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 2, 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, 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-isopropoxypoxide, 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 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 79 ff., 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
5.1. SUMMARY

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 SiO₂ PEALD thin films of 1 nm to 5 nm thickness served as improved surface for subsequent PECVD growth of 15 nm SiOₓ, 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 SiOₓCₓHₓ or SiOₓ and the PEALD grown materials Al₂O₃ or SiO₂. 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 Al₂O₃ on SiOₓCₓHₓ 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 cm³ m⁻² day⁻¹ down to 15.0 cm³ m⁻² day⁻¹ (1 nm Al₂O₃, 6 nm GBL in total) and 7.8 cm³ m⁻² day⁻¹ (5 nm Al₂O₃, 10 nm GBL in total). Highly encouraging results were found for PEALD grown Al₂O₃ cappings on PECVD grown SiOₓ, 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 SiO₂ cappings on SiOₓCₓHₓ 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
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.