C bonds) and sp$^3$-hybridized (C-O and C-C bonds) orbitals. However, this material is of high interest as well as it exhibits, for example, a high fluorescence over a broad wavelength range, while graphene shows no luminescence at all.

### 1.1.3. Physical vapor deposition

While CSD techniques and exfoliation are cost-efficient, so-called vapor phase approaches are considered to yield thin films of superior quality, especially with respect to reproducibility and composition. In general, vapor phase approaches can be divided into two groups: Physical vapor deposition (PVD) and chemical vapor deposition (CVD). In PVD methods, the starting material is usually of the same kind as the desired thin film, e.g. an Al-target for the deposition of Al-metal thin films through sputtering. In contrast to the CSD related methods, PVD techniques are based on the fact that atoms, ions, molecules or (charged) clusters of atoms travel from a source through a vacuum to the substrate to form the desired material and deposition occurs, usually, due to physical phenomena, such as condensation on a substrate. Of course, deposition including chemical reactions and preceding chemisorption on the substrate are known as well for PVD processes. Prior to deposition, the film-forming components must be brought into the gas phase, which can be achieved by different approaches. For example, thermal evaporation of a certain material in a Knudsen cell enables the deposition via a molecular beam, with which also epitaxial growth can be facilitated. Therefore, it is called molecular-beam epitaxy (MBE). This technique allows the deposition of mixed metal oxides, nitrides, chalcogenids and alloys by simply using several Knudsen cells at the same time. In contrast to this, the evaporation of atoms from a target using
CHAPTER 1. INTRODUCTION

laser-techniques is referred to as pulsed laser deposition (PLD) or laser ablation.\cite{39,41}

A third method in PVD to evaporate atoms from a target is sputtering. Commonly, for this technique a noble gas plasma is used. The plasma causes a bombardment of the target surface by positively charged, heavy noble gas ions (usually $\text{Ar}^+$), which cause the ejection of neutral and charged particles/atoms from the surface. Sputtering of a target can be achieved by applying a direct current (DC) to the target (negative electrode, cathode) and the substrate (positive electrode, anode), thereby generating a gas discharge. As charge carriers are accelerated continuously toward the substrate, charging effects occur if insulating materials are deposited, making the deposition of insulators not feasible by this technique. This drawback is overcome by using an alternating current (AC) and high-frequency (HF) sputtering\cite{42,46} is the nowadays commonly used sputter technique for thin film deposition. A more detailed discussion on the generation of plasmas can be found in section 1.5, page 31.

The efficiency of sputter processes can be increased by placing magnets behind the target, thereby generating a magnetic field in close vicinity to the target surface. This approach is called magnetron-sputtering. Due to the superposition of the electric and the magnetic field, the electrons will now move along helical trajectories, increasing the lengths of their pathways. From this, the overall electron density in the target surface vicinity is increased, consequently causing more impacts and a higher sputtering rate. Thereby, obviously the deposition rate is increased as well.

A further improvement can be found in high-power pulsed magnetron sputtering (HPPMS), also called high-power impulse magnetron sputtering (HiPIMS).\cite{42,43} In general, the efficiency of sputtering is increased by higher power input. Since an increased amount of power will directly induce heating to the target, substrate and other components in the deposition chamber, the power supply needs therefore to be operated in short pulse to avoid overheating and damage of these components. In
contrast to DC-magnetron sputtering, HPPMS employs high power densities with low duty cycles $\leq 10\%$, achieved by microsecond short pulses. From this, a high degree of ionization and increased growth rates can be obtained. In addition, the film quality in terms of density and purity is strongly improved.

In general, the described PVD methods are used to deposit alloys or pure metal thin films. However, by introducing a reactive gas, such as ammonia, nitrogen or oxygen, the deposition of metal oxides and nitrides is possible by reactive sputtering. While the metal atoms are ejected by the above mentioned plasma, a reactive gas is introduced into the chamber close to the substrate surface, thereby enabling chemical reactions and the formation of more complex thin films and materials. Also for HPPMS, the usage of reactive gas has been reported, allowing the deposition of oxide and nitride materials together with the benefits from HPPMS.\textsuperscript{[47]}

### 1.1.4. Chemical vapor deposition

All the briefly discussed PVD methods are able to produce thin films and materials of good quality in terms of stoichiometry and impurities, crystallinity and functional properties. However, PVD methods often suffer from certain drawbacks such as line-of-sight-deposition, which makes it challenging to coat three-dimensional structures with a homogeneous thin film in terms of step coverage and overall thickness. In addition, the evaporation of a source material is limited with respect to sensitive components of the reactor chamber, which could be damaged and need extensive and complex protection against the high sublimation temperatures, which are required for several metals.

CVD has been investigated since the mid of the 20th century and today, various books are on hand, providing a substantial overview and detailed information on this thin film deposition technique.\textsuperscript{[48,49]} In CVD, lower temperatures for evap-
oration can be achieved by using metal complexes instead of the pure metal target, which usually exhibit high vapor pressures at reasonable temperatures, mostly below 200 °C. Obviously, the limitations in CVD are directly linked to the precursor’s thermal properties, as a convenient evaporation temperature combined with high thermal stability, i.e. high shelf-life without decomposition, must be on hand. In CVD, a broad variety of precursors can be applied, ranging from inorganic salts, such as simple halide-compounds, up to metal-organic complexes with a user-defined ligand sphere. In particular, employing bulky organic ligands enables the possibility to lower the evaporation temperature together with enhanced thermal stability of the precursor, providing thereby a higher controllability of the process. By this approach, molecular engineered precursors can be obtained, allowing the usage of virtually all metals of the PSE. This technique is referred to as metal-organic chemical vapor deposition (MOCVD) and resembles a common method to deposit thin films of high quality in terms of crystallinity, composition and coverage over large surface areas. Using this technique, also the epitaxial growth of single-crystalline materials can be achieved.

Using different reactive gases, CVD and MOCVD can be used to deposit pure metals (reducing atmosphere using H₂ or oxygen-assisted pyrolysis), oxides (oxygen (O₂) or ozone (O₃)), nitrides (NH₃), sulfides (single-source precursors, H₂S or sulfur) and also selenides and tellurides (alkyl compounds of Te and Se (SeMe₂, SeEt₂ and TeMe₂, TeEt₂) or the pure elements as powders). There are also several so-called single-source-precursors (SSPs), which don’t need a reactive gas to deposit the respective oxides or nitrides. Such SSPs usually comprise respective metal-oxygen or metal-nitrogen bonds already in the precursor. If these SSPs are decomposed in a non-poisoned vacuum, i.e. a highly clean vacuum, the already existing bonds facilitate the formation of the respective oxide or nitride materials without the incorporation of impurities.
1.1. THIN FILM DEPOSITION METHODS

Usually, in CVD and MOCVD the temperature of the substrate is much higher than the evaporation temperature, initiating on the one hand a decomposition of the precursor close to or on the substrate surface and, secondly, providing energy to make the chemical reactions, forming the thin film, more efficient.

While the mechanisms in PVD methods are usually easy to understand and are limited to adsorption, desorption and surface migration, one has to keep in mind that in CVD and MOCVD by-products are generated continuously. This leads to a heavily crowded regime above the substrate surface, where precursor molecules, respective fragments and by-products are permanently adsorbing, desorbing and migrating over the surface, making the prediction of growth more challenging.

CVD approaches are known to yield thin films with excellent properties, especially with respect to crystallinity and the broad variety of easily obtainable materials. As CVD is a continuous process, the growth rates are rather high with up to hundreds of nanometer per minute. Another option, referred to as plasma-enhanced CVD (PECVD), to deposit thin films is the plasma-polymerization of monomers, for example using hexamethyldisiloxane \( \text{O}[\text{Si(CH}_3\text{)}_3]_2 \), HMDSO or hexamethyldisilazane \( \text{HN}[\text{Si(CH}_3\text{)}_3]_2 \), HMDSN to fabricate SiO\(_x\) or Si\(_x\)N\(_y\).[67][68] It should be noted that PECVD is not a PVD related method, as the deposition of the thin film occurs via chemical reactions, rendering it as a CVD technique.

Also considered as gas phase technique but substantially different from CVD is atomic layer deposition (ALD). This technique demonstrates to be, while extensively investigated during the last decades and implemented in state-of-the-art industries (Intel\(^\text{®}\).[70] to be a rather new method for thin film deposition and was patented in 1977 by Suntola et al.[71] For the sake of clarity, ALD and its growth mechanisms will be discussed in section 1.3 in more detail.
1.2. Thin film growth mechanisms in PVD and CVD

The fabrication of thin films is, apart from exfoliation, a bottom-up process. Therefore, the suitability of a deposited material for certain application depends strongly on the how the growth of the thin film takes place. Numerous factors, like temperature, boundary layer (kinetics) and pressure (mean-free path of the atoms and/or molecules) contribute to the growth mechanisms and it is beyond the scope of this thesis to discuss all potential influences from these and more parameters. However, one commonly distinguishes three simple different growth modes:

- Frank-van-der-Merwe growth,
- Stranski-Krastanov growth and
- Volmer-Weber growth.

For the Frank-van-der-Merwe growth mode it is assumed that the growing film has a similar sticking coefficient to both the underlying substrate and the growing thin film. Therefore, homogeneous thin films without peculiar surface structures are obtained.

The Stranski-Krastanov mode assumes a higher adhesion between the first layer of the deposited thin film and the substrate than between the layers of the growing film, causing a island-like growth. This growth mode is favored for the fabrication of quantum-dots, like indium-arsenide, InAs.\footnote{21}

Finally, in the Volmer-Weber growth mode a much higher adhesion of the growing film is found within the film, leading to a island-like-dominated growth, causing the thin film to be of high active surface area. For example, this growth is preferred for the deposition of catalyst materials.

As mentioned above, the film growth during CVD and MOCVD is highly complex as several chemical reactions take place at the same time, but are not necessarily
1.2. THIN FILM GROWTH MECHANISMS IN PVD AND CVD

concerted. A schematic of a CVD process is shown in figure 1.1 illustrating the deposition, employing a generic precursor and reactive gas, forming a binary metal oxide on the substrate surface. In total, six different steps can be distinguished, finally leading to thin film deposition.

1. Diffusion of the precursor and the reactive gas through the boundary layer toward the surface,

2. chemical reactions in the gas phase, forming by-products of various kinds (sometimes also gas phase precipitation),

3. chemisorption of gas phase species on the substrate surface,

4. chemical reactions on the substrate surface,

5. migration/surface diffusion of surface species and

6. desorption of by-products and unreacted precursor molecules.
Assuming the precursors to be simple ones like AlCl$_3$ and oxygen as reactive gas and by neglecting excited and charged states of the different molecules as well as the formation of dimers or even oligomers, a total of eleven different, mostly only short-living, molecular compounds are possible: AlCl$_3$, O$_2$, Al$^{3-}$, $O^{2-}$, Cl$_2$, Cl$^-$, AlCl$_2$O$, AlClO$_2$, AlO$_3$, ClO$^-$ and OCl$_2$. These eleven molecular compounds can now undergo further chemical reactions with each other in every possible permutation and will perform the above listed different steps in a non-ordered fashion. Assuming that those reactions involve in each case only two of these eleven possible chemical compounds, 66 chemical reactions are possible. Considering the complex organic ligands usually used to tailor precursors for application in MOCVD, the outlined example can be further pushed toward unreasonable orders of magnitude. Obviously, this is an exaggerated point of view. However, taking into account the above mentioned exceptions one can easily understand that the prediction of growth mechanisms in MOCVD is extremely challenging and that the incorporation of impurities, especially at lower temperatures, is likely.
1.3. Atomic layer deposition

A series of PVD related deposition techniques suffer from drawbacks like line-of-sight-deposition or poor step-coverage, thereby complicating the coating of high-aspect-ratio structures as found for trenches of DRAM units. CVD and MOCVD processes are, despite the lower evaporation temperatures for the precursors, often operated at high temperatures with respect to the substrate region, \( i.e. \) where the deposition takes place, leading to high growth rates. Such elevated temperatures and high growth rates cause the incorporation of by-products, leading to non-homogeneous thin films with respect to composition as well as roughness, thereby affecting the functional properties. Furthermore, the so called boundary layer above the substrate, caused by the mass transport dynamics, can induce a strong gradient of the thin film thickness. While this issue can be overcome by a tilted susceptor, allowing a more homogeneous film thickness over the whole substrate, the general challenge of inhomogeneous thickness still prevails.

A technique which is able to deal with all these raised issues is atomic layer deposition (ALD), a straight-forward thin film deposition method with unique characteristics in terms of fine-tuned growth modes for high quality thin films. ALD is, in contrast to the continuous deposition in CVD, a discontinuous and cyclic operated process, consisting of two self-limiting half-cycles, also referred to as half-reactions, and was patented in 1977 by Suntola and Antson. It should be noted that a similar technique, back than called "molecular layering" was invented in the Soviet Union in the 1960s. The development of ALD was driven by the demands from the industry with respect to the fabrication of electroluminescent thin film transistors (TTFTs) to build large and efficient displays for mass-production. At this time, ALD was described as atomic layer epitaxy (ALE). However, most of the thin films produced by this technique are amorphous or polycrystalline in their structure and
around the year 2000, the community adopted the term ALD for a more precise description. In addition, the term atomic layer etching, which refers to the precise removal of monolayers, is abbreviated ALE as well. This technique, which is described briefly in section 1.3.2 is of high importance for the semiconductor industry and the acronym ALE is commonly used in the ALD research community. Indeed, both the ALE technique and ALE community originate from the respective ALD counterparts, which is underlined by the fact that in 2014, a satellite-workshop on ALE was part of the international ALD conference. In 2015, this workshop became a stand-alone one-day event at the ALD conference and since 2016, ALD and ALE topics are presented and discussed at this conference without being artificially separated.

The first developed material by ALD was ZnS, which was used for the fabrication of the above mentioned TFTs and in 1983, a giant electroluminescent display, partially fabricated using ALD, was installed at the Helsinki airport, running until 1998. Since its development and patenting, much effort, both in the industry and academia, was dedicated to study and understand established, as well as to develop, ALD processes. Review articles on the topic of ALD cover nearly every aspect, ranging from general overviews over more detailed approaches toward a class of materials, like 2D-materials, or theoretical approaches up to those highly focused ones which cover the progress for only one material, e.g. ZnO. In addition, since 2013 a project called Virtual Project on the History of ALD devotes remarkable effort on the collection of past and presents reports based on ALD. Furthermore, the historical development of ALD since its patenting was summarized by Riikka Puurunen in 2014. It should be noted that in the ALD research community, a fa-

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*ahttp://www.vph-ald.com/*
1.3. ATOMIC LAYER DEPOSITION

A simpliﬁed schematic of an ALD cycle, showing the four fundamental steps in ALD. 1) Precursor dose; 2) Purge and surface saturation; 3) Co-reactant dose; 4) Second purge and monolayer formation of the desired material.


duous blog site is maintained and updated by Jonas Sundqvist, providing detailed information for everybody who is interested in this fascinating technique. It is above the scope of this thesis to discuss every ALD process that has been reported until today. However, the basics of ALD will be outlined and discussed below giving the exemplary details on different aspects of ALD. In particular, plasma enhanced atomic layer deposition (PEALD) will be discussed in section 1.4. In addition, sections 1.3.1 and 1.3.2 will provide a short excursus on the topics molecular layer deposition (MLD) and ALE, which are closely related to ALD.

A schematic of an ALD cycle is shown in Figure 1.2 illustrating the steps leading to ALD-like growth. Similar to CVD, metal-complexes are used as precursors. In a first step, a precursor dose is introduced into the reaction chamber. While the pre-
cursor chemisorbs at reactive surface sites (e.g. hydroxyl-groups, -OH), an excess of the precursor is purged out of the chamber by applying an inert gas purge (second step). During this half-cycle, assuming a sufficiently long enough precursor pulse, a chemisorbed monolayer of the precursor is formed on the substrate surface, virtually covering the whole area. In a third step, a so-called co-reactant is introduced into the chamber. This co-reactant chemically reacts with the earlier chemisorbed monolayer of the precursor fragments, thereby transforming the precursor and depositing exactly one monolayer of the desired material. In a fourth step, a second inert gas purge is applied to get rid of reaction by-products and excess of the co-reactant. These four steps sum up to one ALD-cycle, which can be repeated as often as desired. Comparing this growth mechanisms for an ideal ALD process with those taking place during MOCVD, a much simpler, less complex and more predictable deposition is on hand, making ALD an unique thin film deposition method. From the above outlined process, three so-called ALD criteria can be extracted:

- A temperature-independent growth over a certain temperature range,
- a saturative behavior of the growth rate vs. the precursor dose length and
- a linear correlation of thin film thickness vs. applied number of cycles.

Schematics of these three criteria are depicted in figure 1.3 and are explained in the following.

For a temperature-independent growth, a perfect combination of the precursor’s reactivity and stability must be on hand. From figure 1.3a), four situations can be found, where the boundaries toward temperature-independent growth are overcome and ALD-like growths fails. If the temperature is too low to ensure sufficient chemical reactions between the precursor and reactive site, or if the sticking coefficient is too low (red dots), thin film growth is inhibited. In this case, the formation of
monolayers is unlikely and incomplete coverage of the substrate surface is the consequence. In addition, if the sticking coefficient of the precursor is high enough but the chosen temperature is too low to ensure complete reactions, i.e., cleavage of the remaining ligands and transformation toward the desired material, condensation of the precursor on the substrate surface occurs (blue dots). In this case, the grown films are often non-stoichiometric and the purity is poor, as ligand fragments are incorporated into the growing film. The green dots illustrate parasitic CVD growth at elevated temperatures. In this case, the precursor decomposes readily and gas phase precipitation is likely, causing an increased growth rate. While these films tend to exhibit a higher crystallinity due to thermodynamics, such films are also of poor quality in terms of surface roughness as the growth occurs in a continuous manner and is barely controlled. A fourth situation can be found again at higher temperatures with decreased growth rate (yellow dots). Here, precursor desorption is the major contributing mechanism. In between of all these possible cases, the so-called ALD window can be found. In this temperature range, the reactivity of the metal precursor toward the substrate surface is high enough to form a monolayer without facing decomposition, gas phase precipitation or desorption.

In figure 1.3b), a typical growth rate behavior for a precursor exhibiting sufficient reactivity is shown. If the pulse length is not long enough, the growth rate is
strongly decreased. Obviously, it is hard to tell how long a sufficient pulse needs to be as this depends on the vapor pressure, temperature and reactivity of the precursor. Assuming a precursor dose being long enough to provide the necessary amount of molecules for surface saturation, an even longer pulse will not increase the growth as for this, new reactive surface sites needs to be established. This ideal case assumes that the precursor reacts only with the co-reactant and not with itself, i.e. by inter-molecular reactions.

Hence, assuming surface saturation and temperature-independent growth, the thickness of the growing thin film must be linear in dependency of the applied number of cycles. From these ALD criteria, the following benefits of ALD can be concluded:

- Depositions are possible at rather low temperatures,
- two-dimensional growth of the thin film,
- the grown thin films exhibit low roughness (usually of the same order of magnitude as the underlying surface),
- highly stoichiometric materials can be obtained,
- the thickness can be controlled easily and
- a high degree of reproducibility is on hand.

The reason why ALD yields thin films of high quality is based on the smart combination of low temperatures, in some cases around only below 200 °C, and a fine tuned reactivity of the precursor without gas phase precipitation. In addition, and in contrast to many other deposition techniques from PVD or MOCVD, ALD enables the possibility to coat three-dimensional structures and high aspect-ratios,
1.3. ATOMIC LAYER DEPOSITION

Figure 1.4.: Coverage of high aspect ratios using a) PVD, b) MOCVD or c) ALD. The arrows in the left image resemble the trajectories of incoming atoms/molecules from a molecular beam setup.

as the deposition is rather surface controlled than driven by kinetics. Figure 1.4 illustrates how ALD is able to overcome the line-of-sight deposition problem for complex structures in PVD as well as how the artifacts arising from high deposition rates in MOCVD can be avoided. With respect to Moore’s Law, this is an outstanding breakthrough and makes ALD the method of choice with respect to shrinking device dimensions. By using ALD, the implementation of the 45nm-technology from Intel® was possible, as it allows to produce working and reliable transistors based on high-k materials.

Using ALD, a broad variety of metal oxides, nitrides, sulfides, tellurides, and selenides can be deposited, thereby covering nearly the whole periodic table of elements with respect to the non-artificial produced metals. With respect to the transition-metal oxides TiO₂, ZrO₂ and HfO₂, the rare-earth metal oxides Y₂O₃, Gd₂O₃, Dy₂O₃ and Er₂O₃ as well as p-block oxides like In₂O₃, the success story of using guanidinate-ligands for tris-guanidinate-compounds of the respective metal should be mentioned and demonstrates some kind of breakthrough regarding novel precursor chemistry. Especially for the rare-earth oxides, the respective guanidinate compounds offered the chance to grow thin films at moderate temperatures for high-k application, without facing challenges from major carbon impurities. In addition, the usage of the guanidinate compounds is usually possible without highly reactive co-reactants like ozone and the film growth can be facilitated with high
growth rates using H$_2$O as the co-reactant. In 2016, the p-block amidinate Ca(amd)$_2$ was reported as ALD precursor to deposit CaS, using H$_2$S as co-reactant.\textsuperscript{99}

Pure metal thin films are accessible as well by using H$_2$ as a reducing agent, but the processes exhibit usually low growth rates and a strong pronounced nucleation delay.\textsuperscript{100,101} However, the common approach using H$_2$ as a reducing agent might be overcome in a few years, as several research groups are currently investigating the opportunities from using different reducing compounds. For example, [BH$_3$(NHMe)$_2$] together with the common silver precursor [Ag(fod)(PEt$_3$)] was employed by Mäkelä \textit{et al.} to deposit pure silver thin films.\textsuperscript{102} In addition, Winter \textit{et al.} demonstrated highly efficient ALD processes for copper, titanium and cobalt thin films with high growth rates per cycle (GPC), employing simple precursor compounds like [Cu(dmap)$_2$] together with formic acid and hydrazine, new developed Co-precursors together with formic acid or TiCl$_4$ together with the strong reducing agent 1,4-Bis(trimethylsilyl)-1,4-dihydropyrazine, respectively.\textsuperscript{103,105} Thermal ALD processes to deposit noble metal thin films are also investigated using theoretical approaches, thereby giving an insight into the mechanisms taking place on the substrate surface.\textsuperscript{108} Furthermore, in 2016 Barry \textit{et al.} reported the first successful thermal ALD of pure gold thin films and other groups are investigating the growth process in more detail currently.\textsuperscript{107,108}

1.3.1. Molecular layer deposition (MLD)

Since organic thin films attracted a lot of interest during the last years, which is due to their promising properties for different applications such as energy storing (Li-cells, Na-anodes)\textsuperscript{63,109} and thermoeletric devices,\textsuperscript{110} different groups worked on the development of suiting deposition methods. An interesting technique with high potential is molecular layer deposition (MLD), which is analogous operated as ALD while organic monomers are used as precursors. Based on simple organic reac-
1.3. ATOMIC LAYER DEPOSITION

tions, such as condensation-reactions, the deposition of organic thin films is easily achieved by MLD even at low temperatures. For example, the depositions of polymers like polyimides, polyureas, polyethylene-terephthalate (PET) and many more were reported during the last 20 years.

An even higher potential for the above mentioned applications and others, including gas barriers, can be found in the combination of ALD and MLD to grow inorganic-organic hybrid layers. ALD/MLD processes were shown to enable the fabrication of metal-cone materials, with the first example being reported in 2008 by George et al. for aluminum-alkoxides. Since then, also mangancone, zircones, titanicones, zircones, hafnicones, and vanadicone were reported as well. In 2017, a remote-plasma assisted ALD/MLD process was reported for the deposition of zircones by Zhao et al., demonstrating the possibility to combine the advantages of ALD/MLD materials with the beneficial attributes from plasma-assisted deposition procedures. For such a process, the first half-cycle usually employs a metal-organic precursor and the second half-cycle provides an organic molecule with sufficient reactivity toward the precursor. A simple example for such a process is the combination of TMA with ethylene-glycol (ethan-1,2-diol). As for ALD and a given sufficient reactivity, ligand exchange or condensation reactions take place, forming the hybrid material. In the above mentioned example, the Al-O-bonds are separated by the organic backbone of the glycol molecule. Thus, the combination of the functional properties of both the inorganic part (metal-ions, strong metal-oxygen bonds) and the organic part (tunable flexibility, electronic structure from aryl-groups and bigger conjugated systems) is possible and allows the fabrication of novel materials. Recently it was shown by Svärd et al. that from ALD/MLD even complicated materials can be obtained by applying more complex feeding sequences, allowing the initiation of advanced chemical reactions like ozone-triggered ring-openings.
1.3.2. Atomic layer etching (ALE)

ALD is one of the driving forces behind the development of smaller transistors, which are necessary to meet the demands from our society in terms of faster and more efficient processors, influencing nearly every aspect of our daily life. In this context, the whole fabrication of integrated circuits (ICs), particularly the front-end-of-line (FEOL) process, is based on the patterning of the individual devices on the semiconductor substrate. For this, besides the deposition of high-k materials, insulators and semiconductors, also the etching of the same materials, varying from metal oxides, nitrides and pure semiconductors, is of high importance for precisely engineered computer components like transistors. Today, where Moore’s law brought the semiconductor industry below the nanoelectronic scale, the term precision means in particular the process variability regarding the fidelity on the atomic scale. While ALD allows the deposition of materials on the atomic scale, the removal of materials was operated in the past in a continuous manner using most extensively reactive ion etching (RIE). From a plasma, a mixture of ions, electrons and neutral species, the positively charged ions can be accelerated toward the substrate surface by applying a negative voltage bias to the substrate. Through this, directional etching is achieved, which is important for maintaining critical dimensions of a mask. Without the additional bias, isotropic etching occurs, causing the underlying film to be hollowed out, thereby destroying the device structure. RIE represents a continuous process with fast etch rates, where the removal of a material from the surface and the mass transport into the gas phase occur simultaneously. Thus, as for MOCVD, the volume above the substrate surface is extremely crowded and the delivery of reaction-driving species to the etch front is limited, making the whole process a transport-limited one. From this, the variability can be strongly affected and the process quality, in terms of precision, is decreased. With respect to the vast amount of transistors produced every day, the necessity to develop more
efficient and reliable processes is inevitable. Different approaches to overcome the transport-limitation and the variability were investigated and in some cases, optimized processes were developed, such as switching from batch-reactors to single-wafer reactors or by adding multiple frequencies to the plasma source to decouple the ion and neutral fluxes.\textsuperscript{125,126} However, damage from the plasma to the ICs and inhomogeneities at the etching front still prevail.

A promising technique, which gained a lot of interest over the last years, to overcome these issues is atomic layer etching (ALE),\textsuperscript{122,125,130} that is, analogous to ALD, a self-limiting, discontinuous process. As for ALD, the etching occurs due to sequential surface reactions. ALE processes used on an industrial scale are usually plasma-assisted processes. For example, the surface of a silicon substrate is subjected to Cl\textsubscript{2} gas (or chlorine plasma for higher etching rates), causing the formation of a silicon-chlorine-reactive layer. In a second step, an Ar\textsuperscript{+} ion bombardment activates the removal of the silicon-reactive layer. In between these two steps, excess chlorine and reaction products are purged out of the chamber.

George \textit{et al.} carried out the first reported research regarding a solely chemical driven ALE approach without using plasmas and in 2015, the first self-limiting, thermal (150 °C to 250 °C) ALE process employing HF and [Sn(acac)\textsubscript{2}], namely bis-(acetylacetonate)tin(II), to etch Al\textsubscript{2}O\textsubscript{3} was reported.\textsuperscript{131,132} In this process, the Al\textsubscript{2}O\textsubscript{3} surface is subjected in a first cycle toward [Sn(acac)\textsubscript{2}] and subsequently to HF. Using \textit{in-situ} quartz-crystal-microbalance (QCM), a first prediction of the surface reactions could be proposed: During the first cycle, adsorption of [Sn(acac)\textsubscript{2}], or respective dissociation products, takes place while the HF pulse transforms the first Al\textsubscript{2}O\textsubscript{3} layer into AlF\textsubscript{3}. In the following cycles, dosing of [Sn(acac)\textsubscript{2}] causes the formation of volatile [SnF(acac)] and [Al(acac)\textsubscript{3}]. These reaction products desorb and remove one monolayer of the Al\textsubscript{2}O\textsubscript{3} thin film, which can be transformed to AlF\textsubscript{3} by the next HF-dose. While the etch rates are rather low with only 0.27 Åcycle\textsuperscript{-1}, the thermal
ALE approach can provide new perspectives for the industry and increases the possibilities of IC processing. Currently, investigations are carried out to understand the mechanisms of thermal ALE, employing different chemical compounds, to etch TiN (O$_3$/HF), SiO$_2$ and ZnO (TMA/HF), as well as WO$_3$ (BCl$_3$/HF).
1.4. Plasma-enhanced atomic layer deposition (PEALD)

While ALD and MLD allow the deposition of numerous materials at much lower temperatures compared to conventional CVD processes, the temperatures are in many cases still too high as sensitive structures (e.g. electrical circuits) or polymer substrates might be damaged. While reports on ALD at or close to room-temperature are manifold, the respective processes are, in the most cases, extremely long with respect to precursor doses and purging steps. ALD at room temperatures is also challenging with respect to developing a process following ALD criteria, in particular the criterion on saturation and the formation of monolayers. This is due to the fact that the applied precursors must be heated in nearly all cases to achieve a sufficient vapor pressure. Thus, if the precursor exhibits a higher temperature than the substrate surface, the mechanisms taking place are easily overlaid by condensation on the surface instead of chemisorption. From this, both the reproducibility and thin film quality suffer tremendously. Furthermore, the development and optimization of processes toward ALD growth mechanisms strongly depends on the availability of suitable precursors, exhibiting a high reactivity and ease of handling while having a high vapor pressure at room temperature. While precursors with low reactivity might be used in principle, a complete coverage of the surface is often hindered, thus producing thin films without two-dimensional and inhomogeneous growth, causing the formation of pinholes. With lower deposition temperature, also often a lower density of inorganic materials is accompanied, thereby yielding thin films of poor quality. In addition, low substrate temperatures are not beneficial if a crystalline material is desired.

These shortcomings can be overcome by applying a plasma discharge during the third step of an ALD cycle instead of just pulsing a simple co-reactant, making it a
PEALD has been studied since many years and, as mentioned for ALD above, an blog site has been implemented to serve as an online library, collecting all available resources regarding PEALD. In literature, the terms plasma ALD, PEALD, plasma-assisted ALD, radical-enhanced ALD and energy-enhanced ALD are used more or less synonymously. In principle, one might distinguish between the solely radical-enhanced and the plasma-assisted processes, with the first employing only neutral species and the latter one consisting of a typical plasma, a mixture of ions, electrons and neutral particles. The first one is usually obtained by operating a so-called remote plasma, where long-living radical species are able to travel further than the ions and electrons, which exhibit higher recombination probabilities. However, in nearly all studies the plasma characteristics, ion or neutral fluxes toward the substrate surface are not reported, making a classification within these limitations challenging.

It should be noted that in contrast to PECVD, the plasma consists only of the co-reactant and respective plasma species, while the metal-organic precursor is, ideally, not part of the plasma. This is achieved by the above described discontinuous feeding sequence. In PECVD, the precursor is often called monomer and is polymerized by applying the plasma to the whole gas-mixture, consisting of the monomer and a reactive gas such as oxygen. Therefore, the films deposited by means of PECVD are also called plasma polymers, which is abbreviated PP in some cases. To avoid confusion, throughout this thesis the term PP refers to the polymer polypropylene.

For example, an oxygen plasma can be used instead of water as co-reactant, generating highly energetic plasma species which react with the previous pulsed precursor (Figure 1.5). In principle, the ignition of a plasma is possible with every...
1.4. PLASMA-ENHANCED ATOMIC LAYER DEPOSITION (PEALD)

Figure 1.5.: A simplified schematic of a PEALD cycle. In contrast to an ALD process, the third step includes the generation of a plasma discharge, thereby generating species with high reactivity.

chemical compound which can be vaporized. Obviously, the usage of simple compounds, which are preferably gaseous at room temperature, is the most reasonable approach in this context. For the deposition of oxides, nitrides and pure metal thin films usually oxygen (O$_2$), water (H$_2$O), nitrogen (N$_2$), ammonia (NH$_3$) or hydrogen plasmas are used. Two-Dimensional WS$_2$ has been recently reported as well, employing WF$_6$, H$_2$S and a H$_2$-plasma.

In ALD, usually the parameters evaporation or substrate temperature, pressure, precursor dosing and purging pulse lengths and the co-reactant are those which are used to fine-tune a process toward optimal thin film growth according to ALD mechanisms. In PEALD, parameters like the plasma source, ion fluxes, plasma sheath, electron density, chemical reactions taking place in the plasma and many more will add and should be considered with respect to optimizing a process. Therefore, several merits arise from PEALD, which are listed below, and most of them are directly
connected to the high-energetic plasma species:

- Improved density: The high reactivity from the plasma causes a higher degree of cross-linking.\cite{88,150,151}

- Electronic properties: By applying $\text{H}_2$ or $\text{N}_2$-plasmas, the resistivity of conducting materials can be fine-tuned or doping of oxides is achieved, respectively.\cite{152,153}

- Excellent control of thin film composition: with the high reactivity provided by the plasma, the complete combustion of organic ligands of a precursor is achieved easily. In addition, incorporation of C and N (in the case of oxides) on the surface can be avoided by applying a longer plasma step, thereby favoring the formation of oxides over carbides and nitrides.\cite{149,154,155}

- Higher growth rates: Again, the reactivity of the plasma species allows more readily chemical reactions on the surface, thereby leaving no voids after a cycle, making the deposition more efficient.

- Broader variety of precursors: less reactive precursors can be activated using the high-energy species, thereby enabling the opportunity to fine tune the final materials properties in dependency of the chosen precursor.

- Drastically decreased substrate temperature: While thermally driven reactions on the substrate surface are hindered, the non-thermally ones can be facilitated by the plasma (non-equilibrium).

- Combination of CVD, ALD, MOCVD, PECVD and PEALD: With a plasma source being attached to a reactor chamber, CVD related processes can be combined to deposit composite materials, exhibiting the properties from different deposition techniques or enabling the synergy of different methods. In addition, the post- and pre-treatment of substrates and thin films is possible.
1.4. PLASMA-ENHANCED ATOMIC LAYER DEPOSITION (PEALD)

As mentioned above, one of the biggest advantages of PEALD compared to ALD and other deposition techniques is the ability to deposit thin films at or close to room-temperature. From this, a great potential in terms of coating sensitive substrates arises, making PEALD the method of choice when such substrates are the limiting factor. The reason why PEALD can be operated at such low substrate temperatures is found in the characteristics of a low-pressure plasma, which is discussed in detail in section 1.5. Table 1.2 provides an overview of reported PEALD processes operating at low temperatures, giving the most important details on the deposited materials, precursors, substrates and deposition temperature $T_{\text{dep}}$. It should be mentioned that some of the listed processes operate at elevated temperatures ($\geq 150°C$). However, these processes were reported as "low-temperature" processes in literature.
Table 1.2.: Overview of PEALD processes operating at low temperatures.

<table>
<thead>
<tr>
<th>Material</th>
<th>Precursor</th>
<th>Substrate</th>
<th>T&lt;sub&gt;dep&lt;/sub&gt; (°C)</th>
<th>Ref.</th>
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<td>PP, blend of PET/cotton</td>
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<td>[160]</td>
</tr>
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<td>Quartz/Au</td>
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<tr>
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<td>DMAD&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Silicon, PET</td>
<td>60</td>
<td>[172]</td>
</tr>
<tr>
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<td>DMAD</td>
<td>Silicon, PP</td>
<td>30</td>
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<tr>
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<td>[(hfac)Cu(l)(DMB)]&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Silicon, soda-lime glass</td>
<td>100</td>
<td>[173]</td>
</tr>
<tr>
<td>Ga&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>[Ga(TMHD)&lt;sub&gt;1&lt;/sub&gt;]&lt;sup&gt;5&lt;/sup&gt;</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;/Si</td>
<td>100-400</td>
<td>[174]</td>
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<tr>
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<td>[Ga(NMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;6&lt;/sup&gt;</td>
<td>silicon, SiO&lt;sub&gt;2&lt;/sub&gt;, quartz</td>
<td>60</td>
<td>[174]</td>
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<td>HfO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>TDMAH&lt;sup&gt;7&lt;/sup&gt;</td>
<td>Long period gratings, Si</td>
<td>150</td>
<td>[175]</td>
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<td>In&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Me&lt;sub&gt;2&lt;/sub&gt;ln(EDPA)&lt;sup&gt;8&lt;/sup&gt;</td>
<td>ITO</td>
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<td>[175]</td>
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<td>BDEAS&lt;sup&gt;9&lt;/sup&gt;</td>
<td>Si(100), PET</td>
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<td>FTO, ITO/PET</td>
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<td>60</td>
<td>this work</td>
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<td>TiCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Silicon, PET</td>
<td>80</td>
<td>[179]</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>TTIP</td>
<td>Silicon</td>
<td>70</td>
<td>[179]</td>
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<td>TiCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Silicon</td>
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<td>Silicon</td>
<td>25</td>
<td>[180]</td>
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<td>ZnO</td>
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<td>PMMA&lt;sup&gt;13&lt;/sup&gt;, PC&lt;sup&gt;14&lt;/sup&gt;</td>
<td>25</td>
<td>[179]</td>
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<tr>
<td>ZnO</td>
<td>DEZ</td>
<td>PP, blend of PET/cotton</td>
<td>65</td>
<td>[181]</td>
</tr>
<tr>
<td>ZnO</td>
<td>DEZ</td>
<td>Kapton</td>
<td>200</td>
<td>[182]</td>
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<tr>
<td>ZnO</td>
<td>DMZ&lt;sup&gt;15&lt;/sup&gt;</td>
<td>Silicon</td>
<td>25</td>
<td>[183]</td>
</tr>
<tr>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt;/Zircon</td>
<td>TDMAZr&lt;sup&gt;16&lt;/sup&gt;, EG&lt;sup&gt;17&lt;/sup&gt;</td>
<td>Silicon, PET</td>
<td>80</td>
<td>[182]</td>
</tr>
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</table>

1: Trimethylaluminum, 2: Dimethylaluminum isopropox, 3: [3-(dimethylamino)propyl]-dimethyl aluminum
4: Hexafluoroacetaldehyde Cu(I) (3,3-dimethyl-1-buten), 5: (2,2,6,6-tetramethyl-3,5-heptanedionato) gallium(III),
6: Bis(tris(dimethylamido)gallium(III)), 7: Tetrakis(dimethylamido)hafnium(IV),
8: Dimethyl(N-ethoxy-2,2-dimethylpropanamido)indium, 9: Bis(diethylamino)bis(trimethylalkoxysilyl), 10: Tetrakis(dimethylamido)tin(IV),
11: Pentakis(dimethylamido)tantalum(V), 12: Diethyl zinc, 13: Poly(methyl methacrylate), 14: Polycarbonate,
15: Dimethyl zinc, 16: Tetrakis(dimethylamido)zirconium(IV), 17: Ethyleneglycole
1.5. Principles of plasma

If a gaseous mixture of molecules and/or atoms consists partially or completely of charged particles, it is considered as a plasma. A more precise definition describes a plasma as a quasi-neutral mixture of the mentioned charged particles with collective behavior. The term plasma was introduced in 1928 by Irving Langmuir, while being identified the first time in 1879 by Sir William Crookes and is nowadays considered as the fourth fundamental state of matter (together with solids, liquids and gases). Analogous to solid substances, which will melt and pass into a liquid under energy input, and liquids, which become gaseous after further energy input, a gas can be transferred to the plasma state. Plasmas are generated from gases which are subjected to a high energy input, e.g. by an electric field generated from dc, radio- or microwave-frequency, thereby decomposing molecules and atoms, creating a gaseous mixture of negatively charged electrons and positively charged ions. The corresponding gaseous mixtures can be partially or completely ionized, depending on the energy input, and are generated by heating a gas or subjecting it to strong electromagnetic fields. Strongly ionized plasmas are a phenomenon occurring under extreme situations, e.g. in the interior of stars like the sun or their coronas. Examples for partially ionized plasmas in our daily life are polar lights, lightnings, neon signs for advertising and energy saving lamps.

A multitude of modern applications are based on the industrial application of different plasma techniques, ranging from medicinal treatments for sterilization, wound healing and cancer-related applications, plasma televisions, the deposition of thin films by a broad variety of plasma-assisted processes or the development of a fusion power plant. The science of plasma physics, including the fundamentals and until today developed applications and techniques, is subject of many scientific journals and an enormous effort is spent by many groups all over the world.
to understand and foster the different aspects of plasmas. Thus, it is beyond the scope of this thesis to summarize all details related to plasmas. Several books, focusing on plasma fundamentals, are available and are highly recommended for the interested reader. Nevertheless, important basics of plasma science will be discussed briefly in this section to provide an overview as well as a basic understanding of the later employed, plasma-assisted, deposition techniques, namely PEALD and PECVD. In this context, low-pressure plasmas are discussed in the following.

### 1.5.1. Equilibrium in low-pressure plasmas

As plasmas are gaseous mixtures of negatively and positively charged particles, both the electrical and thermal equilibrium must be considered. After generation of the charged particles, the plasma is quasi-neutral, as the electron and ion density, \( n_e \) and \( n_i \), are equal, \( n_e \approx n_i \). From this, the fractional ionization \( I \) of the plasma can be derived from equation 1.1:

\[
I = \frac{n_i}{n_g + n_i} \quad (1.1)
\]

with \( n_g \) being the neutral gas density. For a completely ionized plasma, \( I \) equals 1, while \( I \ll 1 \) for weakly ionized plasmas. Aforementioned high-pressure plasmas, like the inner part of stars, are usually highly ionized with electrons and heavy particles being in thermal equilibrium with each other, \( T_e = T_i = T \). For low-pressure plasmas, the situation is a different one, as the mean-free-paths of all species is strongly increased. Here, the energy input causes heating of the more mobile electrons, while heavy ions are more or less unaffected and remain with their initial temperature. In addition, the energy transfer from a collision between two heavy atoms or ions is more efficient. Therefore, \( T_i \ll T_e \) and the plasma is considered as non-thermal, *i.e.* a thermal equilibrium between electrons and ions is not on hand. Electron temperatures are usually on the order of \( T_e \approx 1 \text{ eV} \) to \( 10 \text{ eV} \), *i.e.* on the or-
der of magnitude $10^4$ K. It should be noted that the electron temperature is derived from the average kinetic energy, assuming a Maxwell-Boltzmann distribution of the electron kinetic energies. The electron temperature of a plasma is defined as the temperature of that distribution and is derived from equation 1.4

$$E_e = \frac{3}{2}(k_B T)$$

with $k_B$ being the Boltzmann constant ($k_B = 1.380648 \cdot 10^{-23} J K^{-1}$) and $T$ the temperature in K. To obtain the electron temperature in eV, the expression $k_B = 8.617330 \cdot 10^{-5} eV K^{-1}$ is used. On the other hand, the overall temperature is much lower and closer to that of the heavy particles, $T \approx T_i$. These non-thermal plasmas are of high importance for thin film deposition, as the overall low temperature allows the processing of sensitive substrates. Low-pressure plasmas usually contain a charged particle density of about $n \approx 10^8 \text{ cm}^{-3}$ to $10^{13} \text{ cm}^{-3}$, with the neutral gas species density being of the order of $n_g \approx 10^{15} \text{ cm}^{-3}$ to $10^{18} \text{ cm}^{-3}$. Highly energetic electrons from low-pressure plasmas are a main force for excitation, ionization and dissociation processes of atoms and molecules in the gas, thus strongly influencing the occurring chemistry within the plasma. Such high-energetic electrons are found in the tail region of the energy distribution and while the density is usually low, the corresponding amount is sufficient to make low-pressure plasmas highly efficient with respect to deposition applications, such as PECVD and PEALD. In many cases, the electron distribution for such low ionized plasma processes is considered to be Maxwellian-like (as an estimation), with the tail distribution being still a controversially discussed topic among experts.

Furthermore, atoms can be excited by absorption of photons or from inelastic collisions. For these photons, an energy of the difference $\Delta E = E_g - E_{ex}$, with $E_g$ and $E_{ex}$ being the energy of the ground and excited state, respectively, is necessary.
to provide sufficient energy for excitation of electrons. For the energy of the photon, the following relation is given:

\[ E = h \cdot \nu = h \cdot \frac{c}{\lambda} \]  \hspace{1cm} (1.3)

with \( h \) being the Planck constant and \( c = \lambda \nu \) the speed of light in vacuum (\( \nu \) is the frequency and \( \lambda \) the wavelength of the photon). If an atom is excited, it will return to a lower excited or its ground state, thereby emitting a photon with specific energy. This process happens, in average, after a certain time span \( \tau \), which is on the order of ns. Excited states can also relaxate, meaning the radiation-free transition of excited electrons between possible energy levels. Transitions between different energy states, with respect to emission and adsorption, follow certain selection rules for quantum numbers. If the time span \( \tau \) of emission is significantly larger, e.g. in the \( \mu s \)-range, the corresponding species are considered as metastable. This situation can be found if excited states are not able to emit photons according to selection rules for quantum numbers.

The surface chemistry is also dependent on the ion fluxes, as the heavy ions are bombarding the surface, thereby inducing etch and sputter processes. In addition, vacuum ultraviolet (VUV) radiation, exhibiting energies of \( \geq 6.2 \text{ eV} \), i.e. wavelengths \( \leq 200 \text{ nm} \), is able to induce photochemical reactions at the substrate surface, in particular those of polymers.[122]

### 1.5.2. Plasma sheath

As mentioned above, a plasma demonstrates to be quasi-neutral, as \( n_e = n_i \) and exhibits therefore a net charge density of zero, \( e(n_i - n_e) = \rho = 0 \). As the electrons are much lighter and faster than the ions and are of greater or equal temperature compared to the ions, their velocity is higher by at least the factor \( \sqrt{\frac{m_i}{m_e}} \), which is
1.5. PRINCIPLES OF PLASMA

derived from equation 1.4.

\[
\begin{align*}
E_{\text{kin},e} & \geq E_{\text{kin},i} \\
\Leftrightarrow \frac{1}{2}m_e v_e^2 & \geq \frac{1}{2}m_i v_i^2 \\
\Leftrightarrow \frac{v_e^2}{v_i^2} & \geq \frac{m_i}{m_e} \\
\Leftrightarrow \frac{v_e}{v_i} & \geq \sqrt{\frac{m_i}{m_e}} > 1
\end{align*}
\] (1.4)

Thus, electrons will be lost faster to the walls, leaving positively charged ions behind in a volume close to the wall, forming a positively charged sheath with \( n_i \gg n_e \), also called Debye-sheath or space-charge region. Due to this space-charge region, the plasma lies on a more positive potential than the chamber walls (schematically depicted in figure 1.6).

![Figure 1.6: Schematic of a typical potential distribution in a plasma confined between two electrodes.](image)

From this moment on, a positive net charge density \( \rho \) in the plasma sheath is derived. Therefore, a positive potential of the plasma arises with respect to the potential at the electrodes/walls. An electric field, being the negative gradient of the potential, develops within the sheaths. This electric field confines the electrons in the plasma bulk, sustaining quasi-neutrality of the plasma, acting as a barrier for
electrons while positively charged ions are accelerated toward the walls.

### 1.5.3. Plasma sources

Low-pressure plasmas can be generated through different techniques, all aiming toward the heating of electrons from the feedstock gas. Gas discharges are commonly generated by an electric field, DC or RF, creating a high potential difference between two electrodes. As shortly mentioned in section 1.1, RF discharges are favored for the processing of semiconductor materials. In the following, two commonly applied plasma sources, namely capacitively and inductively charged plasmas (CCP and ICP, respectively), are described briefly. In addition, the electron cyclotron wave resonance (ECWR) plasma is discussed as a special case.

**Capacitively coupled plasmas (CCPs)**

If one of two parallel electrodes is grounded while both are connected to a power supply, the setup resembles the principle of a capacitor in an electric circuit. Therefore, such system are called capacitively coupled plasmas (CCP). The power supply in such CCPs is usually a radio-frequency generator ($13.56\, \text{MHz}$). The generated electric field by this radio-frequency between the electrodes ionizes the feedstock gas, as electrons are able to follow the fast oscillation of the alternating electric field. Hence, free electrons (e.g. from cosmic radiation) collide with neutral atoms and molecules and will excite, ionize or dissociate them. From further collisions, an electron-avalanche can be created, providing energy to sustain the discharge. By applying an additional potential as a bias to the substrate, the bombardment of the surface by ions can be further increased.
1.5. PRINCIPLES OF PLASMA

Inductively coupled plasmas (ICPs)

In contrast to CCPs, an inductively coupled plasma (ICP) receives the necessary energy from electromagnetic induction, creating electric currents. For this, the electrode is of coiled shape and is usually wrapped around the vessel or chamber in which the plasma is formed. The coiled shape can be arranged either as a flat or three-dimensional electrode, the latter providing advantages with respect to confining the plasma in a discrete volume. By this setup, an inductively magnetic field is formed, which again induces an electric field in the gas volume, causing the electrons to move on figure-8-like trajectories, thereby gaining sufficient energy to maintain the discharge. Compared to CCPs, ICP plasmas are of higher density.

Electron cyclotron wave resonant (ECWR) plasma: a special case

The electron density of plasmas can be further increased by superimposing the ICP source with a static magnetic field. This can be achieved by Helmholtz-coils, placed in such an arrangement that creates a magnetic field perpendicular to the RF-load coil. The magnetic field splits into a right- and left-handed wave upon entering the plasma region, creating an anisotropy in the plasma.\(^{193,194}\) In contrast to the left-handed wave, the right-handed-wave is able to propagate into the plasma and can cause a resonant plasma excitation by transferring its energy to the plasma. These waves are called electron cyclotron waves,\(^{193}\) and if an odd number of the wavelength of this wave matches the plasma in the direction of the wave vector, resonant excitation is achieved. Indeed, the reactor used for all PEALD experiments described in this thesis comprises such an ECWR plasma source. It should be noted that this kind of plasma source is, in contrast to CCPs and ICPs, much less investigated and understood.
CHAPTER 1. INTRODUCTION

1.6. State of the art: Gas barrier layers

Several daily life goods need to be protected against harming agents to avoid their irreversible degradation. Typical examples are foods, beverages and pharmaceutical products which can be easily destroyed by oxygen gas or water vapor. While cheap polymer materials like PET and PP are commonly applied in the packaging industry, their ability to provide a sufficient gas barrier is limited and further action is necessary to protect the packaged goods. In order to improve the gas barrier performance of the mentioned polymers, organic films from ethylene vinyl alcohol (EVOH) were commercially applied on top of them. Unfortunately, these organic polymers are challenging in terms of recycling and sustainability. In addition, these films are usually applied as several μm-thick films. Another option to improve the barrier performance is the application of metallic thin films, such as aluminum. Thin aluminum films of 10 nm to 100 nm exhibit outstanding barrier properties, but cannot be used when transparency is a desired thin film property. While this approach is also commercially applied, the respective compound materials are not microwave compatible and rather expensive.

Since the nineties, inorganic oxide and nitride materials have been investigated regarding their potential application as GBLs to overcome the mentioned challenges and a lot of effort was devoted on the development of deposition processes and to understand the fundamental mechanisms taking place with respect to transmission of degrading agents, such as oxygen and water. Inorganic oxides and nitrides like SiO$_x$, SiN$_x$, Al$_2$O$_3$ and TiO$_2$ were shown to easily compete with the mentioned organic polymers from EVOH in terms of decreased oxygen and water vapor transmission rates (OTR and WVTR, respectively), even when applied as thin films of below 100 nm. OTR and WVTR values are the common benchmarks for classification of GBLs and are measured in cm$^3$ m$^{-2}$ day$^{-1}$ and g m$^{-2}$ day$^{-1}$, respectively. The
lower the value, i.e. the lower the transported mass of oxygen or water, the better is the performance of the GBL. With respect to OTR, Wertheimer et al. introduced the concept of a critical thickness for a GBL. The critical thickness, \( d_c \), is that thickness where the measured OTR drops by two orders of magnitude. It should be noted that this classification is now 19 years old and that it is based on the investigation of PECVD deposited gas barrier layers on rather thin polymer foils of only 13 \( \mu m \) thickness. Wertheimer et al. carried out a lot of research regarding GBLs on PET, in particular with respect to how defects influence the performance of GBLs and, of even higher importance, how these defects can be visualized, as they are usually too small to be identified by using a simple light microscope.

GBLs of silica-like materials were fabricated preferentially by PECVD, as this technique allows efficient depositions with high growth rates and the obtained GBLs exhibit sufficient low OTR values. Numerous groups carried out research on the topic of GBLs from PECVD and the tables 1.3 and 1.4 gives an overview of the different materials and investigated polymers from the last decade. In addition, the binary oxides \( \text{Al}_2\text{O}_3 \), \( \text{TiO}_2 \), \( \text{HfO}_2 \), \( \text{ZrO}_2 \), \( \text{SnO}_2 \) and different combinations have been investigated as well and the results available from literature are shown in table 1.3 and 1.4 as well. It should be mentioned that reactive sputtering was used for the fabrication of GBLs (\( \text{Al}_2\text{O}_3 \), \( \text{SiO}_2 \), \( \text{TiO}_2 \) and \( \text{ZnSn}_x\text{O}_y \)) as well. Apart from the thickness, it was shown in the past that other parameters can have a strong influence on the GBL performance. For example, the chemical composition of a deposited plasma polymer can be tuned by adjusting the monomer to oxygen ratio, yielding either more organic (\( \text{SiO}_x\text{C}_y\text{H}_z \)) or more inorganic (\( \text{SiO}_x \)) materials. With respect to the interfacial layer of barrier layers on polymers, it was shown that the oxidative degradation during plasma deposition can be inhibited by choosing the right monomer/oxygen ratio, thereby adjusting the atomic oxygen flux. In addition, the \( \text{SiO}_x\text{C}_y\text{H}_z \)-layers were found to promote improved barrier coatings when an organic interlayer
is deposited prior the SiO$_x$ coating.\textsuperscript{[205]} Another parameter is the defect density of a deposited GBL, which was shown to have a strong influence on the GBL performance as well.\textsuperscript{[199,206]} Interestingly, the defect density of PECVD grown materials can be adjusted by controlling the plasma properties in terms of ion and neutral fluxes.\textsuperscript{[207]} For example, a pulsed bias can be applied toward the substrate antenna of the reactor setup, thereby creating an additional electromagnetic field inside the reactor. As charged particles are affected by such an electromagnetic field, the fluxes of ions and neutral can be adjusted toward an optimized growth with suppressed defect formation, enabling the deposition of GBLs with lower defect density and decreased OTR. Irrespective of the defect density, it was shown that the ion current density (ion flux) has an influence on PECVD-grown GBLs regarding their performance.\textsuperscript{[208]} However, a certain degree of defect formation during growth on polymer substrates still prevails and it is known that nano- und macro-defects play a crucial role for the transport of gases and vapors through GBLs. It should be noted that recent studies on a variety of PECVD- and PEALD-grown GBL materials revealed that the mechanisms of diffusion through barrier layers is far away from being solely defect-driven, as established models (e.g. Knudsen-diffusion) do not correlate with experimental results.\textsuperscript{[209,210]} From these studies, a predominant diffusion according to the solid-body model is suggested. However, the temperature-dependent solid-body model (Arrhenius-model) was also found to be limited in terms of explaining experimental results and theoretical behavior. From this, a more complex diffusion model, considering a significant contribution of defect-driven diffusion, must be developed and is a current research subject.

With respect to the defect density as a crucial parameter for the performance of GBLs, the deposition of highly conformal and homogeneous thin films without defect formation is obviously desired. This holds also true when the solid-body diffusion model is considered, as dense and homogeneous thin films should provide less
potential pathways for diffusion. From this, a list of requirements on the deposition process and the final material properties can be derived:

- inorganic materials are preferred over organic polymers,
- the materials should exhibit a high density,
- even for low thicknesses, the materials should exhibit promising OTR/WVTR values,
- the growth must take place without defect formation, i.e. homogeneous growth is desired,
- the process must allow the deposition at low substrate temperatures (polymer substrates) and
- the process should allow to adjust the chemical composition of the material.

In this context, PEALD is the method of choice to deposit thin films of inorganic materials exhibiting a high quality while meeting all the before mentioned requirements. Indeed, it was shown by Mitschker et al. that PEALD coatings of TiO$_2$ exhibit a strongly decreased defect density when compared with SiO$_x$ coatings from PECVD of the same thickness.$^{[207]}$ In addition, the PEALD-grown thin films demonstrated a better barrier performance.

Owing to the increasing demand from the industry regarding the high sensitivity of advanced electrical devices, especially OLEDs, toward water vapor, a lot of research on the fabrication of ultra gas barrier layers has been carried out and has been published during the last ten years. In this context, the term ultra barrier describes GBLs which are able to improve the WVTR of a certain packaging/encapsulation material down to the order of $10^{-6}$ g m$^{-2}$ day$^{-1}$ $^{[213]}$, which is necessary to provide a
life-time of the respective years over a few years. OLEDs are the by far most promising candidates for flexible opto-electronic devices like touch-screens and transparent thin film transistors (TTFTs), which is due their own high flexibility. Unfortunately, OLEDs are irreversibly damaged easily by tiny amounts of water. While normal glass provides superior protection against the ingression of water, it is too brittle for the fabrication of flexible devices. Therefore, an ideal material for OLED encapsulation should exhibit a high wear-resistance like glasses combined with flexibility and a sufficient barrier performance. Polymer substrates such as PET, polyethersulfone (PES) or polyethylene naphthalate (PEN) are the most promising candidates, as they are cheap and highly flexible. The reason that so many groups are working on the development of ultra GBLs is that these polymers are not sufficient in terms of WVTR to avoid degradation of the passivated OLEDs. As for other packaging materials, a solution can be found in adding a GBL on top of these materials, providing the necessary barrier enhancement toward sufficient passivation and strongly prolonged life-times of the devices.

Apart from investigations regarding the process development and thickness-related studies, different groups explored the mechanical properties, in terms of thin film stress and crack formation, as well as the limiting fundamental mechanisms taking place at the interface of GBLs and the surrounding atmosphere. Since 2014, and with respect to this interface, remarkable effort was spent by Perrotta et al. in terms of advanced investigations employing spectroscopic ellipsometry (SE) and ellipsometric porosimetry to determine the porosity and impedance spectroscopy to investigate the surface structure of GBLs grown by PECVD. These extensive studies were performed to understand the influence of nanoporosity on GBL performance in detail and it was shown, by thoroughly monitoring of changes in the refractive indices of both the polymer substrate and the inorganic GBL, that nanoscopic pores absorb vapor molecules which cause a swelling of the polymer.
From this, the molecule permeation could be investigated with respect to kinetics and the extent of permeation. Additional experiments on PECVD-grown SiO$_x$ layers, which were coated with ultrathin (2 nm) PEALD grown Al$_2$O$_3$ coatings could be performed and it was found that PEALD is able to close nanopores on the SiO$_x$ surface. While these analysis techniques provide a strong tool to investigate the mechanisms of diffusion for GBLs, it should be noted that comprehensive investigation is only possible for materials which are not interacting in chemical means with the used probe molecules, such as water, ethanol or toluene. Furthermore, if materials of high densities are investigated, the changes in the refractive index are hard to be measured, making an interpretation challenging.

Until today, a huge amount of research has been carried out regarding the fabrication and improvement of GBLs on polymers using either ALD, MLD, PEALD, PECVD and different combinations of these techniques. Interestingly, most of these research efforts are focusing on the GBL performance in terms of WVTR and with a strong focus toward ultra gas barriers which are necessary for OLED encapsulation. It should be noted that the investigated barrier systems are rather thick coatings $\geq$50 nm and the used polymer substrates are usually high-performance polymers such as PES and PEN. Furthermore, the used substrates are also rather thick with thicknesses between 100$\mu$m and 150$\mu$m, thereby providing an enhanced barrier performance depending on their thickness. Table 1.3 page 46 provides an overview of the progress on GBLs from the last years regarding WVTR deposited by the aforementioned deposition methods, including nanolaminates, and illustrates the GBL material and thickness, substrate and deposition temperature ($T_{dep}$). It must be noted that reports on the investigation of GBLs from the years before 2008 are present. As such literature provides only data which is hardly comparable, due to different measuring techniques and the lack of consistent usage of units, earlier literature is not reported here for the sake of clarity. Reports on the barrier perf-
The performance of GBLs regarding OTR is less often found. The reason for this can be found in a less challenging fabrication of promising oxygen barriers, which is due to the fact that water is polar, while oxygen resembles to be an unpolar agent. Due to the polarity of water, \( \text{H}_2\text{O} \) molecules can interact with gas barrier in terms of adsorption and can accumulate in pores and defects. From this, also the reaction of water molecules with the barrier system is possible, causing an irreversible deterioration of the GBL and further ingress of water. On the other hand, from unpolar oxygen molecules such a behavior is not expected. In addition, molecular oxygen shows much less reactivity, when compared with water, toward inorganic materials such as \( \text{Al}_2\text{O}_3 \), \( \text{SiO}_2 \) and \( \text{TiO}_2 \), making a chemical reaction with strong influence on the GBL performance unlikely. However, OTRs of GBLs are reported in literature and Table 1.4 gives an overview of the results from the last years, focusing again on the GBL material and thickness, substrate, deposition temperature (\( T_{\text{dep}} \)), OTR and the process. As for Table 1.3, literature before 2009 is omitted as the respective reports provide data which is hardly comparable, due to different measuring techniques and the lack of consistent usage of units. In addition, the amount of performed research of the recent years gives substantial evidence that older findings do not match the ramifications of the state of the art. From Table 1.4, it is striking that either thick coatings or thick substrates are used to achieve superior OTR values. In addition, a thick coating does not necessarily produce an outstanding barrier with high performance.
### Table 1.3: Overview of progress on GBLs regarding WVTR deposited by ALD, PEALD and/or PECVD.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (nm)</th>
<th>Substrate</th>
<th>(T_{dep}) (°C)</th>
<th>WVTR (g m(^{-2}) day(^{-1}))</th>
<th>Process</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
<td>50</td>
<td>50 µm PLA</td>
<td>80</td>
<td>0.6</td>
<td>ALD</td>
<td>221</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50 µm PEN</td>
<td></td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
<td>≥ 10</td>
<td>50 µm PET</td>
<td>125</td>
<td>(\leq 5 \times 10^{-3})</td>
<td>ALD</td>
<td>222</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
<td>100</td>
<td>PEN, t.n.r.</td>
<td>100</td>
<td>(10^{-3})</td>
<td>O(_3)-ALD</td>
<td>223</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
<td>40</td>
<td>200 µm PEN, 100 µm PEN, 100 µm PES, 100 µm PET</td>
<td>120</td>
<td>(7.2 \times 10^{-4})</td>
<td>PEALD</td>
<td>224</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
<td>11.8</td>
<td>PES, t.n.r.</td>
<td>50-150</td>
<td>(4 \times 10^{-3})</td>
<td>PEALD</td>
<td>225</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
<td>50</td>
<td>200 µm PEN</td>
<td>100</td>
<td>(3.75 \times 10^{-4})</td>
<td>PEALD</td>
<td>226</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
<td>63</td>
<td>150 µm PET</td>
<td>50</td>
<td>(\leq 10^{-3})</td>
<td>PEALD</td>
<td>227</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)/alucone</td>
<td>55</td>
<td>PET, t.n.r.</td>
<td>80</td>
<td>(9.94 \times 10^{-5})</td>
<td>ALD/MLD</td>
<td>228</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)/plasma polymer-NL</td>
<td>525</td>
<td>200 µm PEN</td>
<td>80</td>
<td>(1.2 \times 10^{-2})</td>
<td>PEALD/PECVD</td>
<td>229</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)/plasma polymer-NL</td>
<td>1000</td>
<td>PEN, t.n.r.</td>
<td>80</td>
<td>(1 \times 10^{-3})</td>
<td>ALD/PECVD</td>
<td>230</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)/plasma polymer-NL</td>
<td>4000</td>
<td>PEN, t.n.r.</td>
<td>80</td>
<td>(1 \times 10^{-4})</td>
<td>ALD/PECVD</td>
<td>231</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)/plasma polymer-NL</td>
<td>130</td>
<td>PEN, t.n.r.</td>
<td>109</td>
<td>n.r.</td>
<td>ALD/PECVD</td>
<td>232</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)/HfO(_2)-NL</td>
<td>50</td>
<td>125 µm PEN</td>
<td>100</td>
<td>(1.4 \times 10^{-4})</td>
<td>PEALD</td>
<td>233</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)/MgO-NL</td>
<td>5.2</td>
<td>Glass</td>
<td>80</td>
<td>(4.7 \times 10^{-6})</td>
<td>ALD</td>
<td>234</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)/TiO(_2)-NL</td>
<td>40</td>
<td>650 µm PES</td>
<td>80</td>
<td>(5 \times 10^{-3})</td>
<td>PEALD</td>
<td>235</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)/TiO(_2)-NL</td>
<td>50</td>
<td>PEN, t.n.r.</td>
<td>100</td>
<td>(9.16 \times 10^{-5})</td>
<td>PEALD</td>
<td>236</td>
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<tr>
<td>SiN</td>
<td>100</td>
<td>50 µm Kapton</td>
<td>125</td>
<td>(7 \times 10^{-3})</td>
<td>PECVD</td>
<td>237</td>
</tr>
<tr>
<td>SiN + (\text{Al}_2\text{O}_3)</td>
<td>100 + 5</td>
<td>125 µm PEN</td>
<td>125</td>
<td>(\leq 5 \times 10^{-3})</td>
<td>PECVD/ALD</td>
<td>238</td>
</tr>
<tr>
<td>Material</td>
<td>Thickness</td>
<td>Substrate</td>
<td>Temperature</td>
<td>Deposition Method</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>-----------</td>
<td>-----------</td>
<td>-------------</td>
<td>------------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>SiN&lt;sub&gt;x&lt;/sub&gt;</td>
<td>200</td>
<td>PET</td>
<td>RT</td>
<td>2 x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>PEVD</td>
<td></td>
</tr>
<tr>
<td>SiN&lt;sub&gt;x&lt;/sub&gt;</td>
<td>10-40</td>
<td>Glass</td>
<td>120</td>
<td>10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td>PEALD</td>
<td></td>
</tr>
<tr>
<td>SiN&lt;sub&gt;x&lt;/sub&gt; + Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; + Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;/HfO&lt;sub&gt;x&lt;/sub&gt; NL</td>
<td>140</td>
<td>Cytop, t.n.r.</td>
<td>100</td>
<td>1.84 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
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<td>300 + 40</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;/Ca/Glass</td>
<td>100</td>
<td>≤2 x 10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td>PEVD/PEALD</td>
<td></td>
</tr>
<tr>
<td>SiON</td>
<td>200</td>
<td>30 µm PET</td>
<td>60</td>
<td>7 x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
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<td>50</td>
<td>PEN</td>
<td>60</td>
<td>8.4 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
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<td>180 µm PET</td>
<td>n.r.</td>
<td>1.1 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
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<tr>
<td>SiO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>415</td>
<td>10 µm PET</td>
<td>RT</td>
<td>4.7 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>PEVD</td>
<td></td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>225</td>
<td>100 µm PEN</td>
<td>RT</td>
<td>5 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>AP-PECVD</td>
<td></td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>200</td>
<td>38 µm PET</td>
<td>RT</td>
<td>2.5 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>PEVD</td>
<td></td>
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<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>800</td>
<td>125 µm PET</td>
<td>RT</td>
<td>2 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
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<td></td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>800</td>
<td>125 µm PEN</td>
<td>RT</td>
<td>2 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>PEVD</td>
<td></td>
</tr>
<tr>
<td>SiO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>100</td>
<td>100 µm PEN</td>
<td>125</td>
<td>1.8 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
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<td></td>
</tr>
<tr>
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<td>80 + 10</td>
<td>100 µm PEN</td>
<td>80</td>
<td>9 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>PEVD/PEALD</td>
<td></td>
</tr>
<tr>
<td>SiO&lt;sub&gt;x&lt;/sub&gt; + Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>100 + 2</td>
<td>c-Si</td>
<td>100</td>
<td>10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td>PEVD/PEALD</td>
<td></td>
</tr>
<tr>
<td>SnO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>110</td>
<td>125 µm PEN</td>
<td>150</td>
<td>10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td>ALD</td>
<td></td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>80</td>
<td>PES, t.n.r.</td>
<td>90</td>
<td>2.3 x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>PEALD</td>
<td></td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>50</td>
<td>200 µm PEN</td>
<td>100</td>
<td>6.32 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>PEALD</td>
<td></td>
</tr>
<tr>
<td>ZnO&lt;sub&gt;2&lt;/sub&gt; (Hf−doped)</td>
<td>t.n.r.</td>
<td>125 µm PEN</td>
<td>150</td>
<td>6.3 x 10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td>ALD</td>
<td></td>
</tr>
<tr>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>80</td>
<td>Glass</td>
<td>80</td>
<td>6.09 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>ALD</td>
<td></td>
</tr>
<tr>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; / Zircon–NL</td>
<td>60</td>
<td>Glass</td>
<td>80</td>
<td>3.1 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>PEALD</td>
<td></td>
</tr>
</tbody>
</table>

t.n.r. = thickness not reported; NL = nanolaminates; RT = room temperature; AP-PECVD: Atmospheric pressure PECVD
1.6. STATE OF THE ART: GAS BARRIER LAYERS

Table 1.4.: Overview of progress on GBLs regarding OTR deposited by ALD, PEALD or PECVD.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (nm)</th>
<th>Substrate</th>
<th>T&lt;sub&gt;dep&lt;/sub&gt; (°C)</th>
<th>OTR (cm&lt;sup&gt;2&lt;/sup&gt; m&lt;sup&gt;−2&lt;/sup&gt; day&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>Process</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-C:H</td>
<td>n.r.</td>
<td>PLA, t.n.r.</td>
<td>n.r.</td>
<td>18.6</td>
<td>PECVD</td>
<td>225</td>
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<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>50</td>
<td>30 μm PP</td>
<td>80</td>
<td>170</td>
<td>ALD</td>
<td>221</td>
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<tr>
<td></td>
<td></td>
<td>25 μm PLA</td>
<td></td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 μm PET</td>
<td></td>
<td>44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10</td>
<td>50 μm PET</td>
<td>100</td>
<td>≤ 5 × 10&lt;sup&gt;−3&lt;/sup&gt;</td>
<td>ALD</td>
<td>222</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25 μm PET</td>
<td>100</td>
<td>≤ 5 × 10&lt;sup&gt;−3&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>125 μm PEN</td>
<td>125</td>
<td>≤ 5 × 10&lt;sup&gt;−3&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>11.8</td>
<td>PES, t.n.r.</td>
<td>50-150</td>
<td>≤ 4 × 10&lt;sup&gt;−3&lt;/sup&gt;</td>
<td>PEALD</td>
<td>225</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PEN, t.n.r.</td>
<td></td>
<td>≤ 4 × 10&lt;sup&gt;−3&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PC, t.n.r.</td>
<td></td>
<td>≤ 4 × 10&lt;sup&gt;−3&lt;/sup&gt;</td>
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<tr>
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<td>12 μm PET</td>
<td>25</td>
<td>1.8</td>
<td>PEALD</td>
<td>249</td>
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<tr>
<td>SiN</td>
<td>50</td>
<td>50 μm PET</td>
<td>RT</td>
<td>≤ 5 × 10&lt;sup&gt;−3&lt;/sup&gt;</td>
<td>PECVD</td>
<td>222</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>225</td>
<td>100 μm PEN</td>
<td>RT</td>
<td>≤ 5 × 10&lt;sup&gt;−3&lt;/sup&gt;</td>
<td>AP-PECVD</td>
<td>243</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>n.r.</td>
<td>50 μm PET</td>
<td>n.r.</td>
<td>≤ 8.2</td>
<td>AP-PECVD</td>
<td>250</td>
</tr>
</tbody>
</table>

t.n.r. = thickness not reported; NL = nanolaminates; RT = room temperature; AP-PECVD: Atmospheric pressure PECVD
1.7. Motivation

A lot of effort has been devoted during the last years to investigate GBLs, mostly carried out on the topic of ultra GBLs with respect to strongly decreased WVTRs for potential OLED encapsulation. For these studies, usually polymer substrates like PET, PEN and PES of around 125 $\mu$m thickness were used, demonstrating good barrier performances even in the uncoated cases. In addition, the deposited materials $\text{Al}_2\text{O}_3$, $\text{SiO}_2$, $\text{TiO}_2$, $\text{ZrO}_2$, $\text{HfO}_2$ as well as their combination in ALD/MLD hybrid materials or together with plasma-polymers were usually applied films with thicknesses above 50 nm, often above 100 nm. Until today, all carried out research in this field indicates that the combination of PECVD grown materials, such as silica-like $\text{SiO}_x$, together with ALD or PEALD grown materials is able to produce high-performance GBLs, if substrates with enhanced intrinsic barrier properties are used and there is no doubt that thicker coatings can provide increased barrier performance.

However, many of these processes still operate at elevated temperatures and while the overall improved performance of thicker GBLs is obvious, the growth of these GBL was not investigated in detail. Furthermore, the influence of limiting factors like thin film nucleation is still not understood completely. For PEALD, which resembles a further development of thermal ALD, another crucial parameter must be considered: To which extent does the precursor chemistry contribute toward an enhanced/decreased barrier performance and how is the precursor chemistry connected to the thin film growth? These questions are of high importance, as PEALD, due to its discontinuous operation, and its efficiency is strongly dependent on the mechanisms taking place at the interface between the growing film and the substrate.

Therefore, one goal of this thesis is the investigation of a potential precursor influence on the thin film growth of GBL materials on PET. For this, established Ti-
precursors and new developed Ti-precursors are directly compared regarding their growth of TiO$_2$ on silicon and PET, thereby investigating the process optimization in terms of thin film growth, film structure and composition as well as barrier performance.

A second goal is the more fundamental investigation of the established approach to combine PECVD and PEALD to fabricate GBLs. This approach is transferred to a more fundamental setup, where thin PET foils (23 µm) are used instead of those which exhibit already good intrinsic barrier performance. For this, SiO$_x$ and SiOCH coatings from PECVD are capped with different ultrathin PEALD coatings, allowing the investigation of both a potential thickness and material influence. In addition, a new approach towards improved barrier coatings from PECVD is investigated, using PEALD grown seeding layers for the subsequent growth of SiO$_x$. In these cases, the combined systems are of 20 nm maximum to allow the detection of little changes in barrier performance induced from the incremental process parameter variations.

The third goal focuses on the fabrication of stackings of different PEALD grown materials, also known as nanolaminates, for GBL application. In this context, both the precursor chemistry as well as the interface of the growing films is investigated with respect to mechanical properties in terms of adhesion and residual thin film stress, which are correlated with the barrier properties of the grown Al$_2$O$_3$/SiO$_2$ dyads.
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References


References


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2. Precursor development for PEALD of titanium dioxide on PET

2.1. Introduction to titanium dioxide and precursor chemistry

Titanium dioxide (TiO$_2$) is a versatile material and is used in a broad field of applications. With a refractive index of $n = 2.874$ at 632.8 nm (rutile), it serves as a highly refracting material, making it the most widely used white pigment. Owing to its semiconducting properties in terms of an electrical band gap of $E_g = 3.0$ eV to 3.2 eV depending on the modification (see below), and its high transparency, it is used in solar cells as photocatalytical material for the UV-initiated degradation of water pollutants, water splitting and the conversion of CO$_2$ into hydrocarbon fuels. Another thin film application of TiO$_2$ is found in optical coatings for dielectric mirrors. Under normal circumstances, TiO$_2$ is present in nature in three different minerals, and resembles either a tetrahedral (anatase and rutile) and orthorhombic (brookite) crystal system (see figure 2.1), with rutile being the most abundant mineral out of these three. It should be noted that in 2015, a fourth modification, namely Riesit which crystallizes in a monoclinic crystal structure, was discovered by Tschauer and Ma. Irrespective of the crystal system out of the three common ones, Ti$^{4+}$ cations have a six-fold oxygen-coordination sphere in these three modi-
Figure 2.1.: Crystal structures of anatase (a), brookite (b) and rutile (c). Red: Ti$^{4+}$, cyan: O$^{2-}$.

ifications, while the amount of Ti-atoms per unit cell differs: Brookite has eight, anatase four and rutile only two Ti-atoms per unit cell. For photocatalytic applications, synthetic anatase-$\text{TiO}_2$ is commonly used while the rutile form exhibits the highest refractive index (with respect to the visible wavelengths), making it the most used brilliant white pigment for paints.

During the last years, $\text{TiO}_2$ attracted a lot of interest as GBL material, owing to its high chemical and mechanical resistance as well as it can be grown easily with established deposition techniques. When used as GBL, the crystallinity of $\text{TiO}_2$ should be low, i.e. the amorphous form is preferred. This is understood easily by considering the application of GBLs in general on flexible polymers and devices. Crystalline materials, which are known to be brittle and likely to fracture upon stress like bending, increase the chance of being damaged, meaning that the formation of cracks in the GBL while handling is likely. Such cracks represent both a vulnerability toward water ingress and, for cracks on the nano-scale, pathways for diffusion of water and oxygen. It should be noted that also the remaining group IV elements, zirconium and hafnium, or more precisely their oxides and metalcone-compounds, have been investigated regarding a potential GBL application as well.

In terms of the deposition of $\text{TiO}_2$ for GBL application, the requirements listed
2.1. INTRODUCTION TO TITANIUM DIOXIDE AND PRECURSOR CHEMISTRY

in section 1.6 must be fulfilled to allow the fabrication of thin films with reliable properties. In PEALD, as for ALD, CVD and MOCVD, the precursor chemistry is of significant importance for the development of deposition processes yielding high-quality thin film materials with respect to these above listed constraints. CVD and MOCVD processes require chemical precursor compounds with low evaporation temperatures, i.e. a high vapor pressure at low temperatures, and a clean decomposition of the precursor, avoiding the incorporation of impurities from a potential ligand in the growing thin film. In addition, the decomposition at low temperatures is favored. ALD has even stronger demands with respect to suitable precursors that can initiate low temperature depositions. As thermal ALD processes usually have long pulse and purging lengths, the respective precursor is heated for longer durations, making thermal stability an important factor for precursor requirements. In addition, a precursor must exhibit a high degree of reactivity toward reactive surface sites on the substrate as well as toward the co-reactant at preferably low deposition temperatures. On the other hand, the reactivity should be low enough to avoid inter-molecular gas phase reactions and auto-catalytic behavior, as it is found for trimethylindium (TMI). Furthermore, non-toxic, non-flammable and non-pyrophoric compounds are obviously favored as they allow easier handling due to less hazardous potential. Finally, the precursor compounds should be cheap to allow an economically efficient process.

Here, PEALD offers the chance to apply a broader range of precursors than conventional thermal ALD as with the plasma, a high energy flux can be created, allowing the formation of a metal oxides even for less reactive precursors. Several PEALD processes to deposit TiO$_2$ have been reported over the last years, using a variety of Ti-precursors like titanium tetrachloride (TiCl$_4$) (1), titanium tetraisopropoxide ([Ti(4-OPr)$_4$], TTIP) (2) and tetrakis(dimethylamido)titanium ([Ti(NMe$_2$)$_4$], TD-MAT) (3). Less common but also used for research regarding PEALD of TiO$_2$ are
precursors based on Cp-substituted compounds, such as tris(methoxy)-trimethylcyclopentadienyl titanium(IV) ([Ti(CpMe)(OMe)] (4), tris(dimethylamido)methylcyclopentadienyl titanium ([Ti(CpMe)(NMe2)] (5), tris(isopropoxide)methylcyclopentadienyl titanium(IV) ([Ti(CpMe)(iOPr)] (6), metal alkoxide-compounds like titanium(IV) methoxide ([Ti(OMe)] (7) and titanium(IV) ethoxide ([Ti(OEt)] (8), as well as titanium(IV) t-butoxide ([Ti(OtBu)] (9). All the mentioned precursors are illustrated in figure 2.2 including their sum formula and, if applicable, standard abbreviation.

In the following, compounds 1-3 are considered, while the remaining precursors are omitted for the sake of clarity. While the usage of TiCl4 (1) often yields thin films with chlorine impurities which are known to affect the electrical properties, the titanium alkoxide compound TTIP (2) shows limitations with respect to the low growth rates per cycle (GPC) at low temperatures. The titanium-amido compound TDMAT (3) on the other hand exhibits several properties which are desired for an ALD or PEALD precursor: liquid at room temperature, both a high reactivity and vapor pressure as well as yielding high growth rates. However, the application of this compound is limited due to a certain thermal instability, causing decomposition if the compound is maintained for longer times at elevated temperatures which are necessary to provide a sufficient precursor dose for surface saturation in ALD. It was shown in 2013 by Dang et al. and in 2014 by Banerjee et al. that the thermal properties of TDMAT can be fine-tuned by a systematical variation of the complex' ligands, yielding Ti-precursor compounds with enhanced thermal stability. In these studies, the amido-ligands were substituted by either a guanidinate ligand (compound 10, tris(diemthylamido)mono(N,N’diisopropyl-2-dimethylamidoguanidinato)titanium(IV)) or by an amino-alkoxide (compound 11, bis(dimethylamido)-bis- (dimethylamino-2-propanolato)titanium), yielding new complexes of titanium exhibiting fine-tuned physico-chemical properties. These two
2.1. INTRODUCTION TO TITANIUM DIOXIDE AND PRECURSOR CHEMISTRY

new Ti-precursors are shown in figure 2.2 as well, illustrating the differences with respect to the coordination sphere. TiCl₄ (1), TTIP (2) and TDMAT (3) have a four-fold coordination sphere, with TDMAT exhibiting rather weak bondings toward the amido-moieties, making it a highly reactive compound. In contrast, the all-nitrogen-coordinated guanidinate compound (10) has a five-fold coordination-sphere, owing to the bidentate guanidinate ligand. On the one hand, this guanidinate ligand increases the thermal stability of the compound due to the more stable bonds between the Ti-atom and the guanidinate backbone. In addition, the bulky guanidinate ligand decreases the reactivity of the compound slightly, thereby decreasing the chance for dimerization, both in the liquid and the gas phase. On the other hand, the
five-fold coordination sphere is rather unlikely for Ti-compounds, making the reaction of the all-nitrogen-coordinated Ti-guanidinate compound with oxygen-sources likely. This fine-tuned reactivity allows the application in ALD as the reactive amido-groups undergo most likely reactions with hydroxyl-groups at the substrate surface, while the guanidinate-ligand stays intact, thereby providing enough reactivity toward a co-reactant. Indeed, a PEALD process using compound 10 was developed in 2014 to produce high-k TiO$_2$ thin films, doped with nitrogen, for semiconductor application.

Compound 11 was obtained by substitution of two amido-groups from TDMAT with the dimethylamino-2-propanolato-ligand, yielding a six-fold coordinated Ti-compound with mixed ligands bonding situation. While two ligands are still coordinated via their nitrogen-atoms, the amino-alkoxide binds through a strong covalent Ti-O bond and an additional nitrogen-Ti coordinative bond, making it a chelating bidentate ligand. From this bonding situation, an even higher thermal stability, combined with a lower vapor pressure, is obtained. Compound 11 is a red-colored liquid at room temperature and can be distilled at 90 °C at a pressure of 0.1 mbar. Using this compound, a MOCVD process for TiO$_2$ was developed in 2014.

With respect to the above outlined research performed regarding new Ti-precursors with engineered physico-chemical properties, the rational synthesis of a mixed mono-aminoalkoxide-tris-amido-Ti-compound was carried out, aiming toward a titanium compound with increased thermal stability (amino-alkoxide ligand) and high reactivity (amido-ligands) allowing the fabrication of TiO$_2$ thin films via PEALD, thereby avoiding the doping from nitrogen atoms or contamination from chlorine. This newly developed titanium compound, namely tris(dimethylamido)-(dimethylamino-2-propanolato)titanium (TDMADT, 12) (see figure 2.2), was obtained from a straightforward ligand exchange synthesis with high yields (> 95%).

The four compounds TDMAT (4), TDMAGT (10), BDMABDT (11) and TDMADT
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(12) exhibit different thermal properties with respect to onset of evaporation ($T_{\text{evap}}$), decomposition temperature ($T_{\text{decomp}}$) and residual masses and from thermogravimetric analysis (TGA) (see figure 2.3), the respective values were obtained and are listed in table 2.1.

![Figure 2.3: TGA of the four Ti compounds TDMAT (4), TDMAGT (10), BDMABDT (11) and TDMADT (12).](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular mass (g mol$^{-1}$)</th>
<th>$T_{\text{evap}}$ ($^\circ$C)</th>
<th>$T_{\text{decomp}}$ ($^\circ$C)</th>
<th>Residual mass at 450$^\circ$C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDMAT (4)</td>
<td>224.18</td>
<td>445</td>
<td>150</td>
<td>$\leq$ 1</td>
</tr>
<tr>
<td>TDMAGT (10)</td>
<td>350.38</td>
<td>148</td>
<td>200</td>
<td>10.5</td>
</tr>
<tr>
<td>BDMABDT (11)</td>
<td>340.34</td>
<td>150</td>
<td>230</td>
<td>14.8</td>
</tr>
<tr>
<td>TDMADT (12)</td>
<td>282.26</td>
<td>60</td>
<td>180</td>
<td>$\leq$ 1</td>
</tr>
</tbody>
</table>

All compounds exhibit a clean one-step evaporation, while for compounds 4, 10 and 12 a clear trend regarding the onset of volatilization and decomposition can be observed. With increasing molecular mass (224.18 g mol$^{-1}$ (4), 282.26 g mol$^{-1}$ (12) and 350.38 g mol$^{-1}$ (10)) of the precursors, both $T_{\text{evap}}$ and $T_{\text{decomp}}$ are shifted toward higher temperatures. Compound 11 exhibits even higher $T_{\text{evap}}$ and $T_{\text{decomp}}$ while the molecular mass (340.34 g mol$^{-1}$) is between compound 10 and 11. That this compound needs higher temperatures for sufficient volatilization is due to the two
amino-alkoxide ligands. With one strong Ti-O bond and an additional Ti-N coordinative bond per amino-alkoxide ligand, this compound is strongly stabilized with respect to its electronic structure, causing a higher thermal stability. In contrast, compound 12 demonstrates an increased thermal stability when compared with TDMAT, accompanied by only a slightly shifted onset of volatilization. In addition, the residual mass is, as for TDMAT, extremely low with a value below 1% for temperatures above 280 °C. For compounds 10 and 11, the residual masses at 450 °C were 10.70% and 14.08%, respectively.

In this chapter, the synthesis and chemical characterization of compound 12 is described in detail. TDMADT (12) was evaluated regarding its thermal behaviour, employing TGA and iso-TGA as well as temperature-dependent $^1$H-NMR studies. Furthermore, this compound was applied in a PEALD process at low temperatures (60 °C) and the findings were compared to similar growth experiments using TDMAT (4). The thin film growth was analyzed employing in-situ QCM, revealing the differences in thin film growth regarding the precursor fragments binding to the film surface during the precursor pulse. The process was investigated and optimized in terms of an ALD window and the linearity of thin film thickness vs. applied number of cycles. The grown TiO$_2$ thin films were were investigated regarding their structure (GIXRD), composition (RBS/NRA and XPS) and functional properties in terms of barrier performance (OTR). For this, TiO$_2$ thin films were deposited on Si(100) and PET substrates.\[32]
References


2.2. An efficient PEALD process for TiO$_2$ thin films employing a new Ti-precursor

The following contribution was accepted for publication December 20\textsuperscript{th} 2015 and was published January 11\textsuperscript{th} 2016. Reproduced from Ref.[32] with permission from the Royal Society of Chemistry. The corresponding Supplementary Information is shown in the Appendix, section A.1 page 132. While in total nine authors (including principal investigators of the SFB-TR 87 project) contributed to this paper, the contribution of the first author was the major one and includes the planning, execution and interpretation of the following experiments and measurements:

- Precursor synthesis, chemical characterization (NMR and temperature-dependent NMR studies), EA and TG analysis,
- thin film depositions \textit{via} PEALD including \textit{in-situ} QCM experiments,
- thin film characterization regarding thickness (Reflectometry), crystallinity (GI-XRD) and composition (RBS/NRA assisted by Dr. D. Rogalla) and
- writing the manuscript.

The following experiments were performed by co-authors, while planning and interpretation of the obtained data was carried out by the first-author:

- Morphology (AFM, I. Giner, University Paderborn, Germany),
- composition (XPS, M. Wiesing and T. de los Arcos, University Paderborn, Germany)
- OTRs (Mocon, F. Mitschker, Ruhr-University Bochum, Germany).

\textsuperscript{a}M. Gebhard and A. Devi \textit{et al.}, \textit{J. Mater. Chem. C}, 2016, \textbf{4}, 1057
An efficient PE-ALD process for TiO$_2$ thin films employing a new Ti-precursor$^\dagger$

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An efficient plasma-enhanced atomic layer deposition (PE-ALD) process was developed for TiO$_2$ thin films of high quality, using a new Ti-precursor, namely tris(dimethylamido)-(dimethylamino-2-propanolato)titanium(iv) (TDMADT). The five-coordinated titanium complex is volatile, thermally stable and reactive, making it a potential precursor for ALD and PE-ALD processes. Process optimization was performed with respect to plasma pulse length and reactive gas flow rate. Besides an ALD window, the application of the new compound was investigated using in situ quartz-crystal microbalance (QCM) to monitor surface saturation and growth per cycle (GPC). The new PE-ALD process is demonstrated to be an efficient procedure to deposit stoichiometric titanium dioxide thin films under optimized process conditions with deposition temperatures as low as 60 °C. Thin films deposited on Si(100) and polyethylene-terephthalate (PET) exhibit a low RMS roughness of about 0.22 nm. In addition, proof-of-principle studies on TiO$_2$ thin films deposited on PET show promising results in terms of barrier performance with oxygen transmission rates (OTR) found to be as low as 0.12 cm$^3$ day$^{-1}$ for 14 nm thin films.

Introduction
Titanium dioxide (TiO$_2$) represents a highly versatile material with applications ranging from self-cleaning and anti-reflecting coatings, photocatalysis (water splitting), transparent conductive oxides and semiconductors.$^{1-4}$ More recently, the application of TiO$_2$ thin films as gas barrier coating has attracted a lot of interest.$^{5-7}$ Similar to SiO$_2$ and Al$_2$O$_3$, the amorphous structure of a densely packed inorganic thin film of TiO$_2$ shows promising barrier performance toward imperiling gases and vapors, such as oxygen and water.$^{8,9}$ The deposition of defect-free thin films is of particular high importance for application as gas barrier coating, as it is known that nano- and micro-defects play a significant role in the diffusion of gases and vapors through barrier layers.$^{10-13}$ In this context, ALD is one of the promising deposition techniques with distinct advantages over other thin film coating methods. Due to the self-limiting growth, highly conformal thin films can be obtained even over large areas or complex surface geometries.$^{14}$ In particular, ALD enables a pinhole free and uniform coating of structures even with high aspect ratios.$^{15}$ In addition, low temperature processes decrease the mechanical stress between an inorganic thin film and a polymer substrate, which is often caused by different thermal expansion coefficients.$^{16}$ The coating of established and emerging high-tech components in state-of-the-art technologies, such as solar-cells and flexible electronics, is especially challenging in terms of sensitive substrate arrangements like integrated circuits or organic light emitting diodes (OLEDs).$^{17,18}$ In particular, the coating of polymers makes processes operating at low temperatures a necessity.$^{18}$ A good option can be found in PE-ALD, where heat treatment of substrates can be decreased near to room temperature, thus meeting the aforementioned requirements without destroying the substrates.$^{19,20}$ In addition, impinging and highly reactive plasma species cause higher degrees of cross-linking within the growing thin film, making it more compact and dense.$^{21,22}$ Thin films of TiO$_2$ have been deposited by ALD using various precursors such as TiCl$_4$,[Ti(OPr$_i$)$_3$] (TTIP) and [Ti(NMe$_2$)$_4$] (TDMAT).$^{23-25}$ Additionally, heteroleptic compounds like amino-alkoxides [Ti(NMe$_2$)$_2$(dmae)$_2$], mixed alkoxide-cyclopentadienyls [Cp$^*$Ti(OMe)$_3$] and alkoxide-amidinates [Ti(OPr$_i$)(NPr-Me-amd)$_2$] of titanium were successfully applied in ALD to grow TiO$_2$ thin films.$^{26-28}$ Several processes to deposit TiO$_2$ by thermal ALD have been described in the literature, including detailed investigations on the mechanisms and thin film characteristics.$^{29,30}$ Detailed investigations on PE-ALD processes to deposit titanium dioxide, including spatial ALD at low temperatures (<100 °C), cover the already mentioned precursors TiCl$_4$, TTIP and TDMAT.$^{17,26,27,31-35}$
In addition, other heteroleptic complexes with bulky chelating groups, namely [Ti(NMe2)3(dmap)] and [Ti(NMe2)3(guan)], were developed and [Ti(NMe2)3(guan)] was successfully applied to grow high-quality TiO2 thin films using PE-ALD. As TDMAT shows limited thermal stability, the partial modification with alkyl-amine ligands is an option to develop precursors with enhanced thermal stability without compromising on the high volatility and reactivity of the parent TDMAT. Herein, we present an efficient PE-ALD process to deposit TiO2 thin films at low temperatures, based on a new five-coordinated Ti-complex, namely tris(dimethylamido) (dimethylamino-2-propanolato)titanium(IV) (TDMADT, 2), Scheme 1 and its characterization.

Owing to the promising physico-chemical characteristics in terms of volatility, reactivity and thermal stability, the new Ti-compound was employed to deposit TiO2 via PE-ALD both on silicon and on PET substrates to investigate the growth characteristics and to fabricate gas barrier coatings (GBC). The results are compared to TiO2 thin films deposited by PE-ALD using the parent TDMAT precursor.

**Experimental section**

**Precursor synthesis and characterization**

Tris(dimethylamido) (dimethylamino-2-propanolato)titanium(IV) (TDMAT, 2). All synthesis reactions and manipulations are performed using standard Schlenk techniques under an atmosphere of argon. Sample preparation for analysis was carried out in an argon-filled glovebox (MBraun LM 100). Hexane (technical grade) was dried and purified using an MBraun solvent purification system (MBraun SPS). The starting compounds TiCl4 (Sigma Aldrich) and LiN(CH3)2 (95%, Sigma Aldrich) were used as received. 1-Dimethylamino-2-propanol (Sigma Aldrich) was added dropwise. After the reaction was completed, the solvent was removed under reduced pressure. The residue, a red liquid, was dried at 50 °C under vacuum to obtain a spectroscopically pure product (8.47 g, 99.3% based on TDMAT).

Elemental analysis for C11H30N4O Ti( % ): found: C, 46.70; H, 10.79; N, 19.82; Ti, 16.95. Calc.: C, 46.78; H, 10.73; N, 19.84; O, 5.67; Ti, 16.98. 1H-NMR (200 MHz, C6D6, 25 °C): δH (ppm) = 1.25, 1.32 [d, d, J = 6.0, 0.9 Hz and d, d, J = 6.1 Hz, 3H, TiOCH(CH3)2CH2N(CH3)2], 2.04–1.91, 2.54–2.26 [m, 2H, TiOCH(CH3)2CH2N(CH3)2], 2.14 [s, 6H, TiOCH(CH3)2CH2N(CH3)2], 3.11, 3.19, 3.35 [s, s, t, 18H, [Ti(NMe2)3(dmap)]. Scheme 1 Schematic structure of the conventional Ti-precursor TDMAT (1) and its new derivative TDMADT (2).

Elemental analysis for C11H30N4O Ti( % ) : found: C, 46.70; H, 10.79; N, 19.82; Ti, 16.95. Calc.: C, 46.78; H, 10.73; N, 19.84; O, 5.67; Ti, 16.98. 1H-NMR (200 MHz, C6D6, 25 °C): δH (ppm) = 1.25, 1.32 [d, d, J = 6.0, 0.9 Hz and d, d, J = 6.1 Hz, 3H, TiOCH(CH3)2CH2N(CH3)2], 2.04–1.91, 2.54–2.26 [m, 2H, TiOCH(CH3)2CH2N(CH3)2], 2.14 [s, 6H, TiOCH(CH3)2CH2N(CH3)2], 3.11, 3.19, 3.35 [s, s, t, 18H, [Ti(NMe2)3(guan)].

**Characterization**

NMR spectra were recorded on a Bruker Avance DPX 200. All spectra were referenced to an internal standard (TMS, δ = 0.00 ppm), while dried deuterated benzene was the solvent in all cases (solvent reference peak is δ = 7.16 ppm). For temperature-dependent NMR studies, deuterated toluene was chosen due to its higher boiling point. Stacked spectra have been normalized to the largest peak. Thermogravimetric analysis (TGA) was carried out on a Seiko TG/DTA 6200/SII device, applying a heating rate of 5 K min−1 under N2 flow (300 ml min−1). For each measurement, a sample mass of about 15 mg was weighed in an aluminum crucible. Elemental analysis was carried out at Microlab Kolbe in Mülheim, Germany. For CHN determination, a Vario EL analyzer from Elementar was used while titanium was measured using a Specod 50 device from AnalytiKlaven.

**Thin film deposition**

All depositions were carried out in a custom built stainless steel showerhead reactor, operating an ECRW plasma at 13.56 MHz. The precursors were filled in stainless steel cartridges maintained at 70 °C and 90 °C for TDMAT (1) and TDMADT (2), respectively. Precursors were pulsed without additional carrier gas. For all depositions, RF power was set to 200 W while the reflected power was 50–55 W. Oxygen (AirLiquid, 99.995%) and argon (AirLiquid, 99.999%) gas flow was monitored during the respective pulse times by mass flow meters. A fixed flow rate of 15 sccm was set for Ar. After evacuation, a base pressure of 5 × 10−6 mbar was reached. For optimizing the ALD process, depositions were performed on polished 2-inch p-type Si(100) wafers. Before each deposition, the substrates were cleaned as follows: After rinsing in boiling isopropanol, acetone and again isopropanol, the substrates were ultrasonicated in HPLC grade water for 10 minutes. PET substrates (Hostaphan RD 23, Mitsubishi Polyester Films, Wiesbaden, Germany, 23 μm thick) were used as received. The temperature of the substrate holder was set to 60 °C for all depositions. Investigations on the ALD window, saturation behavior and linearity were carried out by applying the following optimized deposition sequence: The Ti-precursor was pulsed two times for 40 ms each, separated by an intermediate 200 ms gap. After 500 ms, a two-step purge, each of 50 ms separated by a 100 ms pumping step, took place. After 850 ms, oxygen gas was introduced into the system and the plasma was ignited after 150 ms. The oxygen pulse was also used as the second purging step, lasting in total for 600 ms.
Thin film characterization
Thin film thickness on Si(100) was measured using reflectometry on a FIAngstrom F20 device, applying literature data for the refractive index and extinction coefficient in the range from 400 nm to 1000 nm. Each sample was measured at five different points on the wafer surface to verify the film thickness uniformity across the substrate. In situ QCM measurements were made using an ALD-sample holder attached to a SO-100 Oscillator (6 MHz) and a SQM-160 thin film deposition monitor (JCM, Inficon). For measurements, AT-cut QCM crystals coated with Au and optimized for deposition at 120 °C were used. Atomic force microscopy (AFM) on selected samples was performed using a JPK Nanowizard III Ultra (JPK Instruments AG) equipped with an anti-noise and anti-vibration box. All images were recorded in air using intermittent contact mode. AFM raw data were processed using the open-source software Gwyddion. The composition of thin films deposited on silicon was determined employing Rutherford backscattering spectroscopy (RBS) in combination with nuclear reaction analysis (NRA) at RUBION, the Central Unit for Ion Beams and Radio-nuclides at Ruhr-University Bochum. RBS measurements were made with a 2 MeV He+ beam with a beam intensity of about 60–80 nA. XPS was carried out within an ESCA+ facility (Omicron) at a base pressure of \( <1 \times 10^{-10} \) mbar using monochromated Al-Kα radiation (XM1000, 300 W, 1486.7 eV) and a charge neutralizer (CN 10+, 4.0 eV, 9 µA). Core level spectra were recorded at a constant analyzer energy of 20 eV and at 15° and 60° emission angle relative to the surface normal. The energy calibration was done by shifting the C1s signal of adventitious carbon to 284.8 eV. The measuring depth at the investigated angles is 5.5 nm (15°) and 2.8 nm (60°), respectively. Oxygen transmission rates (OTR) were monitored using a commercial Mocon OXTRAN 2/61 (Mocon Inc., Minneapolis, USA) using the carrier gas method at 23 °C and 0% humidity.

Results and discussion
Precursor evaluation
The new compound TDMADT was evaluated in terms of its chemical and thermal properties in view of its potential application in ALD processes. After isolation of the product, detailed investigations on the thermal properties and decomposition were carried out, employing temperature dependent \(^1\)H-NMR spectroscopy, TGA and isothermal TGA. The synthesis route adopted resulted in high yields (\( >99\% \)) of the target compound and it was found to be spectroscopically pure as verified from NMR analysis. For temperature-dependent \(^1\)H-NMR studies, all measurements were carried out using the same sample while the spectra (Fig. 1) were recorded after 10 minutes at the respective temperature. From these studies it is evident that no decomposition takes place up to 100 °C, as no additional peaks develop and integration of the respective area is constant with changing temperature. The downfield shifted dimethylamido groups at the metal center show a high fluctuation, indicated by the triplet between 3.35 ppm and 4.43 ppm for −50 °C and 100 °C, respectively. At lower temperatures, this triplet becomes less resolved and appears as two broad signals, which might migrate to only one signal at even lower temperatures. The triplet shape vanishes at higher temperatures, showing higher fluctuation of the three amide groups. In addition to the shape of the triplet, the intensity of the two singlets (3.17 ppm and 3.25 ppm) and the triplet changes from a non-equilibrium ratio of 4.5 : 1 : 4.5 at −50 °C to an equal ratio of nearly 1 : 1 : 1 at 100 °C. Interestingly, the multiplet at 1.35 ppm, assigned to the carbon-bonded methyl group of the dmap-ligand, shows the tendency to become better resolved at higher temperatures. While the signal appears as a broad multiplet at −50 °C, it can be identified as a doublet of doublets already at −25 °C. With increasing temperature, it develops again into a multiplet with even sharper peaks. This behavior might be caused by the dimer–monomer exchange phenomenon. At −50 °C, the methyl groups adjacent to the nitrogen atom in the ligand (2.15 ppm) appear as a roughly resolved doublet at 2.15 ppm, which is shifted downfield at higher temperatures and splits into two singlets at 100 °C. The CH₃ group of the ligand is nested around these two singlets, showing manifold coupling both at 1.97 ppm and 2.37 ppm. The proton located at the oxygen-bonded carbon atom exhibits the highest chemical shift at 4.58 ppm with a complex multiplet (cut-out of the selected region in Fig. 1).

The TG analysis of TDMADT revealed single step vaporization and the weight loss characteristics are similar to the parent amide (TDMAT) as shown in Fig. 2, except that the onset temperature for volatilization is shifted to slightly higher temperatures (60 °C). It should be noted that the onset of evaporation as well as the decomposition temperature of 180 °C for the TDMADT (2) follows the trend of the earlier reported compound [Ti(dmap)₂(NMe₂)₂], where two dimethylamido ligands have been substituted by
renders the new compound as a promising precursor for ALD affected. a chelating dmap ligand resulted in an increased thermal that the substitution of one of the parent amide groups with 1 evaporation and decomposition were found to be 100 dmap-ligands. For this compound, temperatures for onset of Fig. 2 TGA curves of TDMAT and its derivative TDMADT. Inset: Iso-TGA of TDMADT at 80 °C and 100 °C.

The volatility, enhanced thermal stability and reactivity renders the new compound as a promising precursor for ALD application. From isothermal TGA at 80 °C and 100 °C (shown as the inset in Fig. 2) a nearly constant weight loss was observed. This indicates that a constant mass transport of the precursor could be achieved during the ALD process.

Growth characteristics

The PE-ALD process, employing the new Ti-compound as precursor, was investigated in terms of surface saturation, ALD window and linearity. In situ QCM was used to determine surface saturation during precursor feed. Here, changes in the frequency of the oscillating quartz crystal are monitored. According to the Sauerbrey equation, the change of the resonance frequency of the quartz crystal can be correlated to mass adsorbed on the substrate during the deposition process. As we found that the employed QCM crystals exhibit a root-mean-square (RMS) roughness significantly higher than that of the usually used substrates like silicon (1.0 μm vs. 0.22 nm), our results are presented as the shift in the frequency of the QCM. Fig. 3 shows the results from two feeding times, 2 × 40 ms and 2 × 150 ms, for TDMADT and one feeding time (2 × 40 ms) for TDMAT.

In each case, the precursor was pulsed two times interrupted by a 200 ms gap. For the two different feedings of TDMADT, surface saturation was achieved after about 1.0 s, indicated by the emerging plateaus. The adsorption of TDMADT causes a frequency shift of 0.75 Hz, which is about 0.3 Hz higher than for TDMAT. As in both cases surface saturation is achieved, the only explanation for this difference in frequency shift is the different molecular mass of the two precursors. This implies that the heavier dmap-ligand is still bonded to the Ti-atom, most likely facing away from the substrate surface, and surface bonding takes place through the cleavage of a Ti-NMe2 bond.

The process was further investigated employing QCM with regard to consistency of repeated cycles. Here, in contrast to saturation studies, a whole and continuous process was investigated. A cut-out from a representative plot of frequency shift vs. time, obtained from a PE-ALD process using TDMADT, is shown in Fig. 4.

From blind experiments (same process without precursor supply) the QCM response was monitored to allow a reasonable interpretation of the obtained data (black squares). During these blind experiments, the plasma pulse is accompanied by a positive frequency shift of 3.25 Hz. When the plasma is turned off, it is expected that the crystal equilibrates to its earlier frequency. Here, a difference of 0.3 Hz remains, indicating that the crystal needs more time for sufficient equilibration. As there was no additional pumping step between plasma-off and the next precursor supply, i.e. between two cycles, it has to be taken into account that this negative frequency shift is always superimposed by the event of precursor
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adsorption, which is expected to be 0.73 Hz from saturation studies.

Therefore, the negative frequency shift during the precursor pulse should be 3.98 Hz. Indeed, we found a frequency shift for this event of 4.48 Hz. As known from blind experiments, the difference of about 0.5 Hz is most likely caused by a thermal non-equilibrium of the crystal. The results from QCM analysis are encouraging, as the ALD criteria of surface saturation and linear increase in thickness are proven preliminary to detailed studies on comprehensive deposition series. In addition, it is most likely that the dmap-ligand of the new compound is still intact and can act partially as an oxygen source. As mentioned above, the difference in RMS roughness between QCM crystals and other used substrates makes the estimation of thin film thickness not feasible. Therefore, as a complementary method for thickness measurement, optical reflectometry was employed in the following sections.

In terms of an ALD window, a temperature-independent GPC of (0.95 ± 0.03) Å per cycle was found for the new precursor for substrate temperatures between 50 °C and 120 °C (Fig. 5a). For substrate temperatures above 120 °C, the GPC drops to about 0.8 Å per cycle, remaining a high growth rate. The observed growth rates for the new compound are rather high and within the broad range of growth rates reported for other Ti-precursors, such as TTIP (0.45–0.7 Å per cycle)\(^{42,43}\), TiCl\(_4\) (0.28–0.65 Å per cycle)\(^{14,44}\) and TDMAT (0.75–2.0 Å per cycle)\(^{35,45}\). Among the known precursors for titanium dioxide thin films, the new compound represents a competitive precursor in terms of obtaining high growth rates.

Furthermore, an ALD window is usually not observed for PE-ALD processes, as the plasma contributes to the whole process with several new parameters, thus affecting the typical ALD behavior. Highly reactive plasma species are also formed among the adsorbed precursor molecules at the substrate, leading to surface migration, reactions, desorption and decomposition. Therefore, if an ALD window is observed during a PE-ALD process, it is even more indicative that the nature of the process is truly following an ALD mechanism, where surface saturation without gas phase precipitation, gas phase reaction or precursor decomposition takes place.

Thickness dependence as a function of ALD cycles was investigated in the range of 100–500 cycles and the data are shown in Fig. 5b. For TDMAT, a GPC of (0.93 ± 0.02) Å per cycle is obtained from the slope of the linear fit for thickness vs. cycles. Applying the same process parameters, GPC increases with 11% for TDMADT to 1.0 Å per cycle. The low standard deviation (error bars) indicates a reproducible layer growth process for both precursors. Furthermore, high homogeneity over the whole substrate is achieved, indicated by a non-uniformity of only 0.2% on a 45 nm thick film, deposited using TDMADT. Taking into account the relation of molecular masses and frequency shifts from QCM saturation studies, it can be assumed that nearly the same amount of precursor molecules adsorbs during one cycle on the surface, resulting in nearly similar GPC.

The growth behavior was further investigated regarding the influence of the plasma pulse length. Fig. 6 shows the GPC values for TDMAT and TDMADT with variation of the oxygen plasma pulse.

When the substrate is exposed to a plasma step of 100 ms or shorter, the growth rates for both precursors are rather high with 1.3 Å per cycle and 0.98 Å per cycle for TDMAT and
TDMAT, respectively. For a plasma pulse of 150 ms, a stronger decrease in GPC is found for TDMAT than for TDMADT, indicating a higher stability of the new precursor towards the applied plasma. For both compounds, a plateau in the growth rate can be found between 150 ms and 300 ms, where in both cases the growth rate is 0.8 Å per cycle. As the plasma oxidizes the ligands of the used Ti-precursors to form TiO₂, high growth rates for short plasma pulses are most likely connected to higher amounts of impurities due to insufficient combustion of the ligands.

Thin film characteristics

The surface features of thin films deposited on Si substrates were investigated by AFM in terms of RMS roughness, and representative AFM images of 24 nm thin films deposited at 60 °C on silicon with an oxygen flow rate of 25 sccm and a plasma pulse length of 150 ms are shown in Fig. 7. From each sample, 1 μm × 1 μm and 500 nm × 500 nm scans were performed. For both precursors, low RMS roughness values, irrespective of the scan size, of 0.36 nm (TDMAT, 1) and 0.22 nm (TDMADT, 2) were found, matching findings from other PE-ALD applications employing TDMAT with RMS roughness values of 0.2–0.31 nm. For TDMAT, AFM revealed the formation of more distinctive hillocks with a height of about 1.6 nm while thin films deposited using TDMADT show a maximum height of only 0.95 nm for surface structures. For both precursors, the formation of single grains is observed, indicating the tendency of both compounds to agglomerate at several nucleation sites during film growth. As the bare silicon substrate exhibits a RMS roughness of 0.22 nm, a true ALD process during which the surface topology of the substrate is mimicked by the growing thin film can be assumed. Interestingly, this finding is even more distinctive for the new precursor TDMADT, as the thin film and the bare substrate show the same roughness.

The composition of the deposited thin films was determined employing RBS and NRA. RBS experiments allow the detection of heavier elements like Si and metals, whereas lighter elements like C and N were detected by means of NRA measurements (Table 1).

As growth rates were found to be temperature-independent within the range from 60 °C to 120 °C, thin films deposited at these temperatures (within the ALD window) were investigated to ensure consistency in composition. Measured and respective simulated RBS spectra are shown in Fig. 8. Besides titanium (1439 keV), silicon (substrate, 1139 keV) and oxygen (710 keV), no other elements were detected. From the spectra in Fig. 8, it is evident that at both deposition temperatures the thin film composition is consistent within the ALD window.

As it is known that the plasma pulse length and the oxygen flow rate, i.e. the amount of oxygen during plasma ignition, do have a strong influence on thin film composition, detailed analysis was carried out on respective deposition series and the results are listed in Table 1. For depositions investigating the influence of the plasma pulse length, the oxygen flow rate was kept constant at 15 sccm. For both precursors, plasma pulse length ≤ 100 ms yields thin
films with high amounts of carbon and nitrogen and the ratio of titanium to oxygen is well above 2.0 and the formation of carbide and nitride species must be assumed. For a plasma pulse of 150 ms, impurities in the thin films grown from TDMAT are still high with 13.0 at% (C) and 17.2 at% (N), respectively. For a 150 ms plasma pulse, TDMADT yields only minor contaminations of 1.7 at% (C) while nitrogen was not detected. Thin films deposited applying a plasma pulse of ≥200 ms show low impurities for both carbon and nitrogen up to 2 at% and nearly perfect stoichiometry, irrespective of the chosen precursors. For TDMAT, a higher oxygen flow rate leads to a significant increase in the oxygen content of the thin films from 43.2% to 63.5%. Using TDMADT yields high oxygen contents already at low flow rates. In addition, using TDMADT yields nearly stoichiometric thin films even at low oxygen flow rates with an O/Ti ratio of 2.2.

The surface chemical composition of representative samples, deposited with 150 ms and 200 ms plasma pulse length, was further characterized using angle-resolved XPS. O/Ti ratios and amounts of C and N in at% are shown in Table 2. Around 2 at% of N was found throughout the samples at both take-off angles and is thus associated with bulk N originating from the precursors. In this regard, the N atomic fraction was observed to be decreased to ≤2 at% at 200 ms pulse length when using TDMADT. The O/Ti ratios are found to be around 1.8 (15') and 1.7 (60'). The deviation of the O/Ti ratio from the expected value of 2 is within the limit of error, taking into consideration that the adventitious carbon surface layer is known to affect XPS quantification. High resolution core level spectra were measured and are shown in Fig. 9.

The C1s spectrum can be assigned to three carbon species peaks: aliphatic C at 284.8 eV, COH and -carbon of carboxylic acids at 285.8 eV, and carboxylic acids at 288.5 eV. The Ti2p spectrum was described by a single doublet corresponding to TiO2 with the Ti2p3/2 component at a binding energy of 458.6 eV. The O1s exhibited one component at 530.0 eV, which can be assigned to TiO2, and a second component at 531.3 eV, which is typical for either surface hydroxylation or O bound to adventitious carbon. The O content bound to adventitious carbon as derived from the C1s spectra amounted to around 30% of the C atomic fraction, which matched quantitatively the atomic fraction of the higher binding energy O1s signal. Thus, the O1s component located at 531.3 eV can be said to be dominated by adventitious carbon without significant evidence of hydroxylation. The N1s core level revealed a single N component at 400.7 eV, which was assigned to interstitial N.

From the results based on the aforementioned process optimization in terms of substrate temperature, the deposition of TiO2 thin films using TDMADT on polymer substrates is promising with respect to application as gas barrier coating. Results from preliminary studies on barrier performance in terms of OTR of TiO2 thin films are shown in Fig. 10. For both precursors, respective analysis was carried out on deposition series with increasing number of cycles, where the range from 20 cycles to 150 cycles was of particular interest.

Table 2 Stoichiometry of PE-ALD TiO2 thin films deposited at 60 °C and 25 sccm flow rate using TDMAT and TDMADT at different pulse lengths as measured by angle-resolved XPS

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Pulse length (ms)</th>
<th>C1s (at%)</th>
<th>N1s (at%)</th>
<th>O1s (at%)</th>
<th>Ti2p (at%)</th>
<th>O/Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDMAT</td>
<td>150</td>
<td>28.1</td>
<td>1.9</td>
<td>50.0</td>
<td>19.9</td>
<td>1.8</td>
</tr>
<tr>
<td>TDMADT</td>
<td>150</td>
<td>28.1</td>
<td>1.9</td>
<td>50.0</td>
<td>19.9</td>
<td>1.8</td>
</tr>
<tr>
<td>TDMAT</td>
<td>200</td>
<td>27.6</td>
<td>2.1</td>
<td>50.3</td>
<td>20.0</td>
<td>1.8</td>
</tr>
<tr>
<td>TDMADT</td>
<td>200</td>
<td>27.0</td>
<td>1.5</td>
<td>51.2</td>
<td>20.4</td>
<td>1.7</td>
</tr>
<tr>
<td>TDMAT</td>
<td>200</td>
<td>42.3</td>
<td>1.9</td>
<td>40.5</td>
<td>15.3</td>
<td>1.7</td>
</tr>
<tr>
<td>TDMADT</td>
<td>200</td>
<td>40.0</td>
<td>2.1</td>
<td>42.3</td>
<td>15.7</td>
<td>1.8</td>
</tr>
<tr>
<td>TDMAT</td>
<td>200</td>
<td>40.5</td>
<td>2.6</td>
<td>41.7</td>
<td>15.2</td>
<td>1.7</td>
</tr>
<tr>
<td>TDMADT</td>
<td>200</td>
<td>41.0</td>
<td>1.7</td>
<td>41.4</td>
<td>15.8</td>
<td>1.6</td>
</tr>
</tbody>
</table>

* Calculation based on the oxide component of the O1s signal at 530.0 eV as derived from the corresponding core level spectra.
A significant change in barrier performance was not observed for thin films deposited with less than 60 cycles (6 nm and 5.6 nm for TDMAT and TDMA DT, respectively). Irrespective of the chosen precursor, thin films showed OTRs in the range of the uncoated PET foil of about 70 cm$^3$ m$^{-2}$ day$^{-1}$. Interestingly, using TDMA DT (2) causes an initial slight drop in OTR after 80 cycles (7.4 nm), while the barrier performance for films deposited using TDMAT (1) remains in the order of the uncoated foil. For 100 cycles (9.3 nm and 10 nm for TDMAT and TDMA DT, respectively), thin films from TDMAT show better barrier performance than those deposited from TDMA DT. A critical thickness, i.e. a drop of at least two orders of magnitude in OTR,$^{12}$ is found in both cases when 150 cycles (15 nm for TDMA DT and 14 nm for TDMA DT) are applied. At this point, differences in the OTR of thin films obtained from the two different precursors are very low. Despite a good barrier performance in terms of OTR for films originating from both precursors below 0.2 cm$^3$ m$^{-2}$ day$^{-1}$, a different nucleation for the two precursors during the first cycles must be assumed, indicated by the discrepancy in OTR values for 80 and 100 cycles. This is also in agreement with AFM results, where thin films from TDMAT show the formation of stronger pronounced hillocks. However, titanium dioxide gas barrier layers with promising performance were successfully deposited on PET substrates using the new compound TDMA DT and a critical thickness of $d_c = 14$ nm was found. In comparison with other ALD gas barrier layers, the performance of our coatings is in good agreement with reported values from the literature. For example, a pure TiO$_2$ thin film of 10 nm thickness on LDPE results in an OTR of 10.0 cm$^3$ m$^{-2}$ day$^{-1}$. In contrast to this, a 128 nm coating of Al$_2$O$_3$ is needed to achieve a barrier coating of 2.0 cm$^3$ m$^{-2}$ day$^{-1}$ on PET.$^{13}$

Conclusions

Using the new compound TDMA DT, [Ti(NMe$_2$)$_3$(dmap)], we successfully demonstrated an efficient PE-ALD process to deposit TiO$_2$ thin films at low temperatures (60 °C), allowing depositions on polymers with low melting points such as PET. The new precursor exhibits high volatility, higher thermal stability compared to TDMAT and a fine-tuned reactivity, resulting in a high growth rate of 0.93 Å per cycle. In situ QCM analysis of PE-ALD experiments revealed a sufficient surface saturation even for very short precursor pulse times of only $2 \times 40$ ms and the presence of the dmap-ligand after surface adsorption. Temperature-independent growth was found in an ALD window between 60 and 120 °C for an optimized PE-ALD process using the new compound, exhibiting a high growth rate of 0.92 Å per cycle. In addition, studies on the thickness vs. number of cycles prove the principle of a true, self-limiting ALD process. Coatings from PE-ALD on silicon were found to be amorphous over the whole temperature range of the ALD window and in comparison to the often used precursor TDMAT, RBS/NRA and XPS revealed the good suitability of this precursor in PE-ALD with regard to thin film composition, exhibiting extremely low amounts of carbon and nitrogen ($\leq 2$ at%). An explanation for this observation could be that the new titanium-complex TDMA DT already comprises a titanium–oxygen bond, thus facilitating the formation of an inorganic thin film more likely at an earlier stage of the PE-ALD process compared to TDMAT, which is an all-nitrogen-coordinated complex. From AFM investigations on 24 nm thick samples, RMS roughness was determined to be 0.22 nm, revealing highly smooth films. From our experiments, the new compound facilitates the formation of TiO$_2$ thin films due to the presence of a Ti-O bond within the precursor. From this, films of higher quality can be obtained in a less processing time. Finally, preliminary studies on the gas barrier performance of TiO$_2$ thin films deposited from TDMA DT on PET substrates show promising results regarding OTR, since values were found to be as low as 0.12 cm$^3$ m$^{-2}$ day$^{-1}$ for a critical thickness of about 14 nm.

Acknowledgements

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Notes and references

3. A combinatorial approach of PECVD and PEALD to deposit GBLs on polymers

3.1. Introduction to composite materials as GBLs on polymers

For the fabrication of GBLs on polymers, PECVD and PEALD techniques are favored, especially owing to their efficiency regarding promising barrier properties of deposited thin films and as these techniques are operated at low temperatures and are capable of yielding dense and homogeneous layers. As depicted in tables 1.3 and 1.4, several groups carried out detailed research on GBLs grown by PECVD and during the last years, PEALD has a attracted interest for this purpose as well. However, most of the reported research focuses mainly on the investigation of ultra GBLs for OLED encapsulation while applications for food or pharmaceutical packaging were not adequately addressed. The major difference between OLED encapsulation and the packaging of food/pharmaceuticals is found in the used substrates. For OLEDs, PEN, PES and PET substrates of 100 nm to 200 nm are of interest, as they provide an already high intrinsic barrier performance which can be further enhanced by depo-
position of the outlined GBLs, as discussed in section [1.6]. For packaging of food, beverages and pharmaceuticals substrates of lower thickness are desired to minimize costs.[12] It should be noted that apart from petroleum-based polymers, polylactic acid (PLA) is currently investigated as potential substitute to produce a high-quality polymer for packaging application.[3]

While the application of organic polymers, e.g. from EVOH, from extrusion or plasma polymerization yields sufficient performance with respect to decreased WVTR and OTR of the respective packaging materials, these GBLs have to be applied as μm thick coatings. In addition, these organic materials are extremely challenging with respect to sustainability and recycling. Using metallic thin films of aluminum is another option and thin films between 10 nm and 100 nm resemble GBLs with enhanced performance.[4] However, such thin films are of concern in terms of recycling, too. Furthermore, they are not microwave compatible and cannot be used when transparency of the packaging material is a criterion.

Another promising option is the deposition of metal oxides for GBL application, combining the benefits of flexibility, high transparency as well as improved barrier performance,[4,5] and different aspects of GBL applications have been investigated, using a variety of deposition techniques (see tables [1.3] and [1.4]). However, recent research gives evidence that the macro-defect density of PECVD grown silica-like plasma polymers has a strong influence on the barrier performance.[6] While this statement is also true for PEALD grown GBLs, the defect density is strongly decreased by this deposition technique and GBLs obtained from PEALD exhibit improved barrier performance together with decreased defect density. In addition, PEALD coatings of TiO$_2$ were shown to exhibit superior barrier performance against water vapor, when compared with different PECVD materials, such as SiO$_x$ or a-Si:H. On the other hand, the fabrication of GBLs by PEALD is, from an economically point of view, not efficient enough. With growth rates of about 0.1 nm cycle$^{-1}$ and
a cycle duration between 1 sec to 30 sec, PEALD is rather slow compared to PECVD processes, where the growth rates are on the order of 1 nm sec$^{-1}$.

From this, the combination of PECVD and PEALD offers another option to fabricate GBLs on polymers, thereby bringing together the benefits from both techniques, creating a synergy of their advantages and ruling out respective drawbacks. The combination of PECVD grown and ALD or PEALD grown GBL materials has been investigated by many groups, focusing on the application of these composite materials for OLED encapsulation, i.e. as ultra GBLs. For this approach, the investigated composites were of thicknesses $\geq 90$ nm. Combinations of PECVD and ALD cover composite materials such as nanolaminates of (SiO$_x$ + a plasma polymer) or thicker PECVD grown silicon nitrides or silica-like oxides with an ALD top layer. For the nanolaminates, different thicknesses and polymer substrates are reported: SiO$_x$/plasma polymer (525 nm on 200 $\mu$m PEN), SiO$_x$/plasma polymer (1000 nm on PEN, thickness not reported), and SiO$_x$/plasma polymer (130 nm on PEN, thickness not reported). A more sophisticated nanolaminate, consisting of SiO$_x$, HfO$_2$ and a plasma polymer was reported in 2016 by Kim et al. All these nanolaminates were fabricated by a combination PECVD (plasma polymer) and thermal ALD (inorganic oxides). The combination of thicker PECVD coatings with an ALD top layer was reported the first in 2009 by Garcia et al. In this contribution, a 100 nm SiN PECVD grown film was coated with a 5 nm SiO$_x$ thin film from PEALD (125 $\mu$m PEN). Recently, in 2016 and 2017, Starostin et al. and Aghaee et al. investigated PECVD grown coatings of SiO$_x$ with PEALD grown SiO$_x$ top layers using porosity ellipsometry to investigate the influence of nanopores on the barrier performance. In these cases, 80 nm and 100 nm of SiO$_x$ were coated with 10 nm and 2 nm SiO$_x$, respectively. However, the instigated systems are comprised of rather thick coatings and gas barrier performance was analyzed for thick films on thick polymer substrates. While these studies are promising with respect to...
PECVD/PEALD grown composite materials for OLED encapsulation, only little is known about the performance of ultrathin films from such a combination.

From an industrial application perspective, the fast deposition rates of PECVD enables an efficient process while the PEALD coatings contribute a strongly improved barrier performance for incapable PECVD GBL coatings. In this context, PEALD grown thin films can be used in two different ways: First, they can be applied as thin capping on a PECVD grown silica-like coating, grown on a polymer substrate. In this case, the PEALD grown thin film acts as a capping for prevailing defects from the PECVD process. In a second approach, the highly homogeneous thin films from PEALD can serve as a seeding-layer on the polymer substrate for subsequent PECVD growth of silica-like films. From this, an improved growth with respect to nucleation and defect formation of PECVD thin film is expected.

In the following, the results from such a combinatorial approach to deposit GBLs are outlined and discussed in detail. For both routes, seeding and capping of PECVD grown thin films, the interaction of thin films with poor barrier performance, if applied as stand-alone GBL on a polymer, is investigated, meaning coatings of low thickness with high OTR values. From this, also an incremental influence from ultrathin PEALD films on the barrier performance of PECVD coatings can be investigated, allowing an understanding of the fundamental interactions of these differently grown thin films. In addition, the investigation of extremely thin seeding and capping layers allows an analysis of thickness- and material-limitation of the proposed combinatorial approach. Furthermore, the influence of the material chemistry of the PECVD grown plasma polymer is investigated. In total, the following systems are investigated:
3.1. INTRODUCTION TO COMPOSITE MATERIALS AS GBLS ON POLYMERS

1. PET + SiO\textsubscript{2} seeding layer (PEALD, thickness variation) + 15 nm PECVD grown SiO\textsubscript{x}.

2. PET + SiOCH (PECVD) + PEALD grown capping layer (Al\textsubscript{2}O\textsubscript{3} or SiO\textsubscript{2}, 1 nm and 5 nm) and

3. PET + SiO\textsubscript{x} (PECVD) + PEALD grown capping layer (Al\textsubscript{2}O\textsubscript{3} or SiO\textsubscript{2}, 1 nm and 5 nm).

These systems are evaluated with respect to morphology, barrier performance and defect density. In addition, the findings regarding barrier performance in terms of OTR for the combined systems are compared to results from investigations of pure PEALD an PECVD coatings to allow a reasonable interpretation of the obtained data. It should be mentioned that a more detailed discussion of precursor chemistry, with respect to Si and Al precursors, can be found in chapter 4 page 99ff.
References


3.2. A combinatorial approach to enhance barrier properties of thin films on polymers: Seeding and capping of PECVD thin films through PEALD

The following contribution was accepted for publication February 25th 2018 and was published first on March 8th 2018. Reproduced from *Plasma Process Polym.*, 2018, 15, e1700209 with permission from WILEY. The corresponding supplementary information is shown in the Appendix, section A.2 page 133. While in total nine authors (including principle investigators of the SFB-TR 87 project) contributed to this manuscript, the contribution of the first author was the major one and includes the planning, execution and interpretation of the following experiments and measurement data:

- PEALD thin film deposition and *in-situ* QCM experiments including process development and optimization with respect to saturation studies and linearity of thin film thickness vs. applied number of cycles,
- thin film characterization regarding thickness (Ellipsometry), crystallinity (GI-XRD) and composition (RBS/NRA assisted by Dr. D. Rogalla, RUBION, Germany) and
- writing the manuscript.

The following experiments were performed by co-authors, while planning and interpretation of the obtained data was carried out by the first author:

- Morphology (AFM, C. Hoppe, University Paderborn, Germany),
- OTRs and defect density (Mocon and SEM, F. Mitschker, Ruhr-University Bochum, Germany) and
A combinatorial approach to deposit gas barrier layers (GBLs) on polyethylene terephthalate (PET) by means of plasma-enhanced chemical vapor deposition (PECVD) and plasma-enhanced atomic layer deposition (PEALD) is presented. Thin films of SiOx and SiOxCyHz obtained from PECVD were grown either subsequently on a PEALD seeding layer (SiO2) or were capped by ultrathin PEALD films of Al2O3 or SiO2. To study the impact of PEALD layers on the overall GBL performance, PECVD coatings with high macro defect densities and low barrier efficiency with regard to the oxygen transmission rate (OTR) were chosen. PEALD seeding layers demonstrated the ability to influence the subsequent PECVD growth in terms of the lower macro defect density (9 macro-defects mm$^{-2}$) and improved barrier performance (OTR = 0.8 cm$^3$ m$^{-2}$ day$^{-1}$), while the PEALD capping-route produced GBLs free of macro-defects.

**KEYWORDS**
cappings, gas barrier layers, PE-ALD, PE-CVD, seedings

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**1 | INTRODUCTION**

Thin films of inorganic oxides such as alumina (Al$_2$O$_3$), silica (SiO$_2$), and titania (TiO$_2$) gained a lot of interest during the last years with respect to their promising performance as gas barrier layers (GBLs) on polymers.$^{[1-8]}$ GBLs must be applied if the packaging material, e.g., polypropylene (PP) or polyethylene terephthalate (PET), is not sufficiently effective enough to protect sensitive goods, such as food, beverages, pharmaceuticals as well as advanced electrical devices like organic light
emitting diodes (OLEDs). Usually, the oxygen transmission rates (OTRs) and water vapor transmission rates (WVTR) of common packaging polymer materials like the mentioned ones are too high, i.e., the barrier performance is too low, with values for OTRs ranging from 530 to 1700 cm$^2$ m$^{-2}$ day$^{-1}$ (PP) and 10$^2$ to 100 cm$^2$ m$^{-2}$ day$^{-1}$ (PET). For example, food packaging application usually requires a barrier performance regarding OTR of 1 cm$^2$ m$^{-2}$ day$^{-1}$.[10] While organic polymers, e.g., ethylene-vinyl alcohol, EVOH[11] or metallic coatings are known to improve the performance of polymers in terms by decreasing WVTRs and OTRs,[12,13] inorganic oxides exhibit additional advantages such as being both recyclable and microwave compatible. In addition, these oxide materials exhibit good barrier performance even when applied as thin films, where organic polymers need to be applied as films with thicknesses in the μm-range.[5,12] For example, the barrier performance of PET regarding OTR can be improved down to 10$^{-1}$ cm$^2$ m$^{-2}$ day$^{-1}$.[10] GBLs based on inorganic oxides and nitrides (e.g., SiN and SiN:H) have been studied since the 1990s and are usually fabricated by sputtering and plasma-enhanced chemical vapor deposition (PECVD).[14–16] While sputtering employs high-cost setups and is accompanied by challenges in terms of its line-of-sight deposition as well as difficulties with respect to the polymer substrates, thin films from PECVD are easier to produce and growth rates in PEALD are on the order of 3 × 10$^{-1}$ nm min$^{-1}$, enabling fast depositions and high throughputs. It was also deduced via PECVD that the introduction of a thin, less oxidized interlayer (SiOxCyHz), deposited from hexamethyldisiloxane (HMDSO), can significantly increase the GBL performance of a subsequently grown SiOx layer from the same precursor.[17–19] During the initial steps of deposition, the surface chemistry of the polymer is also influenced.[20,21] Furthermore, the chemical structure of the deposited inorganic thin films and hence barrier performance can change.[22] Interactions with oxygen in particular, are known to trigger degradative processes at the interface which influences the formation and cross-linking of the barrier film.[18,22] For example, the interface of a polymer and a growing thin film is known to be comprised of a mixture of coating species and etched polymer products.[23,24] As the surface condition is crucial for the development of defects as well, this could potentially result in an increased defect density. Since the transport of permeants through polymers and applied GBL coatings is strongly dependent on defect density and defect size,[22,25,26] gas barrier properties can be improved most efficiently by the deposition of highly cross-linked, dense, and defect-free thin films. In this context, plasma-enhanced atomic layer deposition (PEALD) is a promising deposition technique to achieve superior thin film qualities for different oxide materials like Al$_2$O$_3$, SiO$_2$, TiO$_2$, HfO$_2$, and ZrO$_2$, which have been successfully applied as GBLs.[6,7,27–30] With its self-limiting growth by sequential half-cycles, ALD and PEALD processes are capable of producing pin-hole free and highly conformal thin films. While thermal ALD can be used to deposit many materials already at low temperatures,[31,32] the adaption of PEALD enables depositions even at room temperature by using highly reactive plasma species which can provide a more efficient deposition in terms of shorter cycle times. The low substrate temperatures are an appealing benefit of PEALD especially within the context of coating sensitive polymers. Additionally, materials from PEALD usually exhibit high mass density values.[33] It was shown recently that PEALD grown thin films of TiO$_2$ show a strongly decreased defect density, compared with different PECVD grown SiOx and a-Si:H thin films, which can be correlated with an improved barrier performance toward oxygen gas.[34] Such PEALD thin films demonstrated an improved barrier against water ingress, i.e., lower WVTR values, compared with SiOx of the same thickness.[35,36] Different kinds of polymer substrates (e.g., PET, PP, polyethersulfone (PES), and polyethylene naphthalate (PEN)) and inorganic substrates (e.g., glass and silicon) were investigated to produce improved GBLs, fabricated by means of PEALD.[36,27,37,38] As these studies were performed in the context of OLED encapsulation, the used substrates are usually of a high thickness (≥100 μm). Furthermore, multilayers of Al$_2$O$_3$ thin films (25 nm, PEALD) and a plasma polymer from benzene (125 nm, PECVD), grown from PEALD and PECVD, respectively, exhibited improved moisture barrier performance on PEN.[39] Such a combination is a promising approach to fabricate GBLs, as high deposition rates from PECVD can be combined with the superior thin film quality of PEALD. While combinations of PECVD and PEALD have been reported earlier for thick coatings (≥90 nm) on thick substrates,[7,39–41] these studies did not address the interactions of PEALD and PECVD grown thin films with respect to macro-defects and a potential correlation with barrier performance.

Here, we discuss the results obtained from a combined PECVD/PEALD approach to deposit ultrathin GBLs on PET. The combination of PECVD and PEALD provides the advantages of both techniques to create a synergy with respect to improved GBLs, while respective drawbacks of each deposition technique could be eliminated in due course. In the present study, two different approaches were employed. PECVD thin films were either grown subsequently on highly homogeneous PEALD seeding layers or were capped with PEALD grown thin films. From the seeding-route, an improved growth of PECVD thin films is expected with respect to the defect density and barrier performance. By providing a defined and homogeneous substrate surface interface in terms of surface coverage, surface chemistry and roughness, the formation of macro-defects in the PECVD thin film could be suppressed. The capping-route is expected to improve the prior deposited PECVD surface thin film, since existent macro-defects could be closed, i.e., capped, by the
more efficient PEALD thin films. Combinations of different PECVD materials (more organic SiOxCyHz and more silica-like SiOx) with different PEALD grown oxides (Al2O3 and SiO2) were investigated with respect to barrier performance in terms of OTR and macro-defect density. GBLs from PECVD with rather poor barrier performance were either grown subsequently on a highly homogeneous SiO2 PEALD thin film (seeding) or were coated with a thin PEALD layer (capping). In the first case, the seeding-approach was investigated for SiOx (PECVD) thin films grown on SiO2 (PEALD) thin films of different thicknesses. For the capping route, both SiOxCyHz and SiOx thin films were capped with PEALD grown Al2O3 or SiO2 to enable a material comparison with respect to their barrier performance. Furthermore, the combined barrier systems were analyzed in terms of surface morphology by means of atomic force microscopy (AFM).

2 | EXPERIMENTAL SECTION

2.1 Thin film deposition

PEALD of Al2O3 and SiO2 thin films was carried out in a custom built low-pressure reactor (modular flow). With the grounded and heated (60 °C) substrate holder located between the antennas, an ECR-plasma was generated using radio frequency (13.56 MHz) and a static magnetic flux of 2.8 mT. The power of the plasma was adjusted to 200 and 50 W (forward and reflected, respectively). If not stated otherwise, the plasma discharge length was 150 ms. As precursors, trimethylaluminum (TMA, STREM, min. 98%) and bis-(diethylamino)silane (BDEAS, STREM Chemicals) were used as the respective metal/metalloid source. Both precursors were filled into stainless steel cartridges. TMA was cooled to 0 °C, while BDEAS was heated to 45 °C. As purge and plasma feedstock gas, argon (99.999%, Air Liquide, Alpha Gaz) and oxygen (99.995%, Air Liquide, Alpha Gaz) were used, respectively, with flow rates of 25 sccm in both cases. For each material system, one cycle for the applied standard PEALD process is described below. If not stated otherwise, all thin films were deposited employing the following parameters. Al2O3: a 13 ms dose of TMA was applied as precursor feeding, followed by a 500 ms purge. A 150 ms plasma step was carried out using oxygen gas, followed by a second purge step (250 ms). In total, one cycle lasted for 1750 ms. BDEAS was pulsed for 2 × 25 ms while being interrupted by a gap of 150 ms to achieve surface saturation. Steps two, three, and four (purge, plasma, and purge/pumping) were performed as for TMA with a total cycle time of 1750 ms. PECVD coatings, ranging from carbon containing silicon-based (SiOxCyHz) to silica-like (SiOx) films, were produced in a separate reactor (custom built) with a microwave (MW) driven low pressure plasma. A plasma line antenna is used for coaxial application of MW radiation (fMW = 2.45 GHz) with a maximum peak power of PMW = 3 kW. Hexamethyldisiloxane (HMDSO) was used for the deposition of SiOx:CyHz and SiOx barrier films with different admixtures of oxygen. SiOxCyHz coatings were deposited in a process solely fed with HMDSO and for SiOx, an oxygen to HMDSO ratio of 200 was applied, considering the ratio of gas fluxes (2 sccm HMDSO, 400 sccm O2) through the antenna via mass flow controllers (MFC). MW power was pulsed during film deposition. Processes fed solely with HMDSO were pulsed with an on time of 1 ms and processes with an admixture of oxygen were pulsed with 4 ms on time. The off time was chosen according to the homogeneity criterion. Working pressure was 25 Pa. The experimental setup was described in more detail by Deilmann et al. For process optimization, initially depositions were performed on p-type Si(100), which were cleaned prior to the experiments as follows: Si(100) substrates were first ultrasonicated in HPLC-grade 2-propanol and subsequently dried in an inert-gas stream. The samples were then ultrasonicated in HPLC-grade water and again dried in an inert-gas stream. For gas barrier experiments, thin films were deposited on a 23 μm thick PET foil (Hostaphan RD23, Mitsubishi, Wiesbaden, Germany), which were used as such.

2.2 Thin film analysis

The thickness of Al2O3 and SiO2 thin films deposited on p-type Si(100) was determined by means of a J. A. Woollam M-88 Ellipsometer in the range 300–800 nm using an incident angle of 65°. In situ QCM experiments were carried out using AT-cut quartz crystals (6 MHz) coated with gold and optimized for measurements ranging from room temperature to 60 °C. The custom-built crystal-holder was connected to a SO-100 Oscillator and a SQM-160 thin film deposition monitor (JCM, Inficon). AFM on selected samples was performed using a JPK Nanowizard III Ultra (JPK Instruments AG) equipped with an anti-noise and anti-vibration box. All images were recorded in air using intermittent contact mode. AFM raw data was processed using the open-source software Gwyddion. The composition of the thin films deposited on silicon was determined by employing Rutherford backscattering spectrometry (RBS) in combination with nuclear reaction analysis (NRA). RBS measurements were carried out using a 2 MeV He+ beam, while NRA was performed with a deuteron beam of 1 MeV. For both methods, the intensities were in the range of few nA up to 80 nA on the sample, which was tilted by an angle of typically 7°. Two silicon surface barrier detectors were used, one for RBS (160°) and one for NRA (135°). All recorded spectra were analyzed using SIMNRA software. Quantitative results on the thin film metal/metalloid content were derived from the RBS spectrum, while the NRA spectrum gave the C,
N, and O contents. Oxygen transmission rates (OTR) for films grown on PET were measured using a Mocon OX-TRAN 2/61 (Mocon Inc., Minneapolis, USA) using the carrier gas method at 23 °C and 0% humidity. Error bars reflect the standard deviation from the three independently investigated samples, prepared under the same conditions. Defect densities were quantified by the established technique, based on etching all samples for 1 h in a capacitively coupled oxygen plasma (CCP) and subsequent imaging by SEM.[46–48] Further details on the defect density quantification can be found elsewhere.[34] Reactive oxygen species from a CCP plasma were used to etch the polymer beneath the deposited GBLS. If defects are present in the deposited thin film, reactive oxygen species can travel through these defects and will reach the substrates, which is easily etched by oxygen radicals. As the inorganic oxide GBLS can be considered as chemically inert toward etching by reactive oxygen species, the corresponding etch rates are below the detection limit. The oxygen species cause an isotropic etching of the polymer, leading to hollow structures beneath the GBL. These structures can be detected by scanning electron microscopy (SEM), as they usually exhibit a bright aura around the macro defect, which appears black. As for OTR, standard deviation was obtained from measuring three samples under the same conditions. Spectroscopic ellipsometry (SE) measurements to determine the refractive index of the layers, were carried out using a M-2000D ellipsometer from J. A. Woollam co. with a fixed angle of incidence of 70°. For the measurement in vacuo, the samples were kept under vacuum (5 × 10−6 mbar) for 12 h.

3 RESULTS AND DISCUSSION

3.1 Morphology and barrier performance of PEALD grown GBLS

The development of the PEALD process for Al2O3 and SiO2 from the precursors TMA and BDEAS was investigated in terms of saturation studies (thin film thickness as a function of precursor pulse length) and linearity by employing in situ quartz crystal microbalance (QCM) experiments and is discussed in detail in the Supporting Information (Figure S1). The fabrication of the investigated PECVD thin films of SiOxC2yHz and SiO2 was previously reported.[18,19,22]

The topography of both PEALD materials (Al2O3 and SiO2) was investigated using AFM (Figure 1) to analyze both the surface features and roughness. AFM images of 1 and 5 nm thin films, both for Al2O3 (Figure 1b and c) and SiO2 (Figure 1d and e), deposited on PET, were compared with the pristine PET substrate. The uncoated PET substrate (Figure 1a) exhibits a typical low root-mean-square (rms) roughness of rms = 0.9 nm with a continuous structure of a cross-linked polymer.[49] After deposition of the PEALD thin films, a surface with granular structure for both materials was obtained, which was observed already for the 1 nm thick coatings (Figure 1b) and d) for Al2O3 and SiO2, respectively. The PEALD coatings were relatively smooth with rms-roughnesses of 1.2 and 1.4 nm for the 1 nm coatings of Al2O3 and SiO2, respectively. For SiO2, granular structures with slightly increased size were found for the 5 nm thin film (Figure 1c), while Al2O3 showed similar structural features for the two investigated thicknesses. For both materials, the 5 nm thin films exhibited a lower rms-roughness than the 1 nm thin films, with 1.1 nm (5 nm Al2O3) and 1.0 nm (5 nm SiO2) against 1.2 nm and 1.4 nm, respectively, in the measured area. While thicker films are usually of a higher roughness than their thinner counterparts, the obtained values here are all of the same order of magnitude and resemble PEALD thin films of high homogeneity.

For a meaningful investigation of both the seeding and capping approach for GBLS from the combined PEALD/PECVD processes, the pure PEALD grown materials were evaluated in terms of barrier performance prior to the combined systems. For both PEALD materials, a thickness series was prepared and the respective OTR values are plotted in Figure 2. For Al2O3 and SiO2, thin films of 2.5 nm showed no barrier performance at all with OTR values reaching as high as that for an uncoated PET foil. A decrease in OTR was found for a 5 nm SiO2 coating (about 2 cm3 m−2 day−1). For Al2O3, a thin film of 7.5 nm was necessary to generate a barrier with a similar performance (1.1 cm3 m−2 day−1) as SiO2.

It should be noted that Al2O3 thin films of 60 nm thickness, deposited by PEALD on 12 μm thin PET foil, were reported to result in an OTR of 1.8 cm3 m−2 day−1,[50] while a 10 nm thin film on 50 μm PET was reported to exhibit an OTR ≤5.0 × 10−3 cm3 m−2 day−1.[27] Obviously, a direct comparison of barrier performance is not feasible, as the OTR is strongly dependent on the underlying substrates. At 7.5 nm film thickness, SiO2 showed a performance of 0.3 cm3 m−2 day−1 (decreased by two orders of magnitude). Higher film thicknesses showed no significant improvement in OTR. The constant OTR even for thicker coatings highlights the high quality of the PEALD barrier layer even at low thicknesses. For PECVD coatings of silica-like materials, a thicknesses of at least 30 nm is necessary to achieve similar values.[22] The differences in barrier performance of SiO2 and Al2O3 could be due to hydrolysis effects of the Al2O3 thin films.[51] In addition, the better performance of SiO2 thin films might be connected to a low amount of OH-groups in the SiO2, which are known to be found in porous silica-like materials,[7,41] indicating a low porosity and therefore better barrier performance.
PEALD thin films of the discussed materials are known to improve the GBL performance by more than one order of magnitude, especially for increased thicknesses and for thicker substrates.\(^{[27]}\) Here, a drop in OTR of two orders of magnitude was found for a SiO\(_2\) coating with a critical thickness of 7.5 nm, half the thickness reported by Wertheimer et al.\(^{[1]}\)

Thin films of Al\(_2\)O\(_3\) and SiO\(_2\) from PEALD processes were also investigated regarding their composition employing RBS and NRA. Representative RBS spectra for SiO\(_2\) are shown in the Supporting Information (Figure S2). From the combination of these techniques and the analysis of thin films deposited both on Si(100) and glassy carbon, the stoichiometries and contamination levels were obtained (Table S1). The deposited Al\(_2\)O\(_3\) was found to be oxygen rich, with a ratio for O/Al of 2.0 (ideal: 1.5), while the SiO\(_2\) thin films exhibit nearly perfect stoichiometry (ratio of 1.95 for O/Si; ideal: 2.0). While carbon contamination was between 5 and 6 at\%, nitrogen impurities were found to be negligible.

**FIGURE 1**  AFM images (1 × 1 \(\mu\)m\(^2\)) of Al\(_2\)O\(_3\) and SiO\(_2\) PEALD thin films, grown on 23 \(\mu\)m PET foil at 60 °C; (a) representative AFM image of a bare PET substrate; (b) 1 nm Al\(_2\)O\(_3\); (c) 5 nm Al\(_2\)O\(_3\); (d) 1 nm SiO\(_2\); (e) 5 nm SiO\(_2\)

**FIGURE 2**  OTR of Al\(_2\)O\(_3\) and SiO\(_2\) thin films deposited at 60 °C by PEALD on 23 \(\mu\)m PET foil
3.2 | Seeding route

For the subsequent growth of SiOx by PECVD, SiO2 thin films from PEALD were deposited as seeding layer on PET. The aim of this approach was to optimize the SiOx PECVD growth by providing a defined and homogenous substrate interface in terms of surface features, chemistry and roughness to suppress the formation of defects in the PECVD thin films. SiO2 from PEALD was chosen as seeding material to provide a high similarity of the applied materials and to avoid influences on the final GBLs from lattice mismatches and different thermal expansion coefficients. In this context, the defect densities \( n_{\text{def}} \) of the combined GBLs were evaluated and correlated with the respective OTR values. SiO2 seeding layers of 1, 2.5, and 5 nm were coated with 15 nm SiOx layers and Figure 3 shows the corresponding OTR values as well as defect densities. Error bars were calculated by the standard deviation of defect densities for at least three samples, considering defects with diameters >100 nm, respectively.

The deposition of 1 nm SiO2 (PEALD) and subsequent growth of 15 nm SiOx (PECVD) yielded a barrier film with a similar performance as found for the bare PET foil, with OTR values of about 77 and 72 cm\(^3\) m\(^{-2}\) day\(^{-1}\), respectively. In contrast, a pure 15 nm thin film of PECVD grown SiOx on PET exhibited an OTR of 29 cm\(^3\) m\(^{-2}\) day\(^{-1}\). A higher OTR in combination with a total thickness of 16 nm could be explained by an insufficient surface coverage of the 1 nm PEALD seeding layer, causing the PECVD thin film to have a lower quality as well. In addition, the discontinuous PEALD process and the accompanying low growth rates (compared to PECVD) could lead to etching processes which alter the PET surface, causing deteriorated barrier performance of the overall GBL.

Interestingly, for the 1 nm PEALD seeding layer, defect diagnostics using oxygen etching revealed a defect density of \( n_{\text{def}} = 86 \text{mm}^{-2} \) which is half the amount of defects compared to a directly grown 5 nm SiOx thin film by PECVD on PET. Applying a 2.5 nm seeding layer improved OTR (63 cm\(^3\) m\(^{-2}\) day\(^{-1}\)) slightly when compared with the 1 nm seeding layer, indicating that the film was not entirely closed for the 1 nm seeding-layer, while \( n_{\text{def}} \) was found to be unaffected with a value of 83 defects mm\(^{-2}\). For a 5 nm thick seeding layer, both the OTR and defect density were found to decrease significantly with values of 0.8 cm\(^3\) m\(^{-2}\) day\(^{-1}\) for the OTR and 9 macro defects mm\(^{-2}\), which are remarkable values compared to defect densities of PECVD grown SiOx (>60 macro defects mm\(^{-2}\)). Similarly low defect densities were found in PECVD grown thin films with thicknesses around 100 nm. In addition, the remaining defect density for the GBL comprised of a 5 nm seeding-layer (PEALD) and a 15 nm SiOx (PECVD) exhibited a defect density comparable to that of a 20 nm TiO2 thin film from PEALD, which was reported earlier,\(^{[34]}\) indicating the ability of PEALD coatings to facilitate improved growth of the subsequently grown PECVD SiOx. As \( n_{\text{def}} \) was decreased already for a 1 nm seeding layer with the OTR remaining at the same values as an uncoated PET foil, the OTR seems to be strongly dependent on the overall thickness of the GBL. As reported earlier for GBLs from PECVD,\(^{[34]}\) a decreased macro defect density improved the barrier performance. Compared to GBLs comprised of only one binary oxide from PEALD (Figure 2), the found OTRs were of the same order of magnitude for comparable thicknesses.

A seeded SiOx thin film, grown on 5 nm SiO2, was investigated by AFM to study the SiOx surface morphology (Figure 3b). For this combination of materials, the surface was appeared similar to that of a pure PEALD SiO2 thin film of 5 nm thickness (Figure 1) with the homogenous surface coverage in the measured area exhibiting a granular structure. The rms roughness of this SiOx/SiO2 system (20 nm in total) on PET was found to be 1.4 nm, exhibiting only a slightly increased roughness when compared to a pure 5 nm thin PEALD coating (rms = 1.0 nm), considering the increased thickness of the investigated thin film. The increase in roughness can be explained by considering that the PECVD growth taking place after the PEALD process and thus, the
surface features are more likely to display PECVD features, i.e., increased roughness.

3.3 | Capping route
The capping approach was separated into the capping of SiOₓCₓHₓ and a more silica-like SiOₓ thin film. The SiOₓCₓHₓ thin film usually serves as an interlayer and was found earlier to improve the barrier performance of PECVD grown SiOₓ on PET, acting as a sacrificial layer which is partially oxidized during the continuous growth of SiOₓ. [17–19] Here, these two chemically different layers were capped with either Al₂O₃ or SiO₂ to investigate the materials choice impact on the overall barrier performance. SiOₓCₓHₓ and SiOₓ thin films were 5 nm in thickness for all experiments. In order to investigate a potential thickness influence of the capping layer, the PEALD grown materials were applied either with 1 or 5 nm thickness. As for the seeding-route, the combined systems were analyzed with respect to the defect density and barrier performance regarding OTR. Figure 4a and b show the corresponding plots for both the SiOₓCₓHₓ and SiOₓ layers, capped with Al₂O₃ or SiO₂ of varying thicknesses, respectively.

The combined systems were compared with 5 and 10 nm coatings of SiOₓCₓHₓ and SiOₓ without capping, to allow an estimation of the capping layer influence on the barrier performance and defect density. The OTR values for these PECVD coatings are 63 and 66 cm³ m⁻² day⁻¹, respectively. For each combination, three samples were prepared and evaluated, while each sample was scanned over a total representative area of 0.5 mm² (40 images per sample). For the 5 nm SiOₓCₓHₓ thin film, a 1 nm Al₂O₃ thin film resulted in barrier performance with an OTR of about 15 cm³ m⁻² day⁻¹ and a defect density of only 2 defects mm⁻², which is a remarkably low value and represented a coating being virtually free of any defects on the measured area. A 5 nm coating of Al₂O₃ on SiOₓCₓHₓ resulted in an OTR of about 8 cm³ m⁻² day⁻¹, with the defect density being extremely low with only 1 defect mm⁻². With respect to a 5 nm thin film of SiOₓCₓHₓ on PET, the defect density of the GBL decreased by a factor of 7.7 × 10² and 1.5 × 10³ for 1 and 5 nm capping layers, respectively.

For the capping of 5 nm SiOₓCₓHₓ using SiO₂, a 1 nm capping showed negligible influence on the OTR, being on the same order of magnitude as the bare 5 nm SiOₓCₓHₓ thin film on PET. Interestingly, the defect density was decreased by a factor of 2.4 (1552 defects mm⁻² vs. 35 defects mm⁻²). However, a 5 nm capping layer of SiO₂ exhibited again a strongly decreased defect density with only 156 defects mm⁻², which equals a factor of 10. In addition, this combination exhibits an OTR of only 0.5 cm³ m⁻² day⁻¹, a drop of two orders of magnitude.

Al₂O₃ capping layers grown on 5 nm SiOₓ coatings (Figure 4b) showed similar trends as for SiOₓCₓHₓ with respect to the OTR with values around 12 cm³ m⁻² day⁻¹ (1 nm capping) and 8 cm³ m⁻² day⁻¹ (5 nm capping). Again, the barrier performance could be improved by adding just a 1 nm capping layer. Irrespective of the chosen capping thickness, the formation of defects was substantially suppressed and SEM images revealed a surface free of defects in the measured area, which is an interesting result. For the SiO₂ capping, a similar trend for barrier performance was found as for SiOₓCₓHₓ/SiO₂ combinations: while the 1 nm SiO₂ capping had no influence on the OTR value compared to an uncoated 5 nm SiOₓ thin film (66 vs. 72 cm³ m⁻² day⁻¹), the 5 nm SiO₂ capping exhibited a stronger influence, i.e., an OTR of around 39 cm³ m⁻² day⁻¹. Regarding the defect density, superior results were found again. The combinations SiOₓ/SiO₂ (1 nm) and SiOₓ/SiO₂ (5 nm) both showed strongly decreased defect densities, with only 23 defects mm⁻² and 1 defect mm⁻², respectively, which corresponds to improvements by factors of 9.5 × 10¹ and 1.6 × 10³, respectively. While Al₂O₃ cappings exhibited a stronger influence on defect density, the barrier performance of the PEALD capping materials Al₂O₃ and SiO₂ were different.
An explanation could be that Al₂O₃ exhibits a higher probability to be hydrolyzed by water from ambient air, thereby being degraded and thus exhibiting a lower performance. However, within one material, consistent trends were observed. These findings regarding macro-defect density of combined PECVD/PEALD GBL systems are in agreement with earlier and recent reports of studies on thicker GBLs for advanced moisture barriers,[7,41] where it was shown that single ultrathin ALD coatings have only minor influence on the barrier performance while combinations of thicker PECVD coatings together with ultrathin ALD coatings exhibit strongly improved barrier properties with respect to nano-porosity.

To address a potential influence of nano-defects and pore diameter on defect-assisted permeation of the investigated materials, SiO₂ thin films obtained from PEALD were subjected to spectroscopic ellipsometry (SE) and ellipsometric porosimetry (EP). To evaluate the contribution from nano-porosity toward barrier performance, the samples were subjected to probe molecules (e.g., water) and the change in the refractive index \( n \), depending on a potentially adsorbed layer of these probe molecules, was measured upon changing the relative partial pressure of the probe molecule from 0 to 1 \( (P_{\text{probe}}/P_{\text{sat,probe}}) \) in the EP chamber. Details on the respective evaluation are reported elsewhere.[7] Figure S3 shows the change of the ellipsometric parameter \( \Psi \) and \( \Delta \) as a function of the wavelength and the corresponding fit from a SE measurement under vacuum of a PEALD grown SiO₂ thin film of about 100 nm thickness. The fit was derived from a Cauchy model and revealed only a minor change in the refractive index upon being placed under vacuum within the error \( (\Delta n = 0.0001) \), indicating a highly dense material \( (n \) in atmosphere = 1.4703). For the measurement under ambient atmosphere, the same results were obtained. The fact that the refractive index of the layers does not change upon exposure to atmosphere allows us to conclude that the pore size in the layer is inaccessible to ambient water \( (d = 0.27 \text{ nm}) \), i.e., the deposited amorphous layers are very dense. Therefore, the open nano-porosity content of the SiO₂ film was estimated to be lower than the detection limit of the EP setup \( (0.02\% \) in porosity content for SiO₂ thin films). In addition, the Al₂O₃ thin films were not stable under high partial pressures of water \( (e.g., P_{\text{H₂O}}/P_{\text{sat,H₂O}}>0.5) \)[38,52] which is why a deeper analysis using EP was not feasible.

Representative SEM images of processed samples for the combinations 5 nm SiOₓCᵧHₒ + 1 nm Al₂O₃ and 5 nm SiO₂ + 1 nm SiO₂ with defect indication (i-iii) are shown in Figure 5a and b, respectively. For the sake of clarity, the remaining combinations are shown in Figure S4.

In Figure 5a, one of the rarely found defects in the combined 5 nm SiOₓCᵧHₒ (PECVD) + 1 nm Al₂O₃ (PEALD) system is indicated as “i.” This defect exhibited similar features as those from an earlier investigation on TiO₂ thin films grown by PEALD.[34] The black spot represents the defect itself, while the brighter, white, aura originated from the eroded PET substrate beneath. This is prone to etching by the oxygen radicals and has been used to visualize the otherwise invisible defect structures of inorganic oxides on transparent polymers. From Figure 5a, it can also be seen that defects are not formed around dust particles, indicated by “ii.”

It must be noted that the shown defect “i” was the only one found for the scanned area of 0.5 mm × 0.5 mm, out of three samples for the combination 5 nm SiOₓCᵧHₒ (PECVD) + 1 nm Al₂O₃ (PEALD). For the combined 5 nm SiO₂ (PECVD) + 1 nm SiO₂ (PEALD) system (Figure 5b), defects were nearly exclusively found in the vicinity or beneath dust particles. Indication “ii” shows a bright spot, corresponding to the dust particle. For this particular dust particle, a white aura similar to that of regularly observed defects was observed. An explanation for this could be that oxygen radicals diffused along pathways, induced by the large dust particle. For the capping approach using SiO₂ from PEALD, the majority (>90%) of detected defects were of this variety. From this, the high application potential of PEALD with respect to improved GBLs from the capping approach can be extracted, as defects were obviously formed preferentially at dust-contaminated sites, while the PEALD thin films showed only negligible defect formation over large areas. Most likely, if dust on the sample surface can be avoided, the defect density
can be decreased for SiO₂ coatings down to zero defects mm⁻² as found for Al₂O₃ capping layers.

The different cappings on SiOₓCᵧHₓ and SiOₓ coatings were further investigated using AFM to evaluate the influence of the combined process on the surface topography. Figure 6 shows AFM images of 5 nm SiOₓCᵧHₓ and SiOₓ coatings which were capped with either 5 nm Al₂O₃ or SiO₂ grown by PEALD. For capping layers grown on SiOₓCᵧHₓ (Figure 6, left column, a) and b)), the Al₂O₃ (6a) and SiO₂ (6b) capping exhibited rms-roughnesses of 1.5 and 2.2 nm, respectively. For Al₂O₃, this represents the same order of magnitude as the roughness of a bare PEALD coating on PET (Figure 1). In addition, larger smooth areas with some hillocks but without granular structures were observed for the Al₂O₃ capping. This explains the remarkably low defect density for cappings of Al₂O₃ (Figure 4a) and underlines the high application potential of PEALD to form dense GBL materials without potential pathways for diffusion. On the other hand, the combination SiOₓCᵧHₓ/SiO₂ (6b) was found to have an increased rms roughness with a value of 2.2 nm.

This combination showed also the formation of hillocks which were projected along the z-direction. As the applied PEALD coatings were of a low thickness, the features observed can be assumed to describe the interface of such combined systems. From this, the characteristic morphology of the capped SiOₓCᵧHₓ thin films could be explained by oxidation of the more organic PECVD coating during the subsequent PEALD process. This oxidation and simultaneous growth of the PEALD thin films could cause a deterioration in homogeneity and thereby explain the higher roughness and hillocks.

Combinations of SiOₓ and PEALD grown Al₂O₃ or SiO₂ (6c and 6d) exhibited both a lower rms-roughness (0.9 and 0.4 nm, respectively), while linear structures, most likely caused by the biaxial oriented PET substrate, were observed for the Al₂O₃ capping. It should be noted that the darker spots in Figure 6d do most likely originate from the substrate and are not defects from the cappings. Interestingly, pronounced granular structures were found for the Al₂O₃ capping on SiOₓ. As for this combination, no defects were detected and the applied PEALD cappings seem to provide a highly dense structure which is able to seal the defects in SiOₓ coatings.

Earlier studies suggested that mass transport of oxygen gas and water vapor through inorganic barrier coatings are driven to a major extent by solid-body diffusion instead of Knudsen-diffusion through open pores. The results discussed here support these findings, as for combined systems without defects some oxygen transmission was still occurring.

**Conclusion**

Ultrathin GBLs, fabricated by different combinations of PECVD and PEALD grown materials were investigated with respect to barrier performance (OTR) and defect densities. From a seeding approach, homogenous PEALD thin films of SiO₂ were found to improve the subsequent PECVD growth of
15 nm SiOx substantially in a beneficial way with a decreased defect density by the factor of 2 (1 nm SiO2, PEALD seeding) and 20 (5 nm SiO2, PEALD seeding). Furthermore, a drop in OTR by two orders of magnitude (29.3 cm² m⁻² day⁻¹ (15 nm SiO₂) vs. 0.8 cm² m⁻² day⁻¹ (5 nm SiO₂ + 15 nm SiO₂)) resulted from this decreased density.

The capping approach revealed the superior properties of the Al₂O₃ cappings, irrespective of the chosen thickness (1 and 5 nm) or the chosen underlying PECVD coating (SiO₂CₓHₓ or SiO₂) on PET, with respect to defect density. For Al₂O₃ cappings on SiOₓCₓHₓ, defect density was extremely low with values ≤2 macro-defects mm⁻² (improvement factor of >10³ for a 5 nm capping) while no defects were observed on PECVD grown SiO₂. Regarding barrier performance, an improvement by a factor of 8 was found for 5 nm cappings, compared with the uncoated 5 nm SiO₂CₓHₓ and SiO₂ thin films. Cappings of SiO₂ from PEALD revealed a less pronounced impact on defect formation (improvement factor of 10 for a 5 nm capping) with a strongly improved barrier performance and a drop in OTR by two orders of magnitude when compared with the bare 5 nm SiO₂CₓHₓ thin film on PET (0.5 vs. 63.1 cm² m⁻² day⁻¹). Furthermore, EP indicated extremely low nano-porosity of the PEALD grown SiO₂ thin films below the detection limit (0.02% in porosity content for SiO₂).

In summary, both the PEALD grown seeding and cappings layers had a strong beneficial influence on the barrier performance of thin PECVD coatings and macro defect densities were significantly decreased if not completely suppressed.

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4. Dyads of silica and alumina on polymers via PEALD

4.1. Introduction to multilayer structures of inorganic oxides on polymers

During the last years, there has been a significant focus on GBLs, in particular for the encapsulation of OLEDs, which represent a high potential for flexible displays.\(^9\) As mentioned in section 1.6 page 38 ff., such advanced electronic devices are easily degraded by water vapor and warrants improved GBLs. In this context, the fabrication of nanolaminates, or multilayers (the terms are used more or less synonymously) of inorganic oxides and other materials, such as plasma polymers and hybrid materials, attracted considerable attraction. As the desired GBLs must be transparent and flexible at the same time, inorganic oxides are in the focus of the related research, while metallic thin films are less favored. Different combinations of inorganic oxides (Al\(_2\)O\(_3\)/TiO\(_2\),\(^{2,4}\) Al\(_2\)O\(_3\)/MgO,\(^5\) and Al\(_2\)O\(_3\)/HfO\(_2\)\(^6\)), inorganic oxides mixed with plasma polymers (Al\(_2\)O\(_3\)/plasma polymer\(^7\)) and also ALD/MLD hybrid materials (Al\(_2\)O\(_3\)/Alucone and ZrO\(_2\)/zircone\(^8,9\)) have been investigated and revealed to improve the barrier performance of polymer substrates like PET, PEN and PES down to the order of 10\(^{-6}\) g m\(^{-2}\) day\(^{-1}\) to 10\(^{-4}\) g m\(^{-2}\) day\(^{-1}\) in many cases.
However, the investigated nanolaminate structures are of high thickness (≥ 50 nm) and (even more important) the chosen substrates are rather thick (≥ 100 µm). While these approaches are necessary to obtain strongly improved GBLs, meeting the requirements from OLED devices, a detailed research on the influence on deposition parameters is challenging. For example, studies on the influence of precursor variation on the barrier performance of nanolaminates have not been investigated till date. In addition, the deposition of nanolaminates on thin polymer substrates has not received much attention. While thick nanolaminates have been analyzed regarding barrier performance (WVTR, OTR) and mechanical properties in terms of residual stress, crack formation and adhesion, thinner nanolaminates have not been discussed at all in the literature, with respect to the above mentioned properties.

To obtain a deeper understanding of the fundamental processes taking place during the growth of inorganic oxides on polymers, the investigation of thinner films could be of high importance. As ultrathin films represent a first approximation toward an investigation of the interface between a substrate and a growing film, the correlation of structure-property relation could be possible, enabling understanding and analysis of the growth on a molecular level and in the process to improve the deposition of nanolaminates.

As mentioned above, precursor chemistry and a potential influence on gas barrier properties of nanolaminates from using different chemical compounds for the deposition of a certain material, was not covered yet in the literature. For the most prominent GBL material Al₂O₃, together with silica-like SiOₓ and SiO₂, this could be of high importance also for the industry, as the most commonly applied precursor, in ALD and PEALD, trimethylaluminum (TMA, 1) is highly pyrophoric and difficult to handle. While Al₂O₃ was deposited by ALD or PEALD using different precursors apart from TMA, namely dimethyl-aluminum-isopropoxid ([Me₂AlOPr], DMAI (2)),¹²¹³ and recently tris(dimethylamido)aluminum(III) ([Al(Me₂N)₃], TD-
4.1. INTRODUCTION TO MULTILAYER STRUCTURES OF INORGANIC OXIDES ON POLYMERS

Figure 4.1.: Al precursor compounds for PEALD of $\text{Al}_2\text{O}_3$. 1: Trimethylaluminum; 2: Dimethylaluminum-isopropoxide; 3: Tris(dimethylamido)aluminum(III); 4: [3-(dimethylamino)propyl]dimethylaluminum(III).

Recently, a series of closely related Al-compounds, based on intramolecularly donor-stabilized aluminum(III) compounds, comprising a 3-(dimethylamino)propyl ligand, where reported by Mai et al. and a PEALD process to deposit $\text{Al}_2\text{O}_3$ thin films of high quality, comparable with those deposited from TMA, was developed using the precursor [3-(dimethylamino)propyl]dimethyl aluminum(III) (DMAD, 4). In contrast to TMA (1), the DMAD compound (4) was reported to be non-pyrophoric. While this precursor exhibits lower growth rates in PEALD than TMA (0.7 Å cycle$^{-1}$ vs. 1.4 Å cycle$^{-1}$), the obtained $\text{Al}_2\text{O}_3$ thin films were of high purity and exhibited roughnesses of only 0.27 nm (rms). As this compound shows a high similarity to the commercially applied precursor TMA, owing to the substitution of only one methyl group by the 3-(dimethylamino)propyl ligand, it can be used to investigate the growth of $\text{Al}_2\text{O}_3$ in a comparative study, using both the precursors TMA (1) and DMAD (4).

For silicon-based materials like $\text{SiO}_x$ and $\text{SiN}_x$ from PEALD, a broad variety of established amido-silane precursors, covering homoleptic and heteroleptic compounds, and chloro- or hydrogen-silanes is commercially available: bis(diethylamino)-
CHAPTER 4. DYADS OF SILICA AND ALUMINA ON POLYMERS VIA PEALD

silane ([\(\text{Et}_2\text{N}_2\text{SiH}_2\)], BDEAS),\(^{18}\) bis(dimethylamino)bisilane ([\(\text{Me}_2\text{N}_2\text{SiH}_2\)], BDMAS),\(^{16}\) bis(ethylmethylamino)bisilane ([\(\text{EtMeN}_2\text{SiH}_2\)], BEMAS),\(^{17}\) bis(t-butylamino)bisilane-([\(\text{BuHN}_2\text{SiH}_2\)], BTBAS),\(^{19}\) di(isopropylamino)bisilane ([\(\text{iPrHN}_2\text{SiH}_2\)], DIPAS),\(^{20}\) di-(sec-butylamino)bisilane ([\(\text{Bu}_2\text{NSiH}_3\)], DSBAS),\(^{20}\) diaminosilane ([\(\text{SiH}_2\text{NH}_2\_\text{SiH}_2\)], DMAS), dimethoxy-dimethylsilane ([\(\text{CH}_3\text{OCH}_3\_\text{SiH}_2\)], DMDAS), tris(dimethylamido)bisilane ([\(\text{Me}_2\text{N}_3\text{SiH}_2\)], 3DMAS), tetrakis(dimethylamido)bisilane ([\(\text{Me}_2\text{N}_4\text{SiH}_2\)], 4DMAS),\(^{21}\) trimethylsilane ([\(\text{CH}_3\_\text{SiH}_3\)], TMS),\(^{6}\) tris(dimethylamino)chlorosilane ([\(\text{Me}_2\text{N}_3\text{SiCl}_3\)], 3DMASiCl),\(^{21}\) tetrakis(ethylamido)bisilane ([\(\text{EtHN}_4\text{SiH}_2\)], TEAS),\(^{19}\) hexachlorodisilane ([\(\text{SiCl}_6\)], NPS),\(^{22}\) disilane ([\(\text{Si}_2\text{H}_6\)], DCS).\(^{23}\) In this thesis, the deposition of \(\text{SiO}_2\) thin films via PEALD is carried out using the precursor compound bis(diethylamino)bisilane (BDEAS), owing to its high vapor pressure and high growth rates. In addition, this compound has no chlorine substituents, thereby avoiding the incorporation of chlorine species both in the reactor setup and the final thin films.

In the following section, the results from studies on the growth of inorganic materials (\(\text{Al}_2\text{O}_3\) and \(\text{SiO}_2\)) on polypropylene (PP) during PEALD are discussed. For the growth of \(\text{Al}_2\text{O}_3\), both TMA and DMAD were applied in PEALD processes. Aiming toward the fabrication of nanolaminates on polymers, the respective processes were optimized for depositions at room temperature in terms of precursor saturation. The growth of \(\text{Al}_2\text{O}_3\) and \(\text{SiO}_2\) was monitored using \textit{in-situ} QCM to optimize the process and to ensure high reproducibility. In addition, to allow a transfer of findings toward industrially applied PP foil, functionalized QCM crystals were employed. These crystals were spin-coated with a top-layer of PP (scPP), thereby allowing to monitor the growth features on a model polymer layer. The two different \(\text{Al}_2\text{O}_3\) materials, either grown from TMA or DMAD, and the \(\text{SiO}_2\) thin films
were further investigated regarding their mechanical properties in terms of adhesive strength toward the underlying PP substrate and potential residual stress using Si-sensor chips. Finally, the combination of Al₂O₃/SiO₂ dyads was investigated regarding their barrier performance in terms of OTR and findings were correlated with results from residual stress measurements. The investigated thin films were of maximum 5 nm thickness and OTR measurements were performed on thin PP substrates (26 µm).
References


References


4.2. PEALD of SiO$_2$ and Al$_2$O$_3$ thin films on polypropylene: Investigations of the film growth at the interface, stress and gas barrier properties of dyads

The following contribution was accepted and published January 17$^{th}$ 2018. Reprinted with permission from ACS Appl. Mater. Interf., 2018, 10, 7422-7434. Copyright (2018) American Chemical Society. The corresponding supplementary information is shown in the appendix, section A.3, page 140. While in total 15 authors (including PIs of the SFB-TR 87 project) contributed to this manuscript, the contribution of the first author was the major one and includes the planning, execution and interpretation of the following experiments and measurement data:

- Thin film depositions via PEALD including in-situ QCM experiments,
- thin film characterization regarding thickness (ellipsometry) and crystallinity (GI-XRD) and
- writing the manuscript.

The following experiments were performed by co-authors, while planning and interpretation of the obtained data was carried out by the first author:

- Synthesis of the precursor compound DMAD (L. Mai, RUB, Germany),
- morphology and pull-off tests (FESEM, C. Zekorn, D. Kirchheim and M. Jaritz, IKV/RWTH Aachen, Germany),
- morphology and composition (AFM/XPS, C. Hoppe, University Paderborn, Germany),
- OTRs (Mocon, F. Mitschker, RUB, Germany) and
- residual film stress (L. Banko, D. Grochla, RUB, Germany).
PEALD of SiO₂ and Al₂O₃ Thin Films on Polypropylene: Investigations of the Film Growth at the Interface, Stress, and Gas Barrier Properties of Dyads

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ABSTRACT: A study on the plasma-enhanced atomic layer deposition of amorphous inorganic oxides SiO₂ and Al₂O₃ on polypropylene (PP) was carried out with respect to growth taking place at the interface of the polymer substrate and the thin film employing in situ quartz-crystal microbalance (QCM) experiments. A model layer of spin-coated PP (scPP) was deposited on QCM crystals prior to depositions to allow a transfer of findings from QCM studies to industrially applied PP foil. The influence of precursor choice (trimethylaluminum (TMA) vs [3-(dimethylamino)propyl]-dimethyl aluminum (DMAD)) and of plasma pretreatment on the monitored QCM response was investigated. Furthermore, dyads of SiO₂/Al₂O₃ using different Al precursors for the Al₂O₃ thin-film deposition, were investigated regarding their barrier performance. Although the growth of SiO₂ and Al₂O₃ from TMA on scPP is significantly hindered if no oxygen plasma pretreatment is applied to the scPP prior to depositions, the DMAD process was found to yield comparable Al₂O₃ growth directly on scPP similar to that found on a bare QCM crystal. From this, the interface formed between the Al₂O₃ and the PP substrate is suggested to be different for the two precursors TMA and DMAD due to different growth modes. Furthermore, the residual stress of the thin films influences the barrier properties of SiO₂/Al₂O₃ dyads. Dyads composed of 5 nm Al₂O₃ (DMAD) + 5 nm SiO₂ exhibit an oxygen transmission rate (OTR) of 57.4 cm³ m⁻² d⁻¹, which correlates with a barrier improvement factor of 24 against 5 when Al₂O₃ from TMA is applied.

KEYWORDS: PEALD, dyads, gas barrier, interface, in situ QCM

INTRODUCTION

The fabrication of gas barrier thin films on polymers has gained a lot of interest due to the high demands from the industry in terms of packaging and encapsulation. Degradable goods, such as food, pharmaceuticals, and advanced optoelectronic devices like organic light-emitting diodes (OLEDs), are easily degraded by oxygen and water vapor. Standard packaging materials like poly(ethylene terephthalate) (PET) and polypropylene (PP) show strong limitations with respect to oxygen transmission rate (OTR) and water vapor transmission rate (WVTR), especially when thin foils are used. To increase the barrier performance of such materials, the respective polymers are usually coated with organic thin films of several micrometer thickness. Unfortunately, these materials are challenging in terms of recycling. Plasma-enhanced chemical vapor deposition (PECVD) has been used to deposit inorganic materials like SiO₂ and SiNx on polymers, and roll-to-roll applications have been established as well, demonstrating the versatility of this deposition technique. These inorganic materials demonstrate a high potential for gas barrier layers (GBLs), as they are microwave-compatible, meet requirements on sustainability, and can be applied as thin layers with outstanding barrier applications. However, advanced GBLs must fulfill certain requirements in terms of thin-film quality. It is well known that nano- and microdefects in GBLs play an important role for transport mechanisms through materials and that the chemical composition of the gas barrier layer has an influence on the overall performance as well. In this context, plasma-enhanced atomic layer deposition (PEALD) offers many advantages over established thin-film techniques. In a...
discontinuous PEALD process, two self-limiting reactions on the substrate surface take place, employing a plasma discharge to generate highly reactive species, e.g., atomic oxygen, during the second half-cycle. By applying sequential growth, the thin film thickness is easily controlled and a high degree of reproducibility is achieved, together with a homogeneous surface coverage, suppressing the formation of defects, which are generally found in continuous growth techniques like PECVD. Using PEALD, Al₂O₃, SiO₂, SiNx, and TiO₂ have been deposited successfully to obtain coatings with enhanced gas barrier performance.²⁹⁻³² Beyond binary oxide materials, PEALD is suitable for the growth of nanolaminates with two different metal oxides, as defined interfaces between different materials are assembled and the periodicity of stacking can be controlled easily by alternating a specific number of cycles for each material. Such nanolaminates are able to suppress the formation of nanocrystallites, which provide potential pathways for diffusion along grain boundaries and are detrimental for GBL applications. During the last years, different groups have demonstrated the superior GBL performance of PEALD grown oxide composite materials, such as Al₂O₃/TiO₂ nanolaminates of 40, 50, and 100 nm thickness, to poly(ethylene naphthalate) (PEN), in terms of decreased WVTRs down to the order of 10⁻¹² to 10⁻¹⁰ g m⁻² day⁻¹, making these materials promising for organic light-emitting diode (OLED) applications. Several efforts have been devoted to the investigation of inorganic gas barrier layers, grown by PECVD, on polymers and their mechanical properties in terms of residual stress and adhesion during the last years.²¹⁻²³ Most recently, a detailed study on the residual stress of SiO₂ and SOGCH thin films on PP has been published by Jaritz et al., indicating a dependency between the film stress and GBL performance.³³ However, considering the mechanisms taking place in the PEALD growth of inorganic dyads and nanolaminates on PP, only little is known. In addition, the influence of precursor chemistry on the mechanical and barrier properties has not been investigated in detail, whereas thermal ALD processes were investigated thoroughly by Parsons et al. and George et al.²⁵⁻²⁶ With respect to the discontinuous PEALD method and the polymer nature of the substrate, particular attention must be paid to the initial PEALD cycles, as the polymeric structure of the polymer is prone to be etched easily by plasma species, especially with respect to oxygen plasma.³⁴ In addition, the first cycles of ALD and PEALD processes are known to have a strong effect on the nucleation and thereby affect the final thin-film properties.

Herein, we discuss the growth of Al₂O₃/SiO₂ dyads on PP foil with a focus on the growth mechanisms of the binary oxides (SiO₂ and Al₂O₃) employing in situ quartz crystal microbalance (QCM) analysis. To enable a transfer of findings from these extensive QCM experiments toward the growth on PP, QCM crystals were spin-coated with a defined layer of PP (scPP) prior to the respective experiments. Employing in situ QCM, a comparative study on the growth of Al₂O₃ using two different precursors, namely, TMA and [3-(dimethylamino)propyl]-dimethyl aluminum (DMAD), was carried out. The growth of the materials was further analyzed regarding morphology, employing atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM). Using two different Al precursors, namely, TMA and DMAD, for which we have reported a low-temperature PEALD process recently,²⁹⁻³⁰ the respective Al₂O₃ materials and dyads of Al₂O₃/SiO₂ were investigated regarding their barrier performance in terms of OTR. Furthermore, residual thin-film stress and adhesion measurements were performed to understand the influence of precursor choice on the mechanical properties of dyads and the results were correlated with barrier performance from thin films deposited on PP foil.

**Experimental Details**

**Thin-Film Deposition.** Al₂O₃ and SiO₂ thin films of different thicknesses were deposited in a custom-built (modular flow), cubic (20 cm x 20 cm x 20 cm), low-pressure PEALD reactor. With the grounded substrate holder located between the antennas, an electron (0.2 eV) beam with an intensity of 2.8 mW cm⁻² and an active magnetic flux density of 2.8 mT was employed to generate the plasma discharge. The power of the plasma discharge was adjusted to 200 and 50 W (forward and reflected, respectively). If not stated otherwise, the plasma discharge length was 150 ms. As precursors, bis(dihethylamino)silane (BDEAS, Strem Chemicals), TMA (Strem, min 98%), and DMAD were used as the respective metal/metalloid source. The precursor DMAD was synthesized according to the literature.²⁹⁻³⁰ All precursors were stored in stainless steel cartridges. TMA was cooled to 0 °C, whereas BDEAS and DMAD were heated to 45 °C. Purge and plasma gas, argon (99.999%, Air Liquide, ALPHAGAZ), and oxygen (99.995%, Air Liquide, ALPHAGAZ) were used with flow rates of 2.5 sccm in both cases. For each material, one cycle for the applied standard PEALD process is described below. If not stated otherwise, all thin films were produced according to these parameters. The recipes of these three processes are shown in the Supporting Information (SI) in a graphical illustration (Scheme S1). To investigate the ALD growth characteristics, depositions were performed on Si(100) substrates. Prior to depositions, the Si substrates were cleaned as follows: samples were first ultrasonicated in high-performance liquid chromatography (HPLC)-grade 2-propanol and subsequently dried in an inert-gas stream. Second, the samples were ultrasonicated in HPLC-grade water and again dried in an inert-gas stream. For adhesion and barrier gas measurements, thin films were deposited on a 28.6 μm thick biaxially oriented PP foil (TNS 30, Taghleef Industries LLC, Dubai). To study the growth of SiO₂ and Al₂O₃ on PP, QCM crystals were spin-coated with PP: A 30 nm layer of PP was deposited onto the Au surface of the QCM crystal using the following recipe: 1.6 g of syndiotactic PP was dissolved in 200 mL of p-xylene at 50 °C. The solution (150 μL) was then spin-coated at 5000 rpm with 3000 rpm/s acceleration for 60 s.**

**Thin-Film Analysis.** Thickness of Al₂O₃ and SiO₂ thin films deposited on Si(100) was measured using a J. A. Woollam M-88 Ellipsometer in the range 300–800 nm using an incident angle of 65°, applying values for the refractive index and extinction coefficient from the literature provided by the manufacturer. To calculate the thin-film thickness, a layer model consisting of an infinite thin substrate with a native silicon oxide top layer of 2.0 nm was assumed. In situ QCM experiments were carried out using AT-cut quartz crystals (6 MHz) coated with Au and optimized for measurements ranging from room temperature to 60 °C. The custom-built crystal holder was connected to a quartz-crystal microbalance (QCM) oscillator and an SQM-100 thin-film deposition monitor (JCM, INFICON). X-ray reactivity (XRR) measurements were performed on a Bruker AXS D8 Discover diffractometer with a two-circle θ/2θ goniometer attached to a centric Eulerian cradle and a sealed Cu tube (Cu Kα radiation; λ = 1.5418 Å, 40 kV, 40 mA), which is attached to a focused Göbel mirror yielding a parallel X-ray beam. For XRR, simulated curves were generated using the Bruker LEPTOS software with a model consisting of two sample layers (SiO₂/SiO₃, (2 nm)/Si(100)) or Al₂O₃/SiO₂ (2 nm)/Si(100)). Grazing incidence X-ray diffraction (GIXRD) experiments were performed in a Bruker D8 Discover equipped with an iOS microfocus X-ray source (50 W) with Cu Kα radiation and a VANTEC 500 two-dimensional detector. The measurements were performed at an incident angle of 0.5° with an exposure time of 240 s in a stationary measurement mode. Atomic force microscopy (AFM) on selected samples was performed using a JPK NanoWizard III ULTRA (JPK Instruments AG) equipped with an antinoise and antivibration box. All images were recorded in air utilizing intermittent contact mode with a rectangular Si cantilever-type NSC-
The resonance frequency was about 87 kHz in air, and the scan speed was 1 mm s\(^{-1}\) with a scan resolution of 512 × 512 pixels. AFM raw data were processed using the open-source software Gwyddion.\(^\text{19}\) X-ray photoelectron spectroscopy (XPS) was performed using an Omicron ESCA+ system (Omicron NanoTechnology GmbH) equipped with a hemispherical energy analyzer at a base pressure of <5 × 10\(^{-10}\) mbar. Spectra were recorded at pass energies of 100 eV for the survey spectra. A monochromatic Al K\(\alpha\) (1486.7 eV) X-ray source with a spot diameter of 1 mm and a charge neutralizer (CN10+, 2.0 eV, 5 μA) were used. The take-off angle of the detected photoelectrons was set at 30° with respect to the surface plane. Topographical imaging of the investigated coatings was carried out using a high-resolving field emission scanning electron microscope (Carl Zeiss Microscopy GmbH, Jena, Germany). The microscope is equipped with a standard Everhart–Thornley secondary detector (SE) and an in-lens backscattering detector (SE2) for imaging. To gain quantitative data on bond strength, pull-off tests using an Adhesion Analyser LUMOhFrac 200 by L.U.M. GmbH, Berlin, Germany, were performed in accordance with ISO 4624 and DIN EN 15870. Well-defined test stamps in terms of weight and dimensions are glued on the coated side of the test specimens. A cantilever accelerates eight test stamps and 15 specimens simultaneously with an increase in centrifugal force of 5 N s\(^{-2}\). The bond strength is determined by referring the bond force to the area of fracture. Oxygen transmission rates (OTRs) were measured using a Mocon OX-TRAN 2/61 (Mocon Inc., Minneapolis) using the carrier gas method at 23°C and 0% humidity. The residual stress after deposition was measured using micromachined stress sensors by the curvature method based on Stoney's equation. Micromachined stress sensors with 20 μm thick Si cantilevers were used as substrates to achieve a quantifiable substrate bending with a sufficient measurement resolution. Sensor fabrication and measurement principle are described elsewhere.\(^\text{30}\) These stress sensors were applied in several thin-film investigations and provide a high sensitivity, especially for film thicknesses <100 nm, which is achieved by adjusting the cantilever thickness of the sensors.\(^\text{31,32}\)

### RESULTS AND DISCUSSION

#### Process Development at Room Temperature Using [3-(Dimethylamino)propyl]-dimethyl Aluminum (DMAD).

Thin films of SiO\(_2\) and Al\(_2\)O\(_3\) were deposited by means of PEALD at room temperature, applying optimized feeding sequences and process parameters to achieve self-limiting growth. For the established and commercial applied precursors BDEAS and TMA, ALD-like growth in terms of surface saturation and linearity of thickness vs applied number of cycles on Si(100) was found for precursor doses of 2 × 25 ms and 13 ms with growth rates per cycle (GPC) of 1.05 and 1.4 Å, respectively, which is in agreement with the literature.\(^\text{33,34}\) Corresponding plots of the GPC as a function of precursors pulse length and linearity are shown in the Supporting Information (SI) Figures S1 and S2 for BDEAS and TMA, respectively. For the compound DMAD, which comprises two methyl ligands and an additional 3-(dimethylamino)propyl ligand, a PEALD process at 60°C substrate temperature has been reported recently, exhibiting typical ALD characteristics in terms of surface saturation, ALD window, and linearity with an optimized GPC of 0.61 Å.\(^\text{35}\) As the PP substrates degrade at elevated temperatures of 60°C, the process using DMAD was optimized at room temperature, and the findings in terms of saturation and linearity are shown in Figure 1. From saturation studies with a fixed oxygen plasma pulse length of 150 ms, a maximum GPC of 0.56 Å was found for a precursor pulse length of 120 ms. Figure 1a shows that no further growth occurs for longer precursor doses, indicating growth is taking place according to ALD mechanisms without condensation. Figure 1b illustrates the thin-film thickness as a function of applied number of cycles and for an investigated range between 0 and 250 cycles, and a constant growth rate of 0.56 Å cycle\(^{-1}\) was found from the linear fit, matching the findings from the saturation studies. The found GPCs for TMA and DMAD differ strongly from each other, indicating the influence of the 3-(dimethylamino)propyl ligand on the reactivity toward reactive surface sites on the substrate. Despite the lower growth rates, this precursor was shown to be able to compete with TMA, as the grown thin films were of similar quality in terms of composition and surface roughness.\(^\text{30}\)

**Figure 1.** Growth characteristics of PEALD-grown Al\(_2\)O\(_3\) on Si(100) using DMAD as precursor. (a) Saturation study on DMAD (repeated pulsing) with a fixed plasma pulse length of 150 ms at room temperature. (b) Film thickness vs applied number of cycles at room temperature. The dashed line (linear fit) is to guide the eye.

**Figure 1b.** Illustrates the thin-film thickness as a function of applied number of cycles and for an investigated range between 0 and 250 cycles, and a constant growth rate of 0.56 Å cycle\(^{-1}\) was found from the linear fit, matching the findings from the saturation studies. The found GPCs for TMA and DMAD differ strongly from each other, indicating the influence of the 3-(dimethylamino)propyl ligand on the reactivity toward reactive surface sites on the substrate. Despite the lower growth rates, this precursor was shown to be able to compete with TMA, as the grown thin films were of similar quality in terms of composition and surface roughness.\(^\text{30}\)
shown in Figure 2. The cracks in the thin film and foil are due to intentional cooling and successive breakage to enable better focusing before the measurements were performed. Apart from these cracks, the grown thin films exhibit a homogeneous coverage of the substrate. Although thin films of SiO$_2$ and Al$_2$O$_3$ (DMAD) are featureless and exhibit a highly smooth surface, the Al$_2$O$_3$ (TMA) sample shows some surface structures, mimicking the structure of the underlying biaxial-oriented PP substrate. GI-XRD patterns, shown in the SI Figure S3, revealed that all three materials (SiO$_2$, Al$_2$O$_3$ (TMA), and Al$_2$O$_3$ (DMAD)) were amorphous on Si(100).

As the overall goal is to investigate dyads of these materials as GBLs grown on PP foil using different precursors, a high degree of reproducibility needs to be ensured in terms of thickness control. As a first step, in situ QCM experiments, using standard AT-cut quartz crystals, were performed and the QCM response toward the PEALD process was monitored. The deposited mass, $\Delta m$, of the materials was derived from the Sauerbrey equation ([S1, eqs S1 and S2]). Figure 3a,b illustrates the monitored response, using standard QCM crystals, from 50 PEALD cycles for BDEAS and TMA, respectively, and 25 cycles for DMAD (Figure 3c), and it can be easily seen that for all three processes linearity of the growth process is ensured.
In addition, nucleation delays were not observed after latest three cycles, indicating a sufficient growth even at temperatures as low as 33 °C. For the three processes, total mass gains of 2058.1, 2760.5, and 902.0 ng cm\(^{-2}\) were found for BDEAS, TMA, and DMAD, respectively. Although a linear mass gain and a final crystal habituation at the end of all processes is on hand, the nonequilibration of the QCM crystal during the process and between two cycles suggests an overlapping of cycles. Therefore, it was decided to compare the QCM response from a standard process (10 cycles) to that from a one-cycle experiment and to the one from a prolonged purge experiment after the plasma step. Figure 3d shows the comparison of only 1 cycle (black) against 10 cycles with both a long purge (cyan) and with the standard purge (blue) duretime-delay to understand the PEALD process. Indeed, the prolonged experiment reveals that no overlapping of cycles in terms of insufficient purge is present as the mass gain per cycle (MGPC) matches that from the standard process and the one-cycle experiment exactly. This is also the case for using BDEAS and TMA as precursors. From this, the nonequilibration of the crystal is attributed to heating of the QCM crystal from the high-energetic plasma species. Here, the long purge experiment reveals the same MGPC for DMAD as the one-cycle experiment and the standard process with 35.7 ng cm\(^{-2}\). For BDEAS and TMA, MGPCs of 40.3 and 54.9 ng cm\(^{-2}\) cycle\(^{-1}\) were found, respectively, of which, the value for TMA is in agreement with the values from the literature. These values correspond to molecular surface densities of 4.04 × 10\(^{14}\), 6.48 × 10\(^{14}\), and 4.22 × 10\(^{14}\) molecules cm\(^{-2}\) for the respective precursors, BDEAS, TMA, and DMAD per cycle, although thin-film thickness was measured using ellipsometry. XRR was used to determine the density of the different materials, where the thickness input data were taken from ellipsometry measurements of thin films on Si(100). In all cases, samples of 30 nm thickness were investigated. Respective XRR plots of the measurements (red) and the corresponding fitting curves (blue) are shown in the SI Figure S5a−c for films grown from BDEAS, TMA, and DMAD, respectively. After fitting, densities of around 2.2, 3.23, and 3.53 g cm\(^{-3}\) were obtained for SiO\(_2\), Al\(_2\)O\(_3\) (TMA), and Al\(_2\)O\(_3\) (DMAD), respectively, exhibiting corresponding deviations of 16.7, 18.2, and 10.6% from the bulk material densities. Interestingly, the two different Al\(_2\)O\(_3\) materials show a difference in density. It should be noted that for all depositions the plasma parameters (power, magnetic field), feeding sequence (apart from the precursor dose), and plasma discharge length (150 ms) were kept the same to allow a direct comparison. As for the growth rates discussed above, the found difference in density of the Al\(_2\)O\(_3\) thin films indicates that the precursor choice has a direct impact on the thin-film property. From the literature, it is known that the density of ALD-grown Al\(_2\)O\(_3\) thin films using TMA at low temperatures lower due to higher amounts of hydrogen incorporation. Furthermore, one could speculate that the difference in density can be explained by considering the amount of deposited Al\(_2\)O\(_3\) molecules per cycle for TMA and DMAD. Comparing these values, a ratio of deposited precursor molecules of 1.5 is obtained. For the DMAD process, the lower growth rates could be attributed to the steric hindrance of the 3-(dimethylamino)-propyl ligand in the DMAD precursor that can cause an insufficient surface coverage. The emerging voids on the substrate surface are saturated and closed during the subsequent cycle, which is possible due to the lower reactivity and thus slower growth. From a subsequent nucleation in the DMAD process (coverge of the voids from the second cycle), a material of density higher than that for the TMA process can be obtained. However, additional in situ investigations (IR) need to be performed to confirm this claim. In Situ QCM Measurements: Investigation of the Interface. As it is known that oxygen plasma species easily etch organic polymers like PP, the transfer of results from QCM measurements using bare quartz crystals toward the deposition on polymers is not feasible. Apart from the etching contribution, the surface plots of a PEALD process from an inorganic crystal and makes a direct transfer impossible. To get an understanding of the mechanisms taking place during PEALD on polymers, we therefore decided to investigate not only the growth on the pure, standard QCM crystal surface but also on spin-coated QCM crystals with 30 nm thin PP film. This spin-coated PP (scPP) served as a model layer on the oscillating quartz crystal, enabling the investigation of the QCM response during the growth of inorganic materials directly on PP. Although it has to be considered that these scPP thin films are not exactly of the same kind as the later used biaxial-oriented PP foil for barrier tests in terms of roughness, the chemical composition is comparable and allows, to a certain degree, an understanding of the growth, especially during the initial cycles of a PEALD process. More details on the scPP properties have been reported elsewhere. For all experiments employing scPP/quartz crystals, a new sample was used and all crystals were checked for electrical conductivity and a steady base line at 33 °C. For all three precursors, the same set of experiments were performed: first, one scPP/QCM crystal was used to monitor the growth of two successive runs of 50 cycles (Figure 4a,b for TMA and DMAD, respectively), interrupted by a 60 s break to allow the crystal to equilibrate. Second, a fresh scPP/QCM crystal was subjected to a pretreatment (25 PEALD cycles without precursor, only oxygen plasma) before the deposition took place (Figure 5a,b for TMA and DMAD, respectively). These pretreatment experiments were performed to investigate the growth behavior of the different precursors on both a pristine and conditioned PP surface. Here, the focus lies on the discussion of the two Al precursors, TMA and DMAD. The QCM response for PEALD of SiO\(_2\) using BDEAS and scPP/quartz crystals is shown in the SI Figure S6. The discussion focuses first on the experiments without pretreatment. For convenience, all discussed MGPC values are summarized in Table 1.

In Situ QCM Using scPP without Oxygen Plasma Pretreatment. As we wanted to have detailed look into the growth of Al\(_2\)O\(_3\) on PP using TMA and DMAD, QCM measurements were also performed for the PEALD of SiO\(_2\) using BDEAS to provide a complete comparison. For the Si precursor BDEAS, a detailed description of the QCM response using scPP model layers can be found in the SI. Nevertheless, the two successive runs to deposit SiO\(_2\) were found to deposit different amounts of SiO\(_2\), i.e., 1027.66 ng cm\(^{-2}\) (first run) and 1971.4 ng cm\(^{-2}\) (second run), which could be due to simultaneous etch and growth mechanisms, thereby delaying agglomeration. The second deposition shows a similar mass gain per cycle as the reference measurement using a standard quartz crystal. For TMA (Figure 4a), the situation is different.

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The first run (red) shows no direct etching but a strongly decreased mass gain, which increases slightly after 10 cycles. The overall mass gain of this first run is 510.8 ng cm\(^{-2}\), which is lower by a factor 5.4 compared to the growth on bare QCM crystal. The second deposition (black) shows a less steep slope again and thereby decreased growth, which is overcome after eight cycles by an increased growth rate, yielding a total deposited mass of 827.2 ng cm\(^{-2}\) (factor of 3.3).

In contrast to BDEAS, the second run does not match the MGPC from the experiment using a bare QCM crystal. It should be noted that these systematic QCM studies are the first of their kind and, especially with respect to the formation of a complex interface, diffusion of the precursor into the polymer might play a role. However, this behavior is not fully understood yet. The precursor DMAD again shows a different

![Figure 4. QCM response from QCM crystals, coated with 30 nm scPP: (a) PEALD of Al\(_2\)O\(_3\) (TMA) and (b) PEALD of Al\(_2\)O\(_3\) (DMAD).](image)

![Figure 5. QCM response from QCM crystals, coated with 30 nm scPP, after oxygen plasma pretreatment: (a) PEALD of Al\(_2\)O\(_3\) (TMA) and (b) PEALD of Al\(_2\)O\(_3\) (DMAD).](image)

Table 1. MGPC for the Different QCM Experiments on Both Quartz and scPP/Quartz Using the Precursors BDEAS, TMA, and DMAD

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Run</th>
<th>BDEAS</th>
<th>TMA</th>
<th>DMAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>1st</td>
<td>41.2</td>
<td>55.5</td>
<td>56.1</td>
</tr>
<tr>
<td>scPP without plasma pretreatment</td>
<td>1st</td>
<td>20.6</td>
<td>15.2</td>
<td>35.8</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>39.5</td>
<td>16.5</td>
<td>35.7</td>
</tr>
<tr>
<td>scPP after plasma pretreatment</td>
<td>1st</td>
<td>21.7</td>
<td>43.8</td>
<td>31.4</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>39.4</td>
<td>54.4</td>
<td>35.7</td>
</tr>
</tbody>
</table>
behavior in QCM experiments (Figure 4b). Notably, there is no distinct etching observed during the first run. Furthermore, the first run yields an MGPC of 31.4 ng cm$^{-2}$, which is already close to the MGPC from experiments on quartz (36.1 ng cm$^{-2}$). However, a linear mass gain is observed first after 14 cycles, demonstrating a stronger pronounced nucleation delay as found for deposits on quartz. Interestingly, it should be noted that the small deviations in MGPC and total deposited mass are likely caused by the quality of the used QCM device and must not necessarily indicate changed growth mechanisms.

### In Situ QCM on Crystals with Spin-Coated PP Top Layer: Oxygen Plasma Pretreatment and Precursor Choice

Figure 5 shows the QCM response from experiments using the same precursors and spin-coated crystals, but prior to the deposits, the scPP film was subjected to a pretreatment. This pretreatment consists of 25 PEALD cycles without precursor, i.e., only purges and the oxygen plasma step were operated. As expected, this kind of pretreatment caused an etching effect as can be seen in Figure 5a and S6, showing a stepwise mass loss with a total etched mass of 788.2 ng cm$^{-2}$ (i.e., 31.5 ng cm$^{-2}$ cycle$^{-1}$) for the scPP thin film. Most likely, this kind of pretreatment causes an incorporation of oxygen functionalities in the scPP surface, which makes it more reactive toward precursor molecules. Indeed, from XPS measurements (survey spectra are shown in the SI Figure S7, and core spectra in the SI Figure S8), the C/O ratio changed from 9.4 to 5.6 for the bare and a pretreated PP foil, respectively. Although this shift corresponds to 9.57 and 15.19% O content in the bare and a pretreated PP foil, respectively. Although this finding is in agreement with the literature, where a pretreatment caused an even stronger increase in adhesion forces.

#### Pull-Off Test for Thin Films on PP with and without Oxygen Plasma Pretreatment

As it is known that a certain degree of surface conditioning, in terms of plasma cleaning/etching or by applying a substrate bias, can have a strong influence on the adhesion between the oxide thin film and the polymer substrate, the adhesion between the SiO$_2$ and Al$_2$O$_3$ and the PP foil with and without pretreatment was investigated.

The results of the respective pull-off tests to determine the adhesion are shown in Figure 6. For SiO$_2$ and the Al$_2$O$_3$ from TMA, a similar median adhesive strength was found with mean values of 0.93 and 0.91 MPa, respectively. In both cases, the pretreatment showed some influence as the adhesive strength was found to be increased to 1.27 and 1.17 MPa, respectively. This finding is in agreement with the literature, where a pretreatment caused an even stronger increase in adhesion forces.
bonds at the interface due to more oxygen functionalities, and in due turn an improved adhesion. For DMAD, QCM findings showed no change in the MGPC if a pretreatment was applied, indicating an unchanged interface between the scPP and the Al₂O₃ thin film compared to the untreated scPP. Therefore, the adhesion of Al₂O₃ from DMAD seems to have reached a more or less maximum, with respect to adhesion strength, already for the process without pretreatment. Therefore, applying the pretreatment causes only minor improvement regarding adhesion.

Barrier Performance of Al₂O₃/SiO₂ Dyads on PP and Their Morphology. The precursor choice to grow Al₂O₃, both as single metal oxide and for Al₂O₃/SiO₂ dyads, was investigated regarding a potential influence on the thin-film properties in terms of residual stress and barrier performance. For the dyads, a maximum thickness of 10 nm was chosen, as thicker coatings of the binary oxides SiO₂ and Al₂O₃ showed a constant barrier performance on the used PP foil, i.e., the OTR values were found to reach a maximum even for thicker films. These OTR values of the single oxides for varying thickness are shown in the S1 Figure S9. The uncoated PP foil exhibits an OTR of 1370 cm³ m⁻² day⁻¹. This poor intrinsic gas barrier of the substrate allows us to investigate the immediate influence of the precursor choice. The two combinations for dyads, using either TMA or DMAD for the deposition of Al₂O₃, yielding composite materials were compared to the respective binary oxide compounds. In total, five different systems are schematically described in Figure 7 and are identified as follows: (1) 10 nm SiO₂, (2) 10 nm Al₂O₃ (TMA), (3) 10 nm Al₂O₃ (DMAD), (4) 5 nm Al₂O₃ (TMA)/5 nm SiO₂ and (5) 5 nm Al₂O₃ (DMAD)/5 nm SiO₂.

For the dyads, the respective depositions were performed subsequently after each other without exposing to ambient air, and the measured OTR values are shown in Figure 8. In all cases, three samples of the same system were measured to obtain a statistical value. Interestingly, the pristine single oxides exhibit completely different OTRs, with SiO₂ (1) showing the lowest OTR of 55.8 cm³ m⁻² day⁻¹. For Al₂O₃, the OTR differs strongly for the two precursors. For TMA (2), an OTR of 358.8 cm³ m⁻² day⁻¹ was found, whereas the thin film deposited using DMAD (3) exhibits no barrier at all. Both the material (SiO₂ vs Al₂O₃) and the precursor choice (TMA vs DMAD) have a strong influence on the barrier performance. For the two different dyads, OTRs of 263.6 cm³ m⁻² day⁻¹ (4) and 57.4 cm³ m⁻² day⁻¹ (5) were measured. These findings are of high interest, as the 10 nm thin film of Al₂O₃ from DMAD exhibits no gas barrier at all, but a combination with SiO₂ yields surprisingly good OTRs.

Figure 6. Adhesive strength of SiO₂ and Al₂O₃ (deposited from either TMA or DMAD) thin films on PP foil. All thin films are of 10 nm thickness. The pretreatment (pre-tr.) comprises 25 cycles of an oxygen plasma discharge without applying a precursor.

Figure 7. Schematic of the five different systems investigated regarding their mechanical properties and barrier performance: (1) 10 nm SiO₂, (2) 10 nm Al₂O₃ (TMA), (3) 10 nm Al₂O₃ (DMAD), (4) 5 nm Al₂O₃ (TMA)/5 nm SiO₂ and (5) 5 nm Al₂O₃ (DMAD)/5 nm SiO₂.
As these findings demonstrate some deviations between the different systems, the surface morphology was investigated employing AFM to analyze the thin-film growth on PP. The corresponding AFM images are shown in Figure 9 and follow the same identification as above plus an image of an uncoated PP foil. From the AFM of the uncoated PP foil, the biaxial-oriented structure of the PP is easy to see and exhibits a root-mean-square (rms) roughness of 4.4 nm. In the following, it should be stated that the dark areas originate from the biaxial-oriented substrate. With a rms-roughness of 4.4 nm, the 5 and 10 nm coatings thin PEALD coatings should cover the whole surface with a homogenous thin film. As can be seen in the figure, the 5 nm thin film of SiO₂ exhibits similar surface features as the bare PP foil, and with 3.7 nm, the roughness is close to the one measured for the bare PP. In contrast, both 5 nm coatings of Al₂O₃ either from TMA (2) or DMAD (3), exhibit less structures, and the rms-roughness was found to be lower with values of 1.7 and 2.3 nm in average, respectively. Structures which were found in the SEM images for the Al₂O₃ deposited using TMA can be found here for system 2 as well.

Figure 8. OTRs of the five systems deposited on 23 μm PP foil by PEALD.

Figure 9. AFM images (1 μm × 1 μm) of the five different systems: (1) 10 nm SiO₂, (2) 10 nm Al₂O₃ (TMA), (3) 10 nm Al₂O₃ (DMAD), (4) 5 nm Al₂O₃ (TMA)/5 nm SiO₂, and (5) 5 nm Al₂O₃ (DMAD)/5 nm SiO₂.
In both cases, laterally inhomogeneous film growth could be identified easily as brighter spots in the AFM images. Local granular structures with sizes of several nanometers (up to 25 nm diameter) could explain the lower barrier performance of systems 2 and 3, as gases can easily travel along the particle boundaries, which act as potential pathways through the coating. The found homogeneous surface morphologies are interesting as the same coatings exhibit lower or completely lacking projection against oxygen as found from OTR measurements. For all binary oxide thin films, a closed layer can be assumed. This is also the case for the combined systems 4 and 5 (5 nm Al2O3 + 5 nm SiO2 using TMA and DMAD, respectively) where rms-roughness values of about 0.6 and 0.5 nm were measured. The higher rms-roughness for system 4 can be explained by considering the high noise-to-signal ratio, indicated by the blurred lines. However, for system 4, nucleation spots can be identified, whereas system 5 demonstrates to have a featureless surface. Furthermore, the AFM measurement of systems 4 and 5 reveal linear structures, which most likely arise from the biaxial-oriented PP substrate. These could arise from extrinsic stress induced by heat from the plasma process, causing a certain degree of deformation, i.e., wrinkling, explaining the found linear structures. With respect to OTR measurements, where the dyad systems 4 and 5 show better performance than the respective binary oxides, the surface features of systems 4 and 5 indicate the top SiO2 layer being a crucial factor for improved barrier performance. In addition, the nucleation sites in system 4 explain further the differences in OTR for 4 and 5.

**Thin-Film Stress of SiO2, Al2O3 (TMA), Al2O3 (DMAD), and Respective Al2O3/SiO2 Dyads.** Stress in thin films can harm the effectiveness of gas barriers, especially with respect to the mass transport along cracks. Therefore, the PEALD-grown materials were investigated regarding their residual thin-film stress. The respective depositions were performed on Si stress sensors. To allow a meaningful evaluation of these experiments, the PEALD-grown materials were investigated over a thickness range of 15–45 nm. Thin films of Al2O3 from TMA showed residual tensile stress with lowest values for thicknesses ≥45 nm at around 125 MPa. This residual stress is lower as for Al2O3 thin films grown by thermal ALD using TMA at elevated temperatures of 110–300 °C, where the tensile stress was found to be >200 MPa even for 500 nm thick samples. Compared to other reported PEALD processes to deposit Al2O3, the low values for residual stress are in agreement with values in the literature. In general, intrinsic stress is imposed by, e.g., lattice mismatches and defects. Thermal stress, induced by the temperature difference between the deposition process and application temperature, plays a minor role in the here investigated processes as the depositions were performed at room temperature. Interestingly, the Al2O3 thin films grown from DMAD were found to show a change in the prefix of the measured stress with increasing thickness, i.e., the residual film stress changed from tensile (343 MPa for 15 nm) to compressive stress for thicker films (~160 MPa for 75 nm). The stress thickness behavior of Al2O3 grown by TMA and DMAD indicates a difference in the growth process for these two precursors. This is in agreement with the different morphologies of Al2O3 thin films on PP, as revealed by FESEM (Figure 2). Although the TMA process is capable of replicating the substrate nanostructure, the DMAD process yields a featureless surface. This could explain the lower residual tensile stress of Al2O3 from TMA. As the tensile stress for DMAD Al2O3 films decreases with increasing thickness, it is evident that compressive stress is added incrementally over all measured growth stages to the overall stress. For TMA-grown Al2O3, the stress saturates with increasing thickness, indicating that at later growth stages tensile stress relaxes or that compressive stress components are added. In addition to growth behavior and morphology, the two films exhibit differences in density. Because TMA-grown Al2O3 exhibits a 10% lower density than DMAD-grown Al2O3, it can be assumed that in a denser film of the same amorphous material the conditions to form compressive stress are more favorable. Due to the lower growth rate of the DMAD process (roughly one-third compared to that of the TMA process), a much higher number of PEALD cycles was applied, thereby strongly increasing the total exposure time of the samples toward plasma species. Mayr et al. proposed a stress model for amorphous films, showing that stress can be related to atomic dynamics during particle deposition. In polycrystalline films, compressive stress can be explained with migration of adatoms into the grain boundaries, which can be correlated to adatom mobility. The increased exposure toward plasma species could lead to higher adatom mobility and migration into boundaries of different clusters or domains, thereby generating compressive stress. With respect to Figure 10, for all three materials, clear trends regarding residual stress toward even thinner films, such as 5 and 10 nm, can be foreseen. Although the SiO2 thin films will show even higher compressive stress, both Al2O3 thin films should exhibit higher tensile stress. For both Al2O3 materials, the residual tensile stress for thin coatings explains the poor barrier performance. A combined system of 15 nm SiO2 and 15 nm Al2O3 from TMA showed a residual compressive stress of only ~114 MPa, whereas the same combination using DMAD exhibits a residual tensile stress of 113 MPa. This example...
provides an outlook to tailor the film stress by combining films with a stress thickness behavior of different signs.

**CONCLUSIONS**

PEALLD processes to deposit SiO₂ and Al₂O₃ thin films on PP were investigated in detail with respect to growth mechanisms and functional properties in terms of residual stress and barrier performance. By performing in situ QCM experiments using specifically designed QCM crystals with a scPP top layer, the growth of the inorganic single oxides was monitored in dependence of an oxygen plasma pretreatment and for two different Al precursors. From these investigations, a substantial difference in the growth using commercial Si and Al precursors, namely, BDEAS and TMA, and the recently reported Al precursor DMAD was found. When compared to reference measurements on bare QCM crystals, films deposited with established precursors BDEAS (SiO₂) and TMA (Al₂O₃) exhibit overall lower mass gain per cycle on scPP for the respective oxide materials, whereas the films deposited with DMAD show a remarkable unaffacted mass gain per cycle for both the reference and scPP-coated QCM crystal. For BDEAS and TMA, an O-plasma pretreatment was necessary to obtain similar growth rates, hinting toward the formation of a more diffused interface if no plasma is applied. These findings are supported by stronger adhesive strength between the thin film and industrial PP foil for SiO₂ and Al₂O₃ (TMA) than for Al₂O₃ (DMAD) and PP, indicating the formation of a less diffusive interface when DMAD is used. In addition, the barrier performance of dyads (5 nm Al₂O₃ (either TMA or DMAD) + 5 nm SiO₂) in terms of OTR was found to be improved by a factor of 5 against uncoated PP in the DMAD-based system, whereas the TMA-based system showed an improvement factor of 5. Dyads of 15 nm SiO₂ + 15 nm Al₂O₃ revealed residual stresses of −114 and +113 MPa for TMA and DMAD, respectively. As binary oxide coatings of only 5 nm thickness showed no barrier performance at all for all systems, it can be concluded that the capping with a 5 nm SiO₂ plays a major role for the barrier performance, whereas the underlying Al₂O₃ either deposited from TMA or DMAD, and the accompanied polymer/thin-film interlayer set the limitations for residual thin-film stress. These findings are of high interest with respect to the fabrication of gas barrier layers with tailored residual stress for OLED encapsulation. As the two Al₂O₃ materials, either from TMA or DMAD, were found to exhibit differences in residual thin-film stress, the fabrication of GBLs with tailored residual stress by combination of dyads with different thickness is foreseen. Further studies will deal with the investigation of the interface between the oxide material and the polymer substrate employing IR techniques. In addition, investigations of thicker dyads, multiple stacks on industrial relevant polymers, such as PET and PEN, and their performance in terms of OTR and WVTR will be analyzed.

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**REFERENCES**


5. Summary and Outlook

5.1. Summary

In this thesis, the deposition of inorganic oxides, namely Al₂O₃, SiO₂ and TiO₂ by means of PEALD on the two polymers PET and PP was investigated regarding the application of these materials as GBLs for improved packaging materials. The discussed experiments and results demonstrate a contribution toward the understanding of the fundamentals of the respective PEALD depositions, thereby comprising studies on precursor development and the influence of precursor chemistry on the growth of GBLs on polymers, the combination of PECVD and PEALD as well as correlation of material properties toward barrier performance.

In the first part, the growth of TiO₂ during PEALD on PET was investigated in a comparative study, employing the commercial available precursor TMDAT and a newly developed mixed amino-alkoxide-Ti-precursor, TDMADT. The resulting outcome and more details on the precursor synthesis, characterization and process development were published in 2016 and reproduced in chapter page 59ff. These studies were performed based on the fact that the TDMAT precursor represents, among many beneficial properties such as volatility and reactivity, limited thermal stability. It was shown earlier that the rational precursor development of Ti-precursor compounds yields precursors with fine-tuned thermal properties, making these compounds promising for both PEALD and MOCVD application. As
the here investigated growth on polymers sets two additional limitations, \textit{i.e.} the reactivity toward a polymer substrate and the sensitivity of these substrates toward heat treatment, the motivation for further systematic precursor development is on hand. The new precursor compound TDMADT was obtained from substituting one of the amide-ligands of TMDAT using dimethylamino-2-isopropoxoide, thereby creating a five-fold coordinated Ti-complex with promising thermal properties and sufficient reactivity for PEALD processes. In the comparative study, an efficient PEALD process using TDMADT, exhibiting a similar GPC as TDMAT (0.9 Å cycle\(^{-1}\) vs. 1.0 Å cycle\(^{-1}\)) was developed and the obtained thin films revealed high quality in terms of low roughness (rms = 0.2 nm) and nearly perfect stoichiometry as found from RBS/NRA and XPS studies. Employing \textit{in-situ} QCM, the growth of the two processes, using either TMDAT or TDMADT, was monitored and from the relation of the frequency shifts and possible molecular fragments of the different precursors, it was found that the new precursor chemisorbs to the surface \textit{via} cleavage of two amide-ligands, while the more stable and more bulky dimethyl-amino-2-propanolato ligand stays intact and faces, most likely, upwards with respect to the substrate surface plane. Furthermore, both TDMAT and TDMADT were used to deposit TiO\(_2\) thin films as GBLs on 23 µm PET foil with different thickness and the respective coatings were investigated regarding their barrier performance in terms of OTR. For both compounds, thin films from applying 150 cycles (15 nm for TiO\(_2\) from TDMAT, 14 nm TiO\(_2\) from TDMADT) exhibit OTR values below 0.2 cm\(^3\) m\(^{-2}\) day\(^{-1}\), thereby showing a drop in OTR by two orders of magnitude compared with the uncoated PET foil.

A second major part of this thesis dealt with a combinatorial approach to fabricate GBLs by means of PECVD and PEALD. In chapter 3 page 79ff., this approach was discussed for both a seeding and a capping route. While the approach to combine PECVD and PEALD with respect to GBL application was investigated by several
groups, which was outlined in the chapters 1 and 3, the here performed experiments were designed to investigate the influence of ultrathin PEALD films (1 nm to 5 nm) on the overall barrier performance with respect to macro defect density and barrier performance in terms of OTR. This approach is unique in terms of the chosen barrier layer thickness and the used substrates, which were of only 23 µm thickness. From the seeding approach, in which SiO$_2$ PEALD thin films of 1 nm to 5 nm thickness served as improved surface for subsequent PECVD growth of 15 nm SiO$_x$, a significant impact on the latter measured defect density was found. A PEALD thin film of only 1 nm thickness decreased the defect density by 50%, while a 5 nm PEALD grown seeding layer caused a drop in OTR by two orders of magnitude, indicating a strong influence of the PEALD grown seeding layers on the overall barrier performance of the combined GBL materials.

The capping approach was investigated for four different systems, consisting of the PECVD grown materials SiO$_x$C$_y$H$_z$ or SiO$_x$ and the PEALD grown materials Al$_2$O$_3$ or SiO$_2$. Similar to the seeding approach, the PECVD coating thickness (5 nm) was chosen to exhibit a poor barrier performance to allow the investigation of a potential influence also from ultrathin PEALD thin films of only 1 nm to 5 nm thickness. PEALD grown cappings of Al$_2$O$_3$ on SiO$_x$C$_y$H$_z$ were found to result in a drastically reduced defect density, being ≤2 defects mm$^{-2}$. Furthermore, these cappings decreased the OTR substantial from > 62.0 cm$^3$ m$^{-2}$ day$^{-1}$ down to 15.0 cm$^3$ m$^{-2}$ day$^{-1}$ (1 nm Al$_2$O$_3$, 6 nm GBL in total) and 7.8 cm$^3$ m$^{-2}$ day$^{-1}$ (5 nm Al$_2$O$_3$, 10 nm GBL in total). Highly encouraging results were found for PEALD grown Al$_2$O$_3$ cappings on PECVD grown SiO$_x$, where an ultrathin capping of only 1 nm suppressed the formation of defects completely. Consequently, the defect density was found to be zero macro defects mm$^{-2}$ for both the 1 nm and 5 nm capping. While SiO$_2$ cappings on SiO$_x$C$_y$H$_z$ showed a less strongly pronounced impact on the defect density with 156 macro defects mm$^{-2}$ for the 5 nm, the barrier perfor-
mance found to be affected stronger, as OTR dropped from $>15.0 \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1}$ to $0.5 \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1}$. Regarding barrier performance, similar results were found for SiO$_2$ capping on SiO$_x$, where a 5 nm capping caused a stronger decreased OTR of $38.6 \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1}$. The defect density for SiO$_2$ cappings was found to be strongly decreased compared to the bare PECVD grown SiO$_x$ thin films on PET, with values of 23 macro defects mm$^{-2}$ (1 nm SiO$_2$, 6 nm GBL in total) and 1 macro defect mm$^{-2}$ (5 nm SiO$_2$, 10 nm GBL in total). Here, it was further observed that for $>90\%$ of the detected defects, macro defect formation takes place preferentially at sites contaminated with dust, while larger areas without surface features exhibit only negligible amounts of detectable defects, indicating the superior properties of thin films from PEALD with respect to GBL applications.

In chapter 4, the fabrication of multilayers for a potential GBL application was investigated with respect to stackings of Al$_2$O$_3$ and SiO$_2$ on PP and their mechanical properties in terms of residual stress. The idea followed the one from the seeding/capping approach (chapter 3) in terms of using a polymer substrate exhibiting rather poor barrier performance against oxygen gas and to investigate the influence from thin coatings, deposited by PEALD. In these studies, both the influence from precursor chemistry on the growth of Al$_2$O$_3$ thin films and a potential influence on film growth of Al$_2$O$_3$ and SiO$_2$ from an oxygen plasma pre-treatment of the polymer were investigated. For these studies, the recently reported and novel Al-precursor [3-(dimethylamino)propyl]dimethyl aluminum(III) (DMAD) was compared with TMA to grow Al$_2$O$_3$ via PEALD. From in-situ QCM studies employing functionalized QCM crystals, the growth of Al$_2$O$_3$ was monitored and could be explored with respect to the growth modes in dependency of the applied Al-precursor. For this, QCM crystals were coated with a top-layer of spin-coated PP (scPP), thereby providing an excellent model layer for industrially applied PP foil. From the investigations using the scPP-QCM crystals, a first indication of different growth modes
5.1. SUMMARY

for the two Al-precursors TMA and DMAD was obtained. While the growth of Al₂O₃ on scPP using TMA was decreased in terms of lower amounts of deposited mass per cycle than found for a reference deposition on an uncoated QCM crystal, the DMAD process revealed similar MGPCs for both crystals. It was further observed that the first cycles of the TMA process most likely comprise a rather strong contribution from etching, which could explain the hindered growth and hints toward a more diffusive interface between the scPP and the inorganic oxide. For DMAD, such etching contribution was not found, thus forming, most likely, a more abrupt interface with the substrate. Al₂O₃ thin films from DMAD of 10 nm thickness exhibited no gas barrier when applied on biaxial oriented PP (BOPP), while Al₂O₃ from TMA improved the OTR by a factor of 3.6. For SiO₂ of the same thickness, an improvement of the barrier performance by the factor 23.3 was found, and as for TMA, QCM hints here also toward a more diffusive interface as etching during the first cycles must be taken into account. Considering the findings from in-situ QCM experiments, a more diffusive interface could be beneficial in terms of improved barrier performance, which could be explained by a better sticking of the inorganic thin film on the substrate, due to a gradual increase of the inorganic component. Using Si-sensor chips, the residual stress of the binary oxides was investigated and SiO₂ thin films exhibited compressive stress over a broad thickness range with a lower value of −250 MPa for thicknesses ≥45 nm. Al₂O₃ thin films from TMA showed tensile stress with a lower value of 125 MPa for films ≥45 nm. In contrast, Al₂O₃ from DMAD showed a transition in residual stress from compressive (≤30 nm) to tensile (≥60 nm), with a 45 nm sample exhibiting residual stress close to 0 MPa. This change in residual stress for thicker films could be explained with formation of crystallites, inducing additional stress for thicker films. As GI-XRD revealed no evidence for crystallization, these potential crystallites must be nanoscopic. To investigate the influence from precursor choice on the properties of multilayers of
Al₂O₃ and SiO₂, dyads of 5 nm SiO₂ and 5 nm Al₂O₃, either grown from TMA or DMAD, were investigated regarding their barrier performance and residual stress. Here, the combination of SiO₂/Al₂O₃ (DMAD) exhibited a barrier improvement factor of 22.4 and a residual film stress of 114 MPa (tensile), while the combination with Al₂O₃ from TMA showed an improvement factor of only 4.8 and a residual stress of −113 MPa (compressive). These findings are encouraging, as the barrier performance seems to be dependent to a major degree on the SiO₂ coating while the Al₂O₃ coating can be used to tailor the residual stress of GBL materials, which is of high importance for the encapsulation of flexible display using OLED technology.
5.2. Outlook

The new findings from this thesis work on the PEALD of inorganic oxides on polymers provide a considerable contribution to the understanding of fundamental aspects of thin film growth and GBL applications. In addition, the discussed findings are encouraging for further investigations on this topic as several questions in this context can be answered in more detail.

As the comparison of TDMAT and TDMADT (see pages 59ff.) for PEALD of TiO$_2$ revealed differences with respect to the molecular fragments binding to the substrate surface and an accompanied different stoichiometry of the deposited TiO$_2$ thin films, it is of high interest to investigate other Ti-precursors and to compare the properties of respective thin films. With respect to suitable precursor properties for PEALD processes, the compound bis(dimethylamido)bis(dimethylamino-2-propanolato)titanium (BDMABDT) (page 63) is a promising candidate. Besides excellent thermal properties in terms of stability and volatility, this compound comprises two Ti-O bonds, which could result in even better stoichiometries as those from the process optimization using TDMADT.

With respect to the seeding/capping approach to yield improved gas barrier layers, it is of high interest to analyze the defect structure in more detail, for example using ellipsometric porosimetry to explore the nanoscopic defect structure of different capping/seeding combinations. Apart from binary oxides and the used silica-like PECVD materials, investigations should be carried out to transfer the discussed approach onto ALD/MLD hybrid materials. Such hybrid materials offer the possibility to further fine-tune the mechanical properties of nanolaminates or dyad-structures. With the promising results from the here discussed DMAD precursor, which was found to yield Al$_2$O$_3$ thin films with different behavior in residual stress compared with those deposited using TMA (see chapter 4), the combinations with selected or-
ganic precursor compounds can be used to fabricate materials exhibiting tailored mechanical properties and improved barrier performance.

In the context of GBL materials and investigated binary oxides $\text{Al}_2\text{O}_3$, $\text{SiO}_2$ and $\text{TiO}_2$, the performance of other binary oxides should be investigated as well. It has been shown in the literature that $\text{ZrO}_2$, $\text{HfO}_2$ and $\text{SnO}_2$ exhibit promising GBL performance if applied, together with e.g. $\text{Al}_2\text{O}_3$ or plasma polymers, in nanolaminates or multilayer structures. These materials should be investigated in more detail, with respect to the here discussed experiments, regarding their deposition during PEALD and their influence on the growth of GBLs.

For these materials, the development of respective new precursor compounds should be carried out as well, as suitable precursors for PEALD are either not in hand (Sn) or show limitations with respect to reproducibility and reliability (e.g. tetrakis(dimethylamido) hafnium(IV)). A promising synthesis route could follow a systematic exchange of ligands of established precursor compounds. For example, homoleptic dialkyl-amido-complexes of hafnium and zirconium, like TDMAHf and TDMAZr, could serve as starting compounds for ligand-exchange reactions using the previously employed 3-(dimethylamino)propyl ligand to synthesize new chemical compounds with tailored thermal properties. Such ligand-exchange reactions could generate a broad range of closely related compounds of both mixed dialkylamido-[3-(dimethylamino)propyl] and homoleptic tetrakis[3-(dimethylamino)-propyl]-metal complexes. In addition, the success story of versatile guanidinate- and amidinate-metal complexes can be fostered further by synthesizing mixed and heteroleptic mono-guanidinate-tris-dialkylamido- and mixed mono-amidinato-tris- dialkylamido-metal complexes of hafnium and zirconium. With their bulky side chains, the guanidinate and amidinate ligands offer a further opportunity to synthesize asymmetric ligands, which can influence the thermal properties and reactivity of metal-complexes as well. From such approaches, potential precursors meeting
the requirements of PEALD could be derived, allowing the development of efficient processes to fabricate respective oxide materials for GBL application. It must be noted that these thin metal oxides can serve as high-k materials in transistors as well. Therefore, the development of new Hf and Zr precursors opens a much broader field for research, including the PEALD for high-k applications.

Thin films of Al\textsubscript{2}O\textsubscript{3} were further found to produce GBLs free of macro-defects, demonstrating the high quality of PEALD grown thin films even for low thicknesses. These findings and preliminary results from WVTR-measurements employing Ca-degradation tests are encouraging toward the fabrication of GBLs meeting the demands from OLED encapsulation and further studies should be conducted to develop efficient PEALD processes using new precursors for the metal oxides Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2}, HfO\textsubscript{2} and SnO\textsubscript{2} for similar applications. From this, flexible moisture barrier films could be produced, allowing the encapsulation of lead-free perovskite solar cells and OLED devices. While SiO\textsubscript{2} thin films from PEALD processes were found to exhibit some macro-defects, their barrier performance was superior to that of Al\textsubscript{2}O\textsubscript{3}. It should be mentioned that preliminary results from experiments employing EP measurements on SiO\textsubscript{2} thin films, deposited on Si(100) are highly encouraging as nonoporosity was suggested to be below the detection limit of the used device with respect to detectable changes in the refractive index (under atmosphere \textit{vs. in vacuo}). Similar measurements should be carried out for Al\textsubscript{2}O\textsubscript{3}. In addition, these GBL materials could be investigated employing positron annihilation spectroscopy (PAS). This non-destructive technique enables the chance to measure porosity and to distinguish between vacancies (closed pores) and ordered porosity (open pores).

Considering porosity, the here investigated GBL materials could also act as coatings for membranes to fine-tune both the permeability and selectivity. Since the PEALD grown materials exhibit some permeability even for films without detectable macro-defects, these materials can be used to adjust the selectivity of membranes.
CHAPTER 5. SUMMARY AND OUTLOOK

to separate gases of different mixtures. As for the above mentioned possibility to combine inorganic and organic thin films to obtain hybrid materials for GBL application, the organic component could serve as a surface termination of inorganic materials, thereby giving the chance to regulate the hydrophobicity/hydrophilicity of the respective thin film, which could influence the selectivity of a potential membrane as well. By this approach, a substantial development with respect to enhanced performance separation and selectivity could be accessible.
A. Supplementary information for published contributions
A.1. Supplementary information for "An efficient PEALD process for TiO$_2$ thin films employing a new Ti-precursor"

This page shows the original Supplementary Information as available at The Royal Society of Chemistry.

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2015

Supplementary Information

![Representative XRD pattern of 50 nm TiO$_2$ thin film on Si(100), deposited at 60 °C using TDMAT and oxygen plasma (150 ms, 200 W)](http://www.rsc.org/suppdata/c5/tc/c5tc03385c/c5tc03385c1.pdf)
A.2. Supplementary information for "A combinatorial approach to enhance barrier properties of thin films on polymers: Seeding and capping of PECVD thin films through PEALD"

The following pages show the Supplementary Information as available at Plasma Processes and Polymers. Copyright with Wiley (2018).
A combinatorial approach to enhance barrier properties of thin films on polymers: Seeding and capping of PECVD thin films by PEALD
Maximilian Gebhard, Felix Mitschker, Christian Hoppe, Morteza Aghaee, Detlef Rogalla, Mariadriana Creatore, Guido Grundmeier, Peter Awakowicz, Anjana Devi*

Process development for PEALD of Al₂O₃ and SiO₂
To allow a thorough investigation of barrier materials from a combined and reliable PEALD/PECVD approach, PEALD processes for the fabrication of Al₂O₃ and SiO₂ and were developed and optimized. Al₂O₃ was deposited using trimethylaluminum (TMA), while SiO₂ was formed using bis(diethylamino)silane (BDEAS). These precursors are considered as standard compounds for the ALD of the previously mentioned materials. The depositions of both materials were optimized in terms of their growth rate with respect to the precursor pulse length. Saturation studies were investigated for both precursors at 60 °C and the results for both TMA and BDEAS are shown in Figure S1a and S1b, respectively.
Figure S1: a and b) Saturation studies for the Al and Si precursor TMA and BDEAS, respectively, with each growth rate showing a regime which is independent of the precursor feeding time; c and d) QCM response for the corresponding PEALD processes using TMA and BDEAS to fabricate Al₂O₃ and SiO₂, respectively, with the mass gain plotted in dependence of deposition time and cycles.

For both precursors, the respective growth rates were the same when applied at 60 °C and at room-temperature, indicating that a temperature-independent and ALD-like growth occurs. For TMA, the growth rate per cycle (GPC) was found to be above 1.0 Å cycle⁻¹ already for only a 12 ms precursor dose. However, saturation of GPC was found after a precursor pulse time of 15 ms with a GPC of 1.4 Å cycle⁻¹. As severe problems were encountered with respect to the plasma generation for TMA pulse times >13 ms, a shorter precursor dose instead of 15 ms was selected. From Figure S1a it can be seen that the difference between a 13 ms and a 15 ms precursor pulse is negligible, with a difference in GPC of only 0.1 Å cycle⁻¹. For SiO₂ and the respective precursor BDEAS, saturation was found at a 2×25 ms precursor pulse length with a GPC of 1.1 Å cycle⁻¹. Pulse times below 10 ms were not investigated as the valves used are not able to carry out such a rapid switching between the open and closed positions. The growth
rates per cycle found were in good agreement with literature values and while small deviations arise, these can be most likely attributed to reactor geometry and differences in the applied plasma sources.\textsuperscript{a,b}

The growth of the materials was further monitored by employing \textit{in-situ} QCM to ensure reproducibility and a linear relation between the thickness and applied number of cycles was determined. Figure S1c shows the QCM response from a 50 cycle PEALD process using TMA to produce Al\textsubscript{2}O\textsubscript{3}, while Figure S1d shows the QCM response from a process using BDEAS to deposit SiO\textsubscript{2} with the deposited mass per cm\textsuperscript{2} (\(\Delta m\)) derived from the Sauerbrey-equation, which can be written as

\[
\Delta m = \frac{\Delta f}{S} \quad \text{Equation 1}
\]

with \(\Delta f\) being the frequency shift and with \(S\) being the sensitivity factor for the used crystal:

\[
S = \frac{2\sqrt{f^2 - A/\rho Q\nu}}{\nu Q} \quad \text{Equation 2}
\]

with the quartz crystal density \(\rho Q = 2.64 \text{ g cm}^{-3}\), the shear wave velocity of quartz (AT-cut) \(\nu Q = 3.34 \times 10^5 \text{ cm s}^{-1}\) and the area \(A\). While \textit{in-situ} monitoring of plasma processes must be considered with care due to the abundance of processes and chemical reactions taking place in the gas phase and at the surface, the linear increase in Figure S1c and S1d of the deposited mass is easy to see, providing evidence of highly reliable PEALD processes. As an example, the QCM investigations are described for the SiO\textsubscript{2} process. From this investigation, a deposited mass of 40.7 ng cm\textsuperscript{-2} cycle\textsuperscript{-1} (2033.54 ng cm\textsuperscript{-2} in total for 50 cycles) was found. As the QCM crystals exhibit a much higher active surface area than the used Si(100) samples, a direct transfer of the monitored mass gain into thickness or GPC is rather limited. In addition, XRD experiments revealed amorphous thin films which should have a lower density than the crystalline SiO\textsubscript{2}, making the interpretation of the QCM even more challenging. However, from

the QCM response in Figure S1c and S1d, a nucleation delay during the first three cycles can be assumed for both processes, which is superseded by a linear mode of growth. While a negative QCM response could indicate the presence of an etching processes, we suggest that these features here are caused solely by the heating of the crystal due to the bombardment of the surface by highly energetic plasma species, as etching of inorganic materials like quartz usually needs the utilization of halogenated hydrocarbons or an SF6 plasma.\textsuperscript{c,d} Taking a closer look at the zoomed region in Figure S1d, the PEALD SiO\textsubscript{2} process can be followed in more detail: at the starting point of each single cycle (here, 18\textsuperscript{th} cycle), the deposited mass increases during precursor feeding time, as indicated by the steep positive slope. This slope decreases but remains positive during the argon purge. The abrupt change to a negative response of the QCM, which could be interpreted as etching, is caused by the heat transfer from the plasma ignition to the quartz crystal surface. At the end of the plasma step, the cycle is finished and an abrupt increase, caused by the precursor pulse of the subsequent cycle occurs.

PEALD grown thin films of Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2}, deposited with optimized precursor doses, were investigated regarding their composition using Rutherford-Backscattering spectrometry (RBS) and nuclear reaction analysis (NRA). Details on the quantification of measurements on silicon and glassy carbon can be found in Table S1. In addition, a representative RBS spectrum for SiO\textsubscript{2} is shown in Figure S2. The processes developed here produce SiO\textsubscript{2} thin films with nearly perfect stoichiometry while the Al\textsubscript{2}O\textsubscript{3} coatings were found to be oxygen-rich with a deviation of 25\% from an ideal oxygen to aluminum ratio of 1.5. Both materials show carbon contents of around 6 at.\%, while nitrogen impurities are not detected or are below the detection limit of this technique.

Figure S2: RBS spectra of a 20 nm SiO$_2$ PEALD thin film, grown on Si(100) and glassy carbon at 60 °C.

Table S1: RBS/NRA compositional analysis of thin films deposited on Si(100) and glassy carbon. All thin films were grown at 60 °C applying optimized process conditions.

<table>
<thead>
<tr>
<th>Composition (at.%)</th>
<th></th>
<th></th>
<th></th>
<th>Metal or metalloid</th>
<th>Ratio of O to metal or metalloid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>6.2</td>
<td>0.0</td>
<td>62.5</td>
<td>31.3</td>
<td>2.00</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>5.5</td>
<td>0.3</td>
<td>62.3</td>
<td>31.9</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Figure S3: Ellipsometric parameter $\Psi$ (red) and $\Delta$ (blue) from SE measurements on a 100 nm SiO$_2$ thin films, deposited at 60 °C on Si(100). In black, the corresponding fits of the Cauchy-model are depicted. For better visibility, not all data points are shown.
Figure S4: Representative SEM images of processed samples for the capping combinations a) 5 nm SiO$_x$C$_y$H$_z$ + 5 nm Al$_2$O$_3$, b) 5 nm SiO$_x$C$_y$H$_z$ + 1 nm SiO$_2$, c) 5 nm SiO$_x$C$_y$H$_z$ + 5 nm SiO$_2$, d) 5 nm SiO$_x$ + 1 nm Al$_2$O$_3$, e) 5 nm SiO$_x$ + 5 nm Al$_2$O$_3$ and f) 5 nm SiO$_x$ + 5 nm SiO$_2$. 
A.3. Supplementary information for "PEALD of SiO$_2$ and Al$_2$O$_3$ thin films on polypropylene: Investigations of the film growth at the interface, stress and gas barrier properties of dyads"

The following pages show the Supplementary Information as available at the American Chemical Society. Copyright (2018) American Chemical Society.
Supporting Information

PEALD of SiO$_2$ and Al$_2$O$_3$ thin films on polypropylene: Investigations of the film growth at the interface, stress and gas barrier properties of dyads

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Scheme S1: Recipes for the three PEALD processes using TMA, DMAD and BDEAS to deposit Al₂O₃ and SiO₂.

Figure S1: PEALD growth characteristics of SiO₂ using BDEAS at room-temperature. Thin films were deposited on Si(100) applying a 150 ms oxygen plasma. a) GPC vs. precursor pulse time and b) thickness vs. applied number of cycles using the optimized feeding sequence.
Figure S2: PEALD growth characteristics of Al₂O₃ using TMA at room-temperature. Thin films were deposited on Si(100) applying a 150 ms oxygen plasma. a) GPC vs. precursor pulse time and b) thickness vs. applied number of cycles using the optimized feeding sequence.

Figure S3: GI-XRD patterns of SiO₂, Al₂O₃ (TMA) and Al₂O₃ (DMAD) from PEALD processes. All thin films were of 75 nm thickness.
$$\Delta m = \frac{\Delta f}{S}$$ \hspace{1cm} (1)

with $\Delta f$ being the frequency shift and $S$ being the sensitivity factor for the used crystal:

$$S = \frac{2 \times f_0^2 \times A}{\rho_Q \times v_Q}$$ \hspace{1cm} (2)

with the quartz crystal density $\rho_Q = 2.64 \text{ g cm}^{-3}$, the shear wave velocity of quartz (AT-cut) $v_Q = 3.34 \times 10^5 \text{ cm s}^{-1}$ and the area $A$.

Figure S4: Purge studies for a) BDEAS and b) TMA for the deposition of SiO$_2$ and Al$_2$O$_3$ by means of PEALD.
Figure S5: XRR measurements and fitted curves for 30 nm thin films of a) SiO$_2$, b) Al$_2$O$_3$ (TMA) and c) Al$_2$O$_3$ (DMAD). The fits were derived from adjusting the roughness and density parameters applying a generic algorithm of the used LEPTOS software within physically reasonable ranges. The cost function of the fitting (generic algorithm with 120 generations) decreased in all cases during the fitting routine. As the density from the fitting function is only dependent of the critical angle, it should be mentioned that the shown plots show only the best fitted curves.
In-situ QCM using scPP for BDEAS

The QCM response from PEALD experiments to grow SiO$_2$ using BDEAS on scPP without an additional oxygen plasma pre-treatment is shown in Figure S6a, while Figure S6b shows the results from QCM experiments after an oxygen plasma pre-treatment of the scPP model layer. From the first SiO$_2$ PEALD run using BDEAS, a clear mass loss during the initial cycles is observed, followed by a mass gain dominated regime, which increases slightly after the 33$^{rd}$ cycle. The overall mass gain for this first run is only 1027.6 ng cm$^{-2}$, which is less by a factor of 2.0 compared to the growth on a bare QCM crystal. We suggest that the initial cycles of this run consist of both etching (scPP) and growth (SiO$_2$), where the etching contribution is overcome after 10 cycles. Most likely during these cycles, the growing SiO$_2$ thin film is agglomerating with each cycle. Once this layer is completely closed, only growth on freshly deposited SiO$_2$ occurs and the QCM response follows the expected trend, as the finally closed thin film prevents the underlying polymer to be etched. As can be seen from the plot, the slope of the first run is not as steep as for the experiment performed on a bare QCM crystal, indicating a decreased growth rate. This is most likely due to a strongly decreased amount of reactive surface sites on the scPP, hindering the development of enhanced growth as found for a bare QCM crystal. As there is no material to be etched, the second run (black) shows directly a linear mass gain with a total deposited mass of 1971.4 ng cm$^{-2}$ and a corresponding MGPC of 39.5 ng cm$^{-2}$ cycle$^{-1}$, which is in nearly perfect agreement with the MGPC found for the SiO$_2$ growth directly on quartz. We assume that once a dense film with comparable reactive surface sites, like on a bare QCM crystal, is established, the following deposition exhibits similar growth rates as found for the bare QCM crystal.
Figure S6: QCM response from PEALD of SiO$_2$, using BDEAS. a) QCM response for a bare scPP/quartz crystals and b) QCM response from a scPP-coated quartz crystal after oxygen plasma pre-treatment.

For the first deposition after applying the oxygen plasma pre-treatment, the first 4 cycles show a strongly increased negative QCM response, which is overcome fast and migrates into a steep mass gain (until the 12$^{th}$ cycle) which further migrates to a decreased but linear mass gain after the 15$^{th}$ cycle. The average MGPC of this deposition is 21.7 ng cm$^{-2}$ cycle$^{-1}$. In agreement with the less steep slope of the QCM response, this MGPC is much lower than the
reference measurement on a bare QCM crystal. However, the second deposition run yields a MGPC of 39.4 ng cm$^{-2}$ cycle$^{-1}$, matching the findings from the reference deposition and indicating a comparable growth of SiO$_2$ on the surface of the first deposited SiO$_2$.

Figure S7: XPS survey spectra of the bare PP foil and PP foil after oxygen-plasma pre-treatment.

Figure S8: XPS core level spectra of the C1s peak of the a) bare PP foil and b) plasma treated PP foil.
Figure S9: OTRs of SiO$_2$ and Al$_2$O$_3$ (both from TMA and DMAD) against thin film thickness.
B. Curriculum Vitae
### Academic education

**10/2013 – 12/2017**
Ruhr-University Bochum (RUB), Dr. rer. nat. Chemistry; Grade: Very good  
PhD Thesis: *Plasma-enhanced atomic layer deposition of binary metal oxides as gas barrier layers on polymers*  
Minor subject: Business Administration for Non-Economics, Management Accounting (Grade: very good)

**10/2011 – 6/2013**
RUB, M.Sc. in Chemistry; Grade: 1.0  
Focal point: Functional Materials  
Master Thesis: *Atomic layer deposition of indium oxide thin films employing In-tris-guanidinates and water as precursors; grade: 1.0*

**10/2008 – 9/2011**
RUB, B.Sc. in Chemistry; Grade 2.1  
Bachelorarbeit: *Scandiumcluster in ionischen Flüssigkeiten grade: 1.0*

### Professional experience

Since 01/2018
Argonne National Laboratory, Applied Materials Division, USA, PostDoc Fellow  
- Project development: Defining critical parameters within device manufacturing  
- Execution of projects with external collaboration partners (US Department of Energy)  
- Development of new materials for detector applications

**10/2013 – 1/2018**
RUB, Inorganic Materials Chemistry, Germany, Research Associate  
- Project work within the SFB-TR 87, project development and lead  
- Investigation of structure-property-relationships of inorganic materials and polymers  
- Fundamental research on plasma-assisted thin film deposition  
- International collaborations (India), DAAD-DST-PPP exchange program  
- Successful application for third party funded projects (DFG, EU)  
- Lecturing and supervision of students in internships and tutorials

### Scholarships and honors

**7/2017**
DAAD-Scholarship for attending international conferences

**2017 (2x), 2016, 2015 and 2013**
5 x GDCh-Scholarship for attending international conferences

**5/2013**
Best Poster Prize (E-MRS Spring Meeting, int. Conference, Symposium N)

**10/2011 – 9/2012**
Scholarship „Deutschlandstipendium“ for excellent academic performance

### Extracurricular activities

**2/2015 – 2/2017**
Member of the Executive Board at RUB Research School Plus

**1/2014 – 6/2017**
Representative in the PhD Committee

**9/2010 – 8/2014**
Primary Student Representative of the Faculty Council

**4/2011 – 4/2013**
Member of the Students Council
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