Atomic/molecular layer deposition of hybrid inorganic-organic thin films

Pia Sundberg
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A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Chemical Technology, at a public examination held at the lecture hall 26 at Dipoli Congress Centre on the 12th of December, 2014, at 12.

Aalto University
School of Chemical Technology
Department of Chemistry
Inorganic Chemistry
The possibility to combine the best properties of the two constituents makes inorganic-organic hybrid materials as intriguing candidates for many high-end applications. However, the distinctly different material properties of the inorganic and organic constituents make the fabrication of hybrid materials challenging. For example when using solution deposition techniques, a solvent which works for the organic constituent does not necessarily work well for the inorganic one. Also when considering the potential applications for hybrids, many require the use of high-quality thin films. Atomic and molecular layer deposition (ALD and MLD) techniques are gas-phase deposition methods based on sequential surface-saturated reactions. By combining the two techniques it is possible to deposit high-quality hybrid thin films with accurate thickness and composition control. In this thesis novel inorganic-organic hybrid thin films were deposited using the combination of ALD and MLD.

One of the main challenges when growing hybrid materials using the combined ALD/MLD technique is finding suitable precursors. When flexible linear organic precursors are used in ALD/MLD they may bend and hinder the growth process. In this work rigid aromatic amines, 4,4′-oxydianiline (ODA) and 4-aminophenol (AP) were used to improve the growth rates. Diethyl zinc (DEZ) and TiCl₄, precursors commonly used in ALD, were selected as the inorganic precursors. Successful film growth was observed for all possible precursor combinations, but the growth rates achieved using AP as organic precursor were higher than those obtained using ODA, Ti-AP hybrid exhibiting almost ideal growth. As AP has two different functional groups, more control is achieved in the growth process whereas the ether bond in ODA allows the molecule to bend. From the inorganic precursors TiCl₄, which is stronger Lewis acid and has more ligands than DEZ, catalyzed the deposition reaction better. The cyclic growth process characteristic to ALD and MLD was utilized to make nanostructures consisting of oxides and hybrid materials. The material pairs investigated were TiCl₄+ODA hybrid and TiO₂, DEZ+AP hybrid and ZnO, and trimethylaluminum (TMA) + ethylene-1,2-diol (EG) and Al₂O₃. By varying the hybrid and oxide content in the Ti- and Zn-containing mixtures, it was possible to tune the degree of crystallinity, surface roughness, refractive index, mechanical properties and density in the formed films. The TMA-EG and Al₂O₃ nanolaminates were grown on polylactic acid substrates in order to fabricate a film more suitable for coating biomaterials in packaging applications. When compared to coatings made from pure Al₂O₃ or TMA+EG hybrid, the nanolaminate consisting of TMA+EG and Al₂O₃ layers withstood straining better. The strained nanolaminate was also better oxygen barrier than the strained pure coatings.

Keywords: inorganic-organic hybrid, atomic layer deposition, molecular layer deposition
Tiivistelmä

Epäorgaanis-orgaanisten hybridihutkalvojen valmistus atomi- ja molekyylikerroskasvatuksesta

Julkaisijat

Kemian teknikat korkeakoulu

Yksikkö

Kemian laitos

Sarja

Aalto University publication series DOCTORAL DISSERTATIONS 201/2014

Tutkimusala

Epäorgaaninen kemia

Tiivistelmä


Yksi merkittävimistä haasteista uusien hybrimateriaalien valmistuksessa ALD/MLD-menetelmissä on sopivia lähdekemalien löytäminen. Kun käytetään orgaaniselle lähdekemälle organo-deuterisiä amineja, pientekoot talokemienne kasvun peittäminen. Epäorgaanisista lähdekemielästä TiCl₄:nä, joka on vahvempi Lewis happo ja jolla on

Avainsanat

epäorgaaninen-orgaaninen hybridi, atomikerroskasvattu


ISSN-L 1799-4934 ISSN (painettu) 1799-4934 ISSN (pdf) 1799-4942

Julkaisupaikka Helsinki Painopaikka Helsinki Vuosi 2014

Acknowledgements

The work presented in this thesis was carried out in the Laboratory of Inorganic Chemistry at Aalto University School of Chemical Technology between May 2010 and August 2014. Funding for this work was received from the European Union’s Seventh Framework Programme (FP/2007–2013)/ERC Advanced Grant Agreement, and from the Academy of Finland.

I am sincerely grateful to my supervisor, Professor Maarit Karppinen, for giving me the opportunity to carry out my doctoral studies in the Laboratory of Inorganic Chemistry on such a fascinating subject as atomic/molecular deposition fabricated hybrid thin films, as well as for the guidance and support during these years.

I am deeply grateful for Dr. Anjali Sood for instructions and advice during the work as well as the extensive discussions on the research subject. I would also like to thank Dr. Jari Malm for helping in all the ALD relating questions, Dr. Markus Valkeapää for his guidance in XRR/XRD measurements, Dr. Leena-Sisko Johansson for her expertise in XPS measurements, and Dr. Xuwen Liu for his experience in nanointendation measurements. I am also grateful for all the current and former colleagues and staff of the Laboratory of Inorganic Chemistry for their support during my research.

Finally, I would like to thank my extended family; Raija and Martti, Mia, Jari, and Niklas, Jari and Tanya, Jokke, Zsuzsa and Mauri, who all helped and supported me and made this project a reality. My special thanks go for my husband Aarne, who was always there to discuss anything and encourage me during the hard times. And to Adela, our lovely daughter.

Espoo, November 2014
Pia Sundberg
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# List of Abbreviations and Symbols

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<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
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<td>ALD</td>
<td>atomic layer deposition</td>
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<tr>
<td>AP</td>
<td>4-aminophenol</td>
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<td>CVD</td>
<td>chemical vapor deposition</td>
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<tr>
<td>DEZ</td>
<td>diethyl zinc</td>
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<tr>
<td>EG</td>
<td>ethylene glycol, ethane-1,2-diol</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<tr>
<td>GIXRD</td>
<td>grazing incident X-ray diffraction</td>
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<tr>
<td>GPC</td>
<td>growth-per-cycle</td>
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<tr>
<td>MLD</td>
<td>molecular layer deposition</td>
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<tr>
<td>ODA</td>
<td>4,4’-oxydianiline</td>
</tr>
<tr>
<td>Pc</td>
<td>tetra-t-butyl-Zn-phtahlocyanine</td>
</tr>
<tr>
<td>PVD</td>
<td>physical vapor deposition</td>
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<tr>
<td>RMS</td>
<td>root-mean-square</td>
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<tr>
<td>TAS</td>
<td>dicitratodiperoxotitanate</td>
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<td>TMA</td>
<td>trimethylaluminum</td>
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<td>V</td>
<td>teradecyl viologen</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<td>XRR</td>
<td>X-ray reflectivity</td>
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This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their Roman numerals


Author’s Contribution

**Publication I:**
Researched the relevant literature on the review topic and was the main author of the manuscript.

**Publication II:**
Defined the research plan together with co-authors and had a major role in performing the depositions, conducted the characterization with spectrophotometer, XRR, XRD and XRF, did the wet-etch tests and characterized the etched samples, and was the co-author of the manuscript.

**Publication III:**
Defined the research plan together with co-authors and took part on performing the depositions, conducted the characterization with XRR, GIXRD, AFM, and spectrophotometer, and was the co-author of the manuscript.

**Publication IV:**
Defined the research plan together with co-author, performed the depositions and sample characterization excluding XPS, analysed the characterization results, and was the main author of the manuscript.

**Publication V:**
Defined the research plan together with co-authors and had a major role in performing the depositions, conducted the sample characterization with spectrophotometer, XRR, GIXRD, AFM, and FTIR, as well as wet-etch tests, analysed all these characterization results, and was the main author of the manuscript.

**Publication VI:**
Defined the research plan together with co-authors and had a major role in performing the depositions, supervised and analysed the sample characterization with XRR, GIXRD, AFM, FTIR, spectrophotometer, as well as the wet-etch tests, and was the main author of the manuscript.

**Publication VII:**
Had a supporting role in defining the research plan together with co-authors, performing the depositions, and in the XRR and FTIR measurements, and was the co-author of the manuscript.
1. INTRODUCTION

Inorganic-organic hybrid materials can be defined as materials which consist of both inorganic and organic moieties. Unlike composites, which consists of separate phases of domains size varying from millimeter to micrometer scale, in the inorganic-organic hybrid materials nanometer scale constituents develop a bonding with each other. The combining of the two characteristically different material categories enables in principle the incorporation of different properties from each constituent to the new hybrid material. Electrical conductivity, mechanical strength and thermal stability are examples of the properties which can be gained from the inorganic constituent, whereas the organic constituent can attribute to the flexibility, transparency, and tunable dielectric properties. Due to the introduction of an inorganic-organic material interface it is also possible to achieve completely new or superior properties when compared to those of the pure counterparts.

The history of manmade inorganic-organic hybrid materials goes back several thousands of years. In ancient times these types of mixtures were made to produce colorful paints. For example, the Mayas in the 8th century used plant leaves together with Palygorskite, an inorganic clay, for making extremely durable pigments known as Maya Blue (see Figure 1). The paints have had to endure hard conditions of the jungle and be able to withstand acids, alkalis, organic solvents and biodegradation; even today the colors are still well preserved [1] [2]. Quite amazingly, even though extensively researched, the structure of Maya Blue is still not precisely known.

![Figure 1. A warrior drawn with a background of Maya Blue, an inorganic-organic material made of plant leaves mixed with clay [3].](image)
Industrial-scale interest in the use of inorganic-organic materials dates back to the development of the sol-gel process in 1930s, which enabled the production of hybrid materials by a mild reaction method [4]. Considering the Maya Blue, it is not really surprising that paints and various coatings were among the first industrial applications for inorganic-organic hybrid materials [5]. The versatility of properties makes the hybrid materials an attractive choice for many high-end applications. Today inorganic-organic hybrid materials are widely used in a variety of applications besides paints and coatings, e.g. in cosmetics, automotive industry, medicine, optics and electronics [6].

There are several ways to categorize inorganic-organic hybrid materials. One way stems from the constituent more abundant in the structure, i.e. inorganic-organic or organic-inorganic according to the dominant part. As there are many intermediate cases, this is not a definite way of categorizing, though. Hybrid materials can be also categorized according to their properties and applications or functionality and structure [7]. However, due to the central role of the interface of the two phases, the most commonly employed categorization method separates the hybrids to two classes according to the chemical bonds. Class I hybrids are materials with interactions between the inorganic and organic constituents which are weak, such as van der Waals, hydrogen bonding or electrostatic interactions, while in Class II hybrids the two phases are at least partly connected via strong chemical bonds, i.e. covalent, ionic or Lewis acid-base bonds [4] [6] [7]. When considering these two classes, the films deposited in this work belong to the Class II hybrid materials.

Many of the applications utilizing hybrid materials require that the material is in the form of a high-quality thin film. There are several methods to fabricate hybrid thin films, each with their advantages and disadvantages. For example sol-gel, a method widely used in inorganic-organic hybrid fabrication, is simple method requiring mild conditions and cheap equipment. However, the the films may contain impurities and may have cracks. When using physical vapour deposition (PVD) to deposit thin films, quality of the films is higher, but the equipment needed is expensive. Also unlike in sol-gel, the precursors used in PVD are often toxic and/or corrosive.

Atomic layer deposition (ALD) is a gas-phase thin-film deposition technique which produces conformal, uniform, and pinhole-free inorganic films [8] [9] [10]. The technique was developed in 1960s and 1970s [11] [12] [13] and is currently used for commercial fabrication of a large variety of materials [14]. As ALD is based on sequential deposition cycles, it is not only possible to accurately control the thickness of the resultant thin film, but by introducing another material also fabricate thin-film alloys and nanolaminates. As the composition of such thin-film structures is precisely controlled, it is possible to gradually fine-tune the properties of the films. The strategy has been successfully applied to deposit films with tailored electrical [15] [16] and gas barrier properties [17], refractive index [18] [19] [20], thermal stability [21] and surface roughness [22]. Furthermore, these advantages of ALD can be
extended in fabrication of the hybrid films, produced using the combination of ALD and molecular layer deposition (MLD), a variant of ALD which produces organic thin films.

As the MLD process sets various requirements for the organic precursor candidate, such as sufficient vapor pressure, stability and reactivity at the deposition temperature, finding an inorganic-organic precursor pair working well together is quite a challenge. Also, many organic molecules are flexible and may easily bend and react twice with the active surface sites, hindering the deposition process. These types of double reactions have been seen when using for example ethane-1,2-diol as the organic precursor [23] [24] [25]. Yet another issue is the air-sensitivity often encountered in the hybrid thin films fabricated by the ALD/MLD technique, like seen for example in the ethane-1,2-diol based hybrids [23] [24] [25] as well as in hybrids made using benzene-1,2-diol and benzene-1,3,5-triol [26].

The underlying goal of the present research was to find precursor pairs which would exhibit ideal ALD/MLD growth, i.e. saturated growth with full monolayer coverage, producing air-stable hybrid inorganic-organic thin films. The research conducted using MLD up till today was reviewed\textsuperscript{I}, and novel hybrid materials based on stiff aromatic amines were deposited and characterized.\textsuperscript{II-IV} The sequential growth process was utilized to fabricate mixtures and nanolaminates consisting of oxide and hybrid layers, exhibiting tunable and enhanced properties.\textsuperscript{V-VII}

In this summary part, in Chapter 2 the different techniques to deposit inorganic-organic hybrid thin films, divided to liquid- and gas-phase techniques, are shortly presented. In Chapter 3 the growth process as well as different characterization techniques utilized during the work are described. Chapters 4 and 5 then focus on the fabricated amine based hybrids, and mixture/nanolaminate structures, respectively. Chapter 6 presents the main conclusions regarding the work.
2. TECHNOLOGIES FOR HYBRID THIN-FILM FABRICATION

When considering the applications benefiting from hybrid materials, many require that the material is produced in the form of a thin film. The very same thing that makes combining inorganic and organic moieties such an attractive approach in material design, i.e. distinctively different material properties, makes it also challenging to deposit hybrid thin films. For example when considering solvents used in solution deposition techniques such as spin coating, dip coating and spraying, generally those which work for the organic constituent do not work well for the inorganic part. The organic materials are generally thermally fragile, which may cause complications when using vacuum evaporation techniques through the decomposition or dissociation of the organic part at the evaporation temperature of the inorganic part. Still, there are several viable ways to fabricate inorganic-organic hybrid thin films [27]. In the following subchapters a selection of the most promising methods for the fabrication of inorganic-organic hybrid materials is presented, divided into liquid- and gas-phase processes.

2.1 Liquid-Phase Techniques

The liquid-phase methods used for inorganic-organic hybrid thin-film fabrication are generally simple. The processes do not necessarily require vacuum systems or glove boxes, cutting the equipment costs. Also the handling of non-gaseous precursors is also easier and safer compared to the gaseous ones. However, the quality of the films is generally poorer when compared to those deposited by gas-phase methods. Also the technique used may set limitations on the material selection. In the following subchapters liquid-phase methods used for inorganic-organic hybrid material are shortly described. It should be noted, however, that there are several variations and combinations of the methods presented here; for example self-assembly can be carried out by using a sol-gel route and evaporation-induced self-assembly can even be seen as a variation of the sol-gel method where a surfactant acts as a template. There are also several techniques for the actual thin film application on substrate: 2.1.5 describes the most common ones.
2.1.1 Sol-Gel Methods

The sol-gel technique is widely used for inorganic-organic hybrid material fabrication [7] [4] [27]. A sol-gel process starts with the preparation of a sol, a liquid with dispersed nanoparticles [28]. Sols can be made by mixing colloidal particles in water or by hydrolyzing an alkoxide by mixing with water. The gelation, i.e. the transition from sol to gel, occurs with time through hydrolysis and condensation reactions. During gelation the nanoparticles link together, forming a three-dimensional network. After aging, a period of time during which the forming gel gains strength, the liquid in the network is removed by drying. This is followed by dehydration or chemical stabilization, and finally the densification of the gel is achieved by heating it at high temperatures.

There are several advantages when considering sol-gel. It is relatively simple and cheap method. The temperatures used at the beginning of the process are mild and it can be carried out in atmospheric pressure for large area deposition [29]. A wide range of different materials can be produced. The end product purity is generally high if care is taken in using high purity precursors, although residual contamination in the films can occur. A major issue when considering sol-gel made thin films are the cracks which form during drying and heating, especially when the film thickness is over submicron [30].

2.1.2 Intercalation Reactions

Intercalation reactions are reactions where guest species (ions or molecules) are introduced to a host material. No major changes occur in the structure of the host lattice and the reaction is usually reversible. Intercalation can be used for material fabrication in cases where there is no suitable solvent available for making the hybrid by sol-gel method, either because incompatible solubility of the component materials or insufficient wetting of the substrate with the solvent used for the hybrid [27]. It is possible, however, that during the process in addition to the guest species, also the solvent containing the guest intercalates to the host [31]. Inorganic-organic hybrid materials have been prepared by intercalation of the guest into clays, using for example polyhedral oligomeric silsesquioxane in saponite [32], and ionic liquids (trihydroxyethylmethylammonium iodide, 1-(2-hydroxyethyl)-2-methylimidazolium chloride and 1-benzyl-3-(2-hydroxyethyl) imidazolium chloride) in kaolinite [33]. Other examples of hybrids made by intercalation include polyanilineMoO$_3$ [34] and perovskite-type material (HCH$_2$)$_2$NH$_2$PbI$_4$ [35].

2.1.3 Langmuir-Blodgett Methods

In the Langmuir-Blodgett method a suitable molecule, usually amphiphile, is dissolved in a volatile solvent and then spread at the gas-liquid interphase. After this the molecules are compressed with a movable barrier to alter the local density as well as organization of the molecules [27] [36]. To deposit a monolayer of the material a substrate is passed through the liquid surface. For multilayer structures this passing process is then repeated.
The Langmuir-Blodgett is a relatively simple method, which enables precise control of the monolayer thickness of the forming film. The deposition is homogenous over large areas (several cm$^2$) on large variety of solid substrates. Still, there are several limitations when considering the Langmuir-Blodgett method. The material selection is somewhat limited, as only surfactant-like molecules can be used. The reproducibility is also poor and the growth process is sensitive to impurities. Also only small sized and flat substrates can be coated. The mechanical stability of the films is also somewhat poor [27][36]. Still the technique has been successfully used to make hybrid films. For example chloroform solution of tetra-$t$-butyl-Zn-phthalocyanine (Pc) has been spread on aqueous solution of dicitratodiperoxotitanate complex ammonium salt (TAS) to form a Pc-TAS hybrid. The same group also made teradecyl viologen (V)-TAS hybrids, as well as three layered structures of V-TAS-Pc and Pc-TAS-V [37]. In another study octadecylamine was spread onto an aqueous hectorite clay dispersion to fabricate an organo-clay hybrid film [38].

2.1.4 Self-Assembly Methods

In self-assembly the molecular units form ordered structures spontaneously. The component position is affected by non-covalent or weak covalent interactions, such as hydrogen bonding, Van der Waals interactions, electrostatic interaction and $\pi-\pi$ stacking [39]. Complex nanostructures with atomic precision can be made using self-assembly. The forming structures are relatively defect-free and self-healing. However, the design and fabrication of desired construct can be challenging. Also the internal interfaces of the nanostructures can weaken in time if not strengthened. The self-assembly methods used for inorganic-organic hybrid material fabrication include in situ self-assembly, template-induced self-assembly, evaporation-induced self-assembly, and layer-by-layer assembly [40].

In the in situ self-assembly the fabrication involves inorganic particles formation through different chemical reactions in the organic material matrix [40]. For example Martínez et al. [41] used this approach to make CdS nanoparticles synthesized in hybrid films formed of chitosan, poly(monomethyl itaconate) and silica.

Template-induced self-assembly is a convenient and versatile method for hybrid nanostructure fabrication, where the synthesis is directed by a template [40]. The used templates can be divided to two types, i.e. soft templates with no firm structures and hard templates with solid structures. For example surfactants, polymer, and organic small molecule can be used as soft template, whereas commercial powders and various nanoparticles can be used as hard template. Sakurai et al. [42] used siloxane precursors bearing alkyl chains in the presence of polystyrene opal films as template to grow siloxane-based hybrid films. Depending on the alkyl chain length, either two-dimensional hexagonal structure or a lamellar structure formed during the process.

Evaporation-induced self-assembly is a simple and rapid one-pot synthesis method, involving precursors and surfactant in a highly volatile solvent [40][43]. During the process the solvent evaporation enriches the non-volatile
components, inducing the co-assembly into liquid mesophase. The mesophase then stiffens during polymerization. For example organosilica- and titania-based mesoporous hybrid thin films have been made using this technique [44] [45].

Layer-by-layer electrostatic assembly is one example of layer-by-layer assembly methods [27] [46]. It is in principle a simple and inexpensive thin film deposition method. In layer-by-layer electrostatic assembly the oppositely charged (poly)ions are applied one at a time, separated by a washing step. The process is self-limiting due to the charged species repelling each other. The application of (poly)ions and washing step can be conducted using several different techniques, such as dipping, spinning or spraying. The number of layers and layering sequence can be freely chosen, giving great control over film thickness and composition. For example negatively charged polyoxometallate or polyoxometallate-protected Pt-nanoparticles has been used together with polyaniline, polypyrrole or poly(3,4-ethylene dioxythiophene) [47], as well as negatively charged (poly)sodium 4-styrenesulfonate or tetrasodium-meso-tetra(4-sulfonatophenyl) porphine together with positively charged TiO$_2$ colloids [48] to form hybrid thin films. The interactions of the forming layers when using layer-by-layer assembly are not limited to coulombic attraction. For example layer-by-layer assembly where the formation of the layers was directed by hydrogen bonds has been done using 1-(6-mercaptohexyl)thymine-capped cadmium selenide nanocrystals and poly(3-hexylthiophene-co-oxy diaminopyrimidine-hexylthiophene) [49].

2.1.5 Coating Methods

The application of thin films to a substrate can be in general done by dipping, spinning or spraying as well as by variations of these three methods. In dip coating the substrate is immersed on solution, and then withdrawn from the liquid bath at a constant speed [50]. The structure of the forming films is affected by the precursors, condensation and evaporation rates, capillary pressure, and substrate withdrawal speed. Quite good uniformity can be achieved, as well as very thin films (few nanometers thick) with large area coverage. The disadvantages of dipping include waste of material, slowness and coverage on both sides of the substrate.

In spin coating a small amount of solution is applied on the substrate, followed by high speed spinning of the substrate [51]. Due to the centripetal acceleration the solution spreads out with some of it falling off at the edges, leaving a thin film on the surface. This causes waste of the material used. The film thickness is strongly affected by the used spin speed and time, and good control over the film thickness can be achieved. Even 10 nm thick or thinner films can be obtained by the method. The films obtained by spin coating are uniform and reproducible, but spinning cannot be used on coating large areas.

Spray coating is conducted by spraying the coating material onto the substrate [52]. The method can be used for even when applying coatings on complex topographical structures with large area coverage when depositing for
example paints. The thickness of the films can be easily adjusted in spraying, but the homogeneity of the films is poor.

2.2 Gas-Phase Techniques

The use of liquid-phase techniques is not always appropriate for the desired hybrid thin film fabrication. Also the application may require the use of a vacuum technique when for example gaseous contamination needs to be minimized. In these cases the deposition may be carried out by a gas-phase technique. These techniques can be divided to physical vapor deposition (2.2.1) and chemical vapor deposition (2.2.2) techniques. Atomic/molecular layer deposition, discussed in subchapter 2.2.3, is a variant of chemical vapor deposition: as the chosen method for fabricating inorganic-organic hybrid thin films during this thesis work it is also shortly described.

2.2.1 Physical Vapor Deposition

Physical vapor deposition (PVD) consists of several vacuum deposition techniques, e.g. cathodic arc deposition, electron beam evaporation, thermal evaporation, and sputtering. The deposition process for all techniques can be divided to three steps: evaporation, transportation and deposition [53]. During evaporation the solid or liquid source forms a gas phase. The precise way varies depending on the method used: for example in thermal evaporation the source material is heated whereas in sputtering vaporizing is achieved through bombardment with accelerated ions. Transport step consists of the movement of the atoms or molecules to the substrate. In the last step, deposition, the thin film is generated: in both thermal evaporation and sputtering the atoms or molecules condense on the substrate, forming the film.

There are several advantages when PVD coatings are considered: the forming films generally have good mechanical and thermal properties, many types of inorganic and some organic materials can be utilized to form PVD coatings, and the process is environmentally friendly when compared to e.g. electroplating [54]. The disadvantages associated with the technique include high capital cost, line of sight transfer which causes difficulties when coating surfaces with complex geometries, need of trained personnel for handling processes operated at high vacuums and temperatures as well as need of cooling systems, and slowness of the process. The precise growth rates vary between different PVD techniques as well as processes used, but according to Crowell [55] growth rates achieved are between 10 and 1000 nm per minute.

In inorganic-organic hybrid deposition sputtering has been used by for example Nunes et al. [56] to make nanocomposite thin films of SiO$_2$ and polypropylene, which acted as a matrix for silver dispersion when investigating neural implants.
2.2.2 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is another vapor-transfer deposition process. The solid thin film forms through chemical reactions of the used precursors, either on the substrate surface or near it [57]. There are several variations of CVD, such as low-pressure CVD, plasma-enhanced CVD, atmospheric pressure CVD, and atomic/molecular layer deposition (discussed in subchapter 2.2.3).

When compared to PVD, CVD has several advantages. As CVD is not limited to line of sight deposition, also complex 3 dimensional structures can be deposited by the technique [58]. CVD reactor is relatively simple and does not require ultra-high vacuum, making it easy to carry out any changes needed in the equipment configuration. There are, however, also some disadvantages when compared to PVD. Although lower deposition temperatures can be used in CVD processes, many of the depositions are efficiently done at temperatures of 600 °C and above, which is too high for temperature sensitive substrates. Another disadvantage relates to the precursors used in CVD, which are often hazardous and at times toxic, producing toxic and/or corrosive by-products. The need to neutralize these by-products increases the overall expenses of the process. Also many of the precursors used in a CVD process are expensive. The growth rates are the same order of magnitude as with CVD [55]. Examples of hybrids made using CVD include plasma-enhanced CVD deposited hybrid thin films using cyclohexene and tetraethylorthosilane [59] as well as hexamethylsiloxane and oxygen as precursors [60].

2.2.3 Atomic/Molecular Layer Deposition

Atomic layer deposition (ALD) is a variant of CVD, which is based on sequential surface-saturated deposition cycles. The deposition takes place in a cyclic manner, the process resembling the layer-by-layer assembly method: in ALD each gaseous precursor pulse is separated by a purging pulse of inert gas. The sequential deposition process enables the fabrication of high-quality thin films with excellent atomic-level control over the film thickness. The thin films produced are also conformal to the underlying substrate, pinhole-free, and continuous. The method is, however, slow: according to Leskelä and Ritala [61] typical growth rates of ALD made films vary between 100 and 300 nm per hour, making it an unpractical technique for depositing films with thicknesses of micrometer scale. Recently, a new approach named spatial ALD has gained increasing interest [62] [63]. Spatial ALD can enable up to two orders of magnitude improvement in growth rate as well as operation at close to atmospheric pressures, making it cost-effective laboratory and industrial tool for thin film depositions.

In ALD the films are grown by single atomic layers; in a variant of ALD, molecular layer deposition or MLD, organic polymers can be made where the layers are formed from molecular chains using organic precursors [64]. By combining these two methods it is possible to deposit inorganic-organic hybrid thin films formed of organic molecules covalently bonded to the metal atoms and vice versa [23] [26].
The growth process when depositing hybrid materials using ALD and MLD can be described by a so-called ALD/MLD cycle, depicted on the left side in Figure 2. In ideal case a full monolayer growth is achieved, resulting in hybrid material seen on the right side in Figure 2. As in layer-by-layer assembly, in ALD and MLD the thickness and composition of the forming hybrid film can be accurately controlled. Although as a gas-phase technique ALD and MLD require the use of a specifically designed reactor, the deposition temperatures are generally lower than required in CVD [65].

Figure 2. On the left: ALD/MLD cycle consisting of four separate steps, i.e. 1. pulsing of the first (inorganic) precursor, 2. purging of excess precursor and possible byproducts, 3. pulsing of the second (organic) precursor, and 4. purging. In an ideal case a full monolayer coverage is achieved and an inorganic-organic hybrid material seen on the right is achieved.

If during the ALD/MLD growth process the bifunctional organic molecule would remain straight and the ideal full monolayer coverage would be achieved, it should be possible to acquire high growth-per-cycle (GPC; the average increase in film thickness during one ALD/MLD cycle) values for the hybrid materials. In practice the obtained GPC values are considerably lower. If there are several possible reasons for the low GPC values (see Figure 3). Especially when using flexible linear organic molecules, the growth process is prone to so-called double reactions of the organic precursor molecule on the surface; that is, the molecule may bend and react twice with the surface. This effectively reduces the number of active surface sites, lowering the growth rate. Even if no double reactions take place, the organic molecule may tilt during the growth, reducing the GPC.
Figure 3. Ideally in ALD/MLD the organic precursor reacts with one surface site and remains straight (left). It may also react twice, i.e. so-called double reaction (middle) or tilt (right).

The ALD/MLD technique is described in more detail in the review written of the topic. Also in the review the inorganic-organic materials as well as various nanostructures made using ALD and MLD are discussed.¹
3. EXPERIMENTAL PROCEDURES

As one of the underlining goals of the present work was to find an ideal ALD/MLD process exhibiting saturated growth with full monolayer coverage for growing inorganic-organic hybrid thin films, it was crucial to avoid the unwanted double reactions of the (bifunctional) organic precursor molecules with the surface. To achieve this, aromatic precursors with a stiff backbone, namely 4,4'-oxydianiline (ODA) and 4-aminophenol (AP), were used for fabrication of novel hybrid films. Also the possibility to tune or even enhance the properties of the resultant film was explored by depositing nanostructures consisting of different combinations of hybrid and oxide layers. In addition to ODA and AP, ethane-1,2-diol (ethylene glycol, EG) was used as an organic precursor in making some depositions. Precursors commonly used in conventional ALD were selected for the inorganic precursors, i.e. diethyl zinc (DEZ), TiCl₄, and trimethylaluminum (TMA). The structures of the precursors used in this work are shown in Table 1.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Abbreviation</th>
<th>Source and purity</th>
<th>Ref.</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-aminophenol</td>
<td>AP</td>
<td>Aldrich, 99%</td>
<td>III, VI IV</td>
<td></td>
</tr>
<tr>
<td>4,4'-oxydianiline</td>
<td>ODA</td>
<td>Fluka, &gt;98%</td>
<td>II, VI</td>
<td></td>
</tr>
<tr>
<td>Ethane-1,2-diol</td>
<td>EG</td>
<td>Riedel de-Haën, ≥99.5%</td>
<td>VII</td>
<td></td>
</tr>
<tr>
<td>Diethyl zinc</td>
<td>DEZ</td>
<td>Aldrich, 52 wt% Zn (minimum)</td>
<td>III</td>
<td></td>
</tr>
<tr>
<td>TiCl₄</td>
<td>TiCl₄</td>
<td>Strem Chemicals Inc. Sigma-Aldrich, ≥ 99.995%</td>
<td>II, IV, V</td>
<td></td>
</tr>
<tr>
<td>Trimethylaluminum</td>
<td>TMA</td>
<td>SAFC Hitech, electronic grade purity</td>
<td>VII</td>
<td></td>
</tr>
</tbody>
</table>

The techniques used for the film characterization included X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, X-ray reflectivity (XRR), grazing incident X-ray diffraction (GIXRD), spectrophotometric modelling, atomic force microscopy (AFM) and nanoindentation. In the following subchapters 3.1 and 3.2, the deposition process parameters employed and the most important characterization methods as well as how the ideal GPC values were calculated are discussed in more detail.
3.1 Thin-Film Depositions

Most of the films where fabricated using the F-120 reactor by ASM Microchemistry Ltd: only the TMA+EG nanolaminate films were fabricated using the SUNALE™ reactor by Picosun. A pressure of 2 to 4 mbar was kept in the F-120 reactor during the thin film depositions. Nitrogen gas was used for purging any excess precursor molecules and gaseous by-products, and also as a carrier gas for precursor delivery. The inorganic precursors, i.e. diethyl zinc (DEZ), TiCl₄, and TMA were kept in reservoirs outside the reactor at room temperature during the depositions. The organic precursors, i.e. AP, ODA, and EG required heating to achieve sufficient vapor pressure for the deposition process, see Table 2. Due to the different design of the two reactors, the heating temperatures for the organic precursors are not comparable: whereas in the F-120 reactor the organic precursors are placed in small glass crucibles inside the reactor and heated with a heating element, in the SUNALE™ reactor the containers are larger, connected to the gas lines through valves and with a different heating couple placement.

Table 2. Heating temperatures required for organic precursors.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Abbreviation</th>
<th>Reactor</th>
<th>Heated to (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane-1,2-diol</td>
<td>EG</td>
<td>SUNALE™</td>
<td>98</td>
</tr>
<tr>
<td>4-aminophenol</td>
<td>AP</td>
<td>F-120</td>
<td>111</td>
</tr>
<tr>
<td>4,4’-oxydianiline</td>
<td>ODA</td>
<td>F-120</td>
<td>~150</td>
</tr>
</tbody>
</table>

Si(100) was used as a substrate material during on all the depositions. In the TMA and EG based experiments, also polylactid acid and cellophane as substrates were used.

One ALD/MLD deposition cycle consisted of pulsing of the inorganic precursor, followed by purging with nitrogen, then pulsing of water or the organic precursor, again followed by purging. For self-limiting growth the pulsing and purging times should be sufficiently long, ensuring that the surface is saturated with the precursor and that any excess precursor is removed together with possible by-products. In case of the mixtures and nanolaminates, the growth process consisted of alternate deposition cycles for the oxide and hybrid materials. The pulsing and purging times used are summarized in Table 3.
Table 3. Precursor pulse and purge times used in the depositions.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Material</th>
<th>Deposition temp. (°C)</th>
<th>Precursor</th>
<th>Pulse (s)</th>
<th>Purge (s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid</td>
<td>TiCl₄+ODA</td>
<td>160-490</td>
<td>TiCl₄</td>
<td>1.5</td>
<td>3</td>
<td>II</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ODA</td>
<td>3</td>
<td>3 or 30</td>
<td></td>
</tr>
<tr>
<td>Hybrid</td>
<td>TiCl₄+ODA</td>
<td>160-310</td>
<td>TiCl₄</td>
<td>1.5</td>
<td>3</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ODA</td>
<td>14</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>Mixtures</td>
<td>TiCl₄+ODA</td>
<td>280</td>
<td>TiCl₄</td>
<td>1.5</td>
<td>3</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ODA</td>
<td>14</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td></td>
<td>TiCl₄</td>
<td>1</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>water</td>
<td>1.5</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Hybrid</td>
<td>DEZ+ODA</td>
<td>160-220</td>
<td>DEZ</td>
<td>5</td>
<td>8</td>
<td>unpublished</td>
</tr>
<tr>
<td>Hybrid</td>
<td>TiCl₄+AP</td>
<td>120-220</td>
<td>TiCl₄</td>
<td>1.5</td>
<td>3</td>
<td>IV</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ODA</td>
<td>24</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Hybrid</td>
<td>DEZ+AP</td>
<td>140-330</td>
<td>DEZ</td>
<td>3</td>
<td>4</td>
<td>III</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AP</td>
<td>7</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Hybrid</td>
<td>DEZ+AP</td>
<td>140, 280</td>
<td>DEZ</td>
<td>60</td>
<td>90</td>
<td>unpublished</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AP</td>
<td>35</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>mixtures, nanolaminates</td>
<td>DEZ+AP</td>
<td>140</td>
<td>DEZ</td>
<td>3</td>
<td>4</td>
<td>VI</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AP</td>
<td>7</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>DEZ</td>
<td>1.5</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>water</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Nanolaminate</td>
<td>TMA+EG</td>
<td>100</td>
<td>TMA</td>
<td>0.1</td>
<td>6</td>
<td>VII</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>EG</td>
<td>0.3</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TMA</td>
<td>0.1</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>water</td>
<td>0.1</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Characterization Techniques

The chemical state of the deposited films was investigated using FTIR. In particular, the presence of the organic backbone in the hybrid structure could be confirmed by the measurements. In the FTIR measurement, infrared radiation is passed through the measured sample. As different types of bonds absorb IR radiation of different wavelengths, the technique can be used to obtain information regarding the molecular structure of ALD/MLD-grown films quickly and nondestructively. As also bands originating from the Si substrate can be seen in the measured spectra, subtraction of a clean Si substrate spectrum from the spectra for the samples was necessary. However, even this process was not enough to remove all the disturbing peaks, especially those often seen around 600 cm⁻¹ and 1100 cm⁻¹. Yet another factor which made the interpretation of the spectra more challenging was the relative low thickness of the films: the thickness of the present films was typically in the range of 50-150 nm, and the intensity of the peaks was quite low.

From the FTIR spectra measured for films deposited using aromatic amines, the presence of aromatic ring in the structure could be confirmed from the strong peak around 1500 cm⁻¹ (see Figure 4). The absence of peaks relating to –OH and -NH also gave good indication of how the reaction might take place during the deposition, suggesting how the actual bonding may occur. Bands relating to C-N, C-O and aromatic-O-aromatic (Ar-O-Ar) could be often seen in the spectra. There is also the possibility to see bands relating to metal-O and metal-N bonds in the spectra, although in practice only metal-O peaks were clearly seen for the mixture thin films. Some information of what
happens to the films during a reaction in ambient air could be also gained. For example in case of the unstable Ti-ODA films, a broad feature around 3300 cm\(^{-1}\) could be attributed to the absorbed moisture.\(^{11}\)

![Figure 4. FTIR spectra for a Ti-ODA film aged in ambient air and a Zn-AP : ZnO mixture film.](image)

The surface chemistry of the Ti-ODA and AP-based films was evaluated by high resolution XPS measurements.\(^{11,16}\) In XPS the sample is irradiated with a beam of X-rays (monochromated Al K\(_\alpha\) in this research). The energy of the X-ray photon is adsorbed by a core-level electron. In case the energy is large enough, the electron is emitted from the surface with a kinetic energy. The kinetic energy depends on the X-ray photon energy and binding energy of the core electron. Identification of elements and concentration determination are done by analyzing the kinetic energy and intensity of the emitted electrons, see Figure 5. As the electrons originate from the 0-10 nm depth of the sample surface, the technique is sensitive to any contaminations such as oxygen and carbon from air as was also seen for the investigated hybrid films.\(^{11,14,15}\) It would be, however, possible to prevent the contamination by air by conducting the investigation \textit{in situ} in ALD environment, like done for example by Swaminathan \textit{et al.} who studied the evolution of chemical bonding by pulsing H\(_2\)O on Ge(100) substrates before depositing Al\(_2\)O\(_3\) by ALD \cite{66}.

![Figure 5. XPS spectra for as-deposited and aged Ti-AP hybrid thin films.](image)
In this research XRR was used to measure the thicknesses and densities of the hybrid films.\textsuperscript{H-VI} The method was also used for the layer-structure determination of nanolaminate structures.\textsuperscript{VI,VII} In XRR X-rays are reflected from the sample surface and the intensity of the X-rays reflected are measured. The X-ray interference can be seen in a reflectivity profile (Figure 6) as oscillations known as Kiessing fringes. The shorter the period, $\Delta \theta$, between the Kiessing fringes is the thicker the film is. Information regarding the density of the film can be gained from the amplitude of the Kiessing fringes as well as the critical angle, $\theta_c$, for total reflection. For denser films the critical angle is higher. The amplitude of Kiessing fringes depends on the density difference of the film and the substrate: when the difference is larger, the amplitude is higher. Large surface roughness causes faster decay rate on X-ray reflectivity. Higher interface roughness can be seen in the decrease of Kiessing fringe amplitude at higher angles [67]. In practice the densities of the films and layer thicknesses as well as densities of nanolaminates (see Figure 6 (b)) were determined using fitting programs from X’Pert Reflectivity software by PANalytical.
Experimental Procedures

Figure 6. XRR pattern (blue) and fitting data (red) for (a) a Ti-ODA hybrid thin film and (b) nanolaminate consisting of ~30 nm thick Zn-AP and ~10 nm thick ZnO layers.

The surface topography of the films was studied using AFM. In AFM the surface is scanned using a probe consisting of a cantilever and a tip. The measurements in the present work were conducted using the tapping mode. In this mode, a small piezoelectric element is used to force the cantilever to oscillate near its resonant frequency. The tip is then brought near the sample surface, where the repulsive or attractive forces decrease the amplitude of the oscillations. During the imaging the surface is scanned at a constant amplitude. The vertical displacements required to maintain the constant amplitude are displayed as a height image, giving information on sample topography. As there are only short, intermittent contacts between the tip and the sample surface, the mechanical damage from the measurement on the sample is limited.

The ideal GPC values for each hybrid material were calculated from the bond lengths acquired by the ChemBio3D Ultra software. A hybrid thin film chain was drawn with the software and a calculation to minimize the energy of
structure was conducted. After this length of each bond obtained and total chain length for straightly standing molecule calculated, see Figure 7. The estimated values for each hybrid are presented in Table 4. As this type of estimation does not take into account any possible bond angles except those concerning aromatic ring, it is only a rough estimation of the ideal GPC value.

![Figure 7. Bond lengths for Zn-AP hybrid](image)

<table>
<thead>
<tr>
<th>Hybrid</th>
<th>Ideal GPC value (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-AP</td>
<td>9.1</td>
</tr>
<tr>
<td>Zn-AP</td>
<td>9.2</td>
</tr>
<tr>
<td>Ti-ODA</td>
<td>14.9</td>
</tr>
<tr>
<td>Zn-ODA</td>
<td>14.6</td>
</tr>
</tbody>
</table>

Table 4. Estimated ideal GPC values Ti-AP, Zn-AP, Ti-ODA and Zn-ODA hybrid films calculated from bond lengths.
One of the major objectives of the work was to shed light on the factors affecting the hybrid film growth and ultimately find a precursor pair which would exhibit essentially ideal ALD/MLD growth. To achieve this, a systematic investigation of all four possible deposition process combinations when using TiCl$_4$, DEZ, ODA and AP as the precursors was conducted. From the inorganic precursors, TiCl$_4$ is a stronger Lewis acid and has four ligands while DEZ is weaker acid and has only two ligands. The major differences between ODA and AP can be observed from Table 1: ODA is homobifunctional with two –NH$_2$ groups and consists of two aromatic rings with an ether bond in between, whereas AP is heterobifunctional with both –OH and -NH$_2$ groups and consists of only one aromatic ring. The formed Ti-ODA, Zn-ODA, Ti-AP and Zn-AP were deposited at temperature ranges of 160-490, 160-220, 120-220, and 140-330 °C, respectively (see Table 3).

### 4.1 Chemical State of Films

Hybrid thin films were successfully grown with all the amine + inorganic metal pairs investigated. For all the hybrid films, the FTIR spectra (see Figure 8) showed a strong peak around 1500 cm$^{-1}$ and a weaker one at 1610-1630 cm$^{-1}$ which both originate from the aromatic ring. Bands from C-N and C-O as well as Ar-O-Ar stretch could also be seen. No peaks could be seen relating to N-H or O-H, indicating that the organic precursor has indeed reacted with the inorganic precursor. As even weak peaks relating to –NH could be observed, it seems likely that when TiCl$_4$ was used, T=N imidobonding or a cross-linked structure was formed. In case of the DEZ based films, it would seem that the forming structure is rather straight (see Figure 9).
Figure 8. FTIR spectra for representative Ti-AP, Zn-AP, Ti-ODA and Zn-ODA hybrid thin films.

Figure 9. Ideal structures suggested for the hybrid films: (a) Ti-AP hybrid with imido bonding, (b) Ti-ODA hybrid with cross-linking, and (c) Zn-AP hybrid.

The XPS measurements confirmed the presence of the metal, nitrogen, carbon and oxygen in the hybrid Ti-ODA, Ti-AP and Zn-AP hybrid thin films. However, due to contamination the carbon and oxygen measurements were judged to be only qualitative. An additional carbon feature relating to carbon in a carbonyl group could also be observed for Ti-ODA and Zn-AP, likely originating from surface oxidation. Also TiO$_2$ was seen present on the surface in the Ti-ODA hybrid, probably from reaction of Ti-Cl with moisture.
4.2 Film stability in ambient air

With the exception of Ti-ODA films deposited above 250 °C, the hybrid films were unstable at least to some degree. For all but Ti-AP the instability could be seen visually in change of the outward appearance as a color change and/or the film turning milky, see Figure 10(a). The Ti-AP hybrid retained its outward appearance after exposed to air (Figure 10(b)); the instability of Ti-AP was first verified by XRR measurements, where a slight decrease in overall thickness was observed. From the FTIR studies performed a broad feature around 3300 and 3200 cm⁻¹ in the FTIR spectra could be seen for the Ti-AP films and Ti-ODA films deposited below 250 °C, suggesting that the hybrid reacts with moisture in ambient air.¹,²

![Figure 10](image.png)

Figure 10. Photos of (a) Zn-ODA hybrid, and (b) Ti-AP hybrid. Both films had been exposed to ambient air for several months.

The hybrid made using DEZ and AP was stable in ambient air during winter time. The average molar fraction of water in air in Finland during the winter, from November to April, is below 0.005. During the summer, especially from June to September, the Zn-AP hybrid films showed unstable behaviour. The average water content rises above 0.01 during these four months. Decomposition of AP in the Zn-AP hybrid structure could be seen in the FTIR spectra, where new peaks corresponding to N-H and unsaturated C=C carbon as well as a decrease in peak intensity of aromatic ring could be seen.³ The Zn-ODA films deteriorated quickly, the color changing from royal blue (interference colour related from the film thickness) to brown with milky cast in only few minutes when taken from the reactor. However, no bands which could be associated to moisture or to reacted hybrid could be seen in the FTIR spectrum for the Zn-ODA films. Due to this high instability of the Zn-ODA hybrid, the films were stabilized by depositing 200 cycles of ZnO as a capping layer to investigate the growth process; even then the films dimmed after extended exposure to ambient air.

4.3 Film growth

The precursor pulse lengths needed for surface-saturated growth were investigated at deposition temperatures of 310, 140, 160 and 140 °C for the Ti-ODA, Ti-AP, Zn-ODA and Zn-AP hybrid films, respectively. The effects of the length of the organic and inorganic precursor pulses on the resultant GPC values are presented in Figure 11 and Figure 12, respectively.
Figure 11. Growth-per-cycle (GPC) for the (a) Ti-AP, (b) Ti-ODA, Zn-ODA, unpublished (c) and Zn-AP, unpublished hybrids with different organic precursor pulse lengths measured by XRR. Note that the values for the Zn-ODA system are for films capped with 200 cycles of ZnO. The respective deposition temperatures and pulse lengths of the inorganic precursor used for the Ti-AP, Ti-ODA, Zn-ODA, and Zn-AP hybrids were 140 °C and 1.5 s, 310 °C and 1.5 s, 160 °C and 5 s, and 140 °C and 3-120 s (see labels).
Both the DEZ-based processes required longer organic precursor pulses to achieve surface-saturated growth when compared to those based on TiCl₄. For the Zn-ODA films an ODA pulse as long as 16 s in minimum was required. It should be noted that there was a significant difference in the GPC values determined for the Zn-ODA films grown with a 4-s long ODA pulse with different growth processes: the films grown using a 200-cycle ZnO capping layer and 1000 cycles of hybrid had a GPC value of 0.05 Å per cycle whereas the films grown for 4000 cycles without the capping layer showed a GPC value of 0.2 Å per cycle. It may be that the unstable Zn-ODA absorbs water, increasing the film thickness and thus greatly affecting the measured GPC.

Figure 12. Growth-per-cycle (GPC) for the (a) Ti-AP, (b) Ti-ODA, Zn-ODA, and (c) Zn-AP hybrids with different inorganic precursor pulse lengths measured by XRR. The values for the Zn-ODA system are for films capped with 200 cycles of ZnO. The respective deposition temperatures and pulse lengths of the organic precursor used for the Ti-AP, Ti-ODA, Zn-ODA, and Zn-AP hybrids were 140 °C and 5 s, 310 °C and 3 s, and 160 °C and 24 s, and 140 °C and 7-50 s (see labels).
value which would cause a more noticeable difference in the uncapped and thicker film. It is also possible that in the laminate structure in which the hybrid layer is deposited between two ZnO layers, the interfaces may not be perfectly sharp, which would be likely to introduce more measurement uncertainty. This seems to be a plausible explanation when considering the density values obtained for the ZnO layer: the values fluctuated largely, between 2.0 and 4.1 g cm\(^{-3}\), and were moreover considerably lower than the values typically reported for pure ZnO (5.4-5.7 g cm\(^{-3}\)).\(^{III,VI}\) It may also be that the Zn-ODA hybrid does not grow well on ZnO (and vice versa), and due to a long nucleation period lower GPC values are obtained for the films with less deposition cycles.

The Zn-AP films were first believed to require an AP pulse length of 7 s to achieve surface-saturated growth.\(^{III}\) However, when the DEZ pulse length was in later experiments prolonged from the 3 s originally employed (see Figure 11 (c)), the highest GPC value was achieved at an AP pulse length of 35 s.

As for the Ti-containing films, the Ti-ODA films were found to grow in an essentially linear manner when the ODA pulse length was 3 s.\(^{II}\) It is however clear from Figure 11 (b) that the growth was not fully surface-saturated; only for the ODA pulse lengths longer than 12 s the GPC remained constant.\(^{VI}\) The Ti-AP films grew in a surface-saturate manner with an AP pulse length of only 5 s. From these results it would seem that the reactivity of the inorganic precursor towards the organic precursor has a huge effect on the required pulse lengths of the organic precursor: TiCl\(_4\) as a stronger Lewis acid catalysed better the deposition reaction when using ODA and AP as organic precursors. Another relevant factor may be the number of ligands: TiCl\(_4\) has four ligands whereas DEZ has only two, which could enhance the growth of the Ti-containing hybrids.

The effect of the inorganic precursor employed was also clearly seen when comparing the pulse lengths of TiCl\(_4\) and DEZ with the amines used. For TiCl\(_4\), the relatively short pulse length of 1.5 s was enough to achieve surface-saturated growth (see Figure 12 (a) and (b)).\(^{II,IV}\) Actually, in case of Ti-ODA a slight increase in the GPC value could be observed when a 1.0-s long pulse was used; this indicates that TiCl\(_4\) has an etching effect on the film.\(^{II}\) Similar etching effects were seen also for DEZ: the GPC values clearly dropped for the Zn-ODA and Zn-AP hybrids when the pulse length was increased.

The general growth trend for all the hybrids but the Ti-ODA was the same: after a temperature range where the GPC remained rather constant, a decrease on the value can be seen (see Figure 13). Most likely this is due to desorption of the precursor molecules from the film surface, which is enhanced when the temperature is increased. Similar growth behaviour due to precursor desorption has been reported by for example Dameron et al. [23] and Peng et al. [70]. For the Ti-ODA hybrid the GPC values increased with increasing deposition temperature, most likely due to the etching effect of byproduct HCl which is more efficiently purged from the reactor at higher deposition temperatures.\(^{II}\) Although in Figure 13 the highest deposition temperature used for the Ti-ODA hybrid is 310 °C with ODA pulse length of 14 s,\(^{VI}\) when
pulse length of 3 s was used good quality films were obtained at temperatures up to 490 °C which is the highest temperature which can be used to grow films with F-120 type reactor. The GPC values for the Zn-ODA films were extremely low regardless what deposition temperatures were used for the thin film deposition.

![Figure 13](image.png)

**Figure 13.** Growth-per-cycle (GPC) for the Ti-AP, Zn-AP, Ti-ODA and Zn-ODA hybrid thin films at different deposition temperatures. The pulse lengths used during the depositions were 1.5 s TiCl\(_4\)/5 s AP, 3 s DEZ/7 s AP, 1.5 s TiCl\(_4\)/14 s ODA, and 5 s DEZ/4 s ODA, respectively.

The rather low GPC values for the Zn-AP films shown in **Figure 13** were obtained with DEZ and AP pulse lengths of 3 and 7 s, respectively. However, in later series of experiments at deposition temperature of 140 °C with longer DEZ and AP pulse lengths (up to 50 an 25 s, respectively) it was noticed that the GPC increased up to 11.6 Å per cycle. When the deposition temperature of 280 °C was used with longer pulse lengths, the GPC value of 36.7 Å per cycle was obtained. As the calculated chain length of Zn-AP is only 9.2 Å, it is clear that more experiments are required to understand what happens during depositions when longer precursor pulse lengths are used. It should be noted that no sign of possible decomposition during the deposition process could be seen from the ex situ FTIR measurements done on the Zn-AP films.

The Ti-AP hybrid system was by far the most well behaving growth process. The highest GPC values, i.e. 10-11 Å per cycle, were for the Ti-AP hybrids deposited at temperatures between 120 and 160 °C. These values are close to the value estimated based on the anticipated bond lengths for a straight Ti-AP chain, i.e. 9.1 Å per cycle. There are only two other reported systems exhibiting growth so close to ideal, both using hexa-2,4-diyn-1,6-diol as the organic precursor [71] [72].
As can also be seen from Figure 13, growth rates for the AP-based hybrids were higher than those for the ODA-based ones. Steric hindrance could explain this since ODA with two aromatic rings is a relatively big molecule. The ODA molecule may also bend from the ether bond between the rings which both increases its bulkiness and enhances the probability of the unwanted double surface reactions. The AP molecule is smaller, stiffer and moreover bifunctional with both –OH and –NH₂ groups; bifunctionality of AP is believed to make the deposition process more selective and thereby essentially better controlled as there should be a preference for the inorganic precursors that are weak Lewis acids to react first with the –OH group and only after that with the –NH₂ group.

4.4 Film properties

The root-mean-square (RMS) roughness of the Ti-ODA, Ti-AP and Zn-AP hybrids was extremely low. Such smoothness is typical for amorphous materials. The amorphous nature of the films was further confirmed from the GIXRD measurements as no diffraction peaks originating from the hybrid materials could be observed.

![Figure 14. (a) The AFM images, and (b) GIXRD patterns for Ti-ODA, Ti-AP and Zn-AP hybrid films.](image)

The densities of the hybrid films were found to be quite low and closer to organic polymers [73] than to those of the corresponding oxides. The densities of Ti-ODA and Ti-AP hybrid films were estimated to be 1.6 [71] and 1.9-2.2 g/cm³ [74] respectively, whereas ALD grown TiO₂ films have an approximate density of 3.7 g/cm³ [74]. The Zn-AP films had a density of 1.5-1.7 g/cm³, whereas densities reported for ZnO films have varied a bit, from 5.4 to 5.7 g/cm³ [75].

The refractive index values for the Ti-containing hybrids, i.e. 1.8 ± 0.1 for Ti-ODA hybrid deposited at temperatures above 270 °C [76] and 1.86-1.91 for Ti-AP hybrid deposited at temperature range of 120-180 °C [76] were clearly lower than 2.48 obtained for pure TiO₂, but higher than for typical polymers with
refractive indices between 1.350 and 1.7100 [76]. No reliable refractive index values were obtained for the Zn-ODA films due to the highly unstable nature of the films. The refractive index of Zn-AP hybrid films (~1.94 ± 0.01 regardless of deposition temperature) and ZnO (1.87) were quite close to each other.
Due to the cyclic deposition process of ALD and MLD, it is inherently easy to combine two or more different materials to form various nanostructures. As the materials employed can have distinctly different properties, mixing provides a potential way of fine-tuning the properties; mixing is simply achieved by controlling the number of each deposition cycle. In past ALD has been used to combine at least two different inorganic materials to form structures with tailored electrical [15] [16] and gas barrier properties [17], refractive index [18] [19] [20], thermal stability [21] and surface roughness [22].

Mixtures, superlattices and nanolaminates can be made from e.g. an oxide and a hybrid, by varying the number of deposition cycles of each material. A mixture is formed when the number of deposition cycles of each material is kept low and, in case in which no full monolayer coverage is not achieved, the materials form a homogeneous mixture. In case the growth occurs in a more controlled manner, the structures formed have distinctly separate layers and are called superlattices, [77] [78] [79] [80] see Figure 15(a). When depositing nanolaminates (Figure 15(b)), the number of cycles is increased and at least one of the material layers achieves nanometer scale thickness.

During the present research, the feasibility of fine-tuning the properties by mixing an oxide and a hybrid was tested. The precise effect of mixing different material layers was studied by by using Ti-ODA hybrid together with TiO$_2$, Zn-AP hybrid combined with ZnO, as will be discussed in subchapters 5.1-5.4.V.NI
Nanostuctures can also exhibit enhanced properties when compared to the parent materials. To improve the mechanical properties of pure Al\textsubscript{2}O\textsubscript{3} coating, and consequently barrier properties when strain is applied, nanolaminates consisting of Al\textsubscript{2}O\textsubscript{3} and alucone were deposited (subchapter 5.5).

5.1 Chemical State of Films

The mixtures were fabricated by alternating the number of hybrid and oxide deposition cycles. FTIR measurements were able to verify the presence of the aromatic backbone only for the Ti-ODA:TiO\textsubscript{2} mixtures with mixture ratios of 1:1 and 1:2; as the oxide content increased, the degree of hybrid in the mixture was not sufficient for the FTIR detection anymore. However, the nitrogen content measured by XPS gave a good indication of the amount of hybrid in the structure: the measured values followed well the trend calculated from ideal structures. Also the titanium content obtained from XPS data followed the expected trend, following inversely that of nitrogen.

The FTIR studies carried out on selected Zn-AP:ZnO mixture samples clearly showed the peaks originating from AP in the molecule. From XPS measurements the amount of Zn and N in the Zn-AP:ZnO mixtures with ratios of 1:3 and 1:1 followed the trend of calculated from the assumed growth sequence, whereas the more hybrid containing 3:1 film resembled the pure Zn-AP hybrid.

5.2 Film Growth and Quality

The Ti-ODA mixtures and Zn-AP containing structures were deposited at temperatures of 280 and 140 °C, respectively. When considering the linear growth predicted from the pure constituents, the obtained GPC values for both Ti-ODA and Zn-AP containing mixtures were lower. As the pure hybrids were amorphous and oxides crystalline, when combining the two materials the amorphous hybrid may force renucleation of the forming oxide crystals. This could also be seen at the ZnO layer thicknesses of the nanolaminate structures which were less than the target values. The renucleation slowed down the growth rate, and reduced the degree of crystallinity of the films. In case of Ti-ODA hybrid mixtures, the decrease of crystallinity was supported also by the almost linear reduction in RMS roughness (see Figure 16 (a)-(d)). Although not as profound as with Ti-ODA, Zn-AP addition still had a smoothing effect on RMS roughness (see Figure 16 (e)-(h)).
The refractive indices of Ti-ODA:TiO$_2$ mixtures followed well the linear trend expected from the pure components. The incorporation of Zn-AP hybrid to ZnO caused a clear drop in the density of the formed structure.

5.3 Mechanical Properties

One aim when making inorganic-organic materials is to control the mechanical properties of forming hybrid films by varying the precise hybrid:oxide ratio. The effect of mixing hybrid to an oxide was studied with Ti-ODA hybrid and TiO$_2$, as well as with Zn-AP hybrid and ZnO.

According to the nanoindentation measurements done on Ti-ODA hybrid with peak load of 5 μN, it was concluded that the hardness and reduced modulus values for the pure hybrid were 0.8 and 17.9 GPa, respectively. For the TiO$_2$ containing films the noise level at shallow depth, surface roughness, and material pile-up around the indenter were the major error sources. To improve the statistics of measurements for TiO$_2$ and mixtures, nine additional indents were carried out at a peak load of 40 μN. From these measurements it was concluded that incorporating TiO$_2$, which is considerably harder and has a higher reduced modulus value than pure Ti-ODA hybrid, enhanced both hardness and reduced modulus values of the mixtures, see Table 5.

<table>
<thead>
<tr>
<th>Film thickness (nm)</th>
<th>1:6</th>
<th>1:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (GPa)</td>
<td>11.4 ± 2.1</td>
<td>7.0 ± 0.6</td>
</tr>
<tr>
<td>Reduced modulus (GPa)</td>
<td>168.7 ± 39.5</td>
<td>139.1 ± 24.2</td>
</tr>
</tbody>
</table>

Also the Zn-AP hybrid is a soft material (hardness ~ 2 GPa), with contact modulus of ~ 50 GPa. ZnO, although still quite soft, is essentially harder and stiffer than the Zn-AP hybrid. Incorporation of increasing amounts of ZnO to the Zn-AP was seen to have only a small effect on the mechanical properties up to the ratio 1:1. When the ratio was 1:3, small improvement in the mechanical properties could be observed. From the laminate structures it was observed...
that thicker ZnO layers had stronger impact on the films than thinner oxide layers, making the structures harder. From these experiments it seems that in order to obtain harder and stiffer films when using Zn-AP and ZnO, not only the oxide concentration of the material but also the thickness of the oxide layer has a great influence on the mechanical properties.\textsuperscript{VI}

\subsection*{5.4 Chemical Stability}

When combining organic and inorganic materials, the chemical stability of the inorganic materials is one of the attributes aimed for. By mixing TiO\textsubscript{2} to Ti-ODA hybrid the chemical stability of the films was greatly improved. Whereas pure Ti-ODA hybrid was found to react with isopropanol, ethanol, water, 1 M NaOH, HCl and concentrated H\textsubscript{2}SO\textsubscript{4}, only the prolonged treatment with concentrated H\textsubscript{2}SO\textsubscript{4} was seen to have any effect on the tested 1:6 and 1:1 mixture films.\textsuperscript{V}

No similar improvement on chemical stability could be achieved by adding ZnO to Zn-AP, mixtures behaving much the same way as pure hybrid when treated with various solvents. There was one interesting exception, though: when the 1:3 Zn-AP:ZnO mixture was treated with acetone, it seemed that a backbone consisting mostly of ZnO still remained. As the acetone seems to selectively remove the organic part leaving the inorganic backbone intact, the treatment could be used to produce porous ZnO structures where the pore sized are controlled by varying the hybrid content in the structure.\textsuperscript{VI}

\subsection*{5.5 Barrier Properties}

Thin film of pure Al\textsubscript{2}O\textsubscript{3} has good barrier properties \textsuperscript{[81]}, but loses them when strain is applied, making it unsuitable for packaging applications \textsuperscript{[82]} \textsuperscript{[83]}. In order to find better coating material for biopolymers, a comparison of pure Al\textsubscript{2}O\textsubscript{3}, pure TMA+EG hybrid, and various nanolaminate structures of Al\textsubscript{2}O\textsubscript{3} and TMA+EG were investigated.

Straining of pure Al\textsubscript{2}O\textsubscript{3} showed that the material is brittle: in the SEM images of Al\textsubscript{2}O\textsubscript{3} grown on polylactic acid films wide cracks could be seen to form after straining (\textbf{Figure 17(a)}). The straining of the films also caused a decline in barrier properties, seen as an increase in water vapor and oxygen transmission rates. \textsuperscript{VII}

TMA+EG hybrid films were not mechanically stable or good barriers, either: cracks formed when the films were strained (\textbf{Figure 17(b)}). Although the cracks formed when using alucone were not as wide as with Al\textsubscript{2}O\textsubscript{3}, there were more of them. \textsuperscript{VII}

However, when five-layer laminates consisting of Al\textsubscript{2}O\textsubscript{3} and TMA+EG were deposited, a clear improvement could be seen on the mechanical properties when compared to the pure Al\textsubscript{2}O\textsubscript{3} and TMA+EG coatings as the number of cracks clearly decreased and the width of them was not large (\textbf{Figure 17(c)}). Also when comparing pure and various laminate structures strained 3 %, the oxygen transmission rates increase to range of 120-325 cm\textsuperscript{2}/m\textsuperscript{2} d 10\textsuperscript{5} Pa for all
but one: for the laminate consisting of 2-4 nm thick Al₂O₃ layers and 9-10 nm thick TMA+EG layers the oxygen transmission rate does not change when strain is applied, remaining at constant value of 30 cm²/m² d 10⁵ Pa.⁷⁷

**Figure 17.** SEM images of biaxially oriented polylactic acid film with (a) pure Al₂O₃ strained to 4 %, (b) pure alucone strained to 3%, and (c) Al₂O₃ + alucone nanolaminate strained to 3%.
6. CONCLUSIONS

In this work the strongly emerging combined atomic and molecular layer deposition technique for realizing new types of layered inorganic-organic materials was employed to successfully fabricate four different types of novel inorganic-organic hybrid materials based on Ti and Zn and aromatic amines, *i.e.* 4,4'-oxydianiline (ODA) and 4-aminophenol (AP). Although the Ti-ODA hybrid thin films were stable in ambient air, the growth processes for the ODA-containing systems were slow. The growth-per-cycle (GPC) values achieved by using the heterobifunctional AP to deposit hybrid films were considerably higher. Most importantly, the Ti-AP hybrid films seemed to grow almost ideally, requiring rather short pulsing times to yield excellent GPC values. The AP-based films were also quite stable in air.

To find out which factors affect the growth of the forming hybrid material, a systematic comparison of TiCl$_4$, DEZ, ODA and AP based hybrid films was also conducted. All the different precursor combinations yielded hybrid thin films as intended. To achieve fully surface-saturated surface reactions a longer inorganic precursor pulse was required in the processes where DEZ was used as the inorganic precursor compared to the TiCl$_4$-based processes. Apparently of the two inorganic precursors, TiCl$_4$ as a stronger Lewis acid exhibits stronger reactivity towards the organic ODA and AP molecules.

Also higher GPCs could be achieved when AP rather than the bulkier ODA was employed as the organic precursor. Steric effects, caused by the overall size of the organic precursor, seem to play a major role in ALD/MLD processes, as well as the ether bond which allows the ODA molecule to bend. Another important factor was the heterobifunctionality of the AP molecule; AP has both –OH and –NH$_2$ as reactive groups, which reduces the probability of the unwanted double surface reactions, as both the Ti–Cl and Zn–CH$_2$–CH$_3$ surface species apparently prefer one of the groups over the other and thus react more readily with a fresh AP molecule rather than an AP molecule already bonded to another surface species.

The comparison of how the different structures of organic precursors so far utilized in hybrid thin film fabrication affect the growth is, by far, not complete. Additional information could be gained by comparing the growth of a linear and an aromatic molecule, as well as carrying out depositions where the functional groups are varied in a more systematic manner. For example the growth of 4-aminophenol based hybrids could be compared to those based on hydroquinone (with two –OH groups) and 1,4-diaminobenzene (with two –NH$_2$ groups).
The construction of mixtures and nanolaminates by varying the number of deposition cycles of inorganic-organic hybrid and oxide materials, provided a possibility to tune different material properties. Although the overall growth seemed to suffer from the combining of hybrid and oxide materials, still many properties could be controlled by combining the two distinctly different materials. Degree of crystallinity, density, surface roughness, and mechanical properties could be altered by the varying amounts of the used hybrid and corresponding oxide in the structure. The chemical stability of the Ti-ODA hybrid was greatly improved by incorporating TiO$_2$ to the forming structure. Although no such improvement was observed when adding ZnO to Zn-AP, the treatment with acetone seemed to leave the inorganic backbone intact. This might provide a simple way for making porous ZnO structures.

Nanostructures are also interesting as the material interfaces make it possible to achieve enhanced material properties. Nanolaminates constructed using Al$_2$O$_3$ and TMA+EG showed overall improvement on barrier properties when strained, although further study is required for the coatings to be sufficient for commercial applications.
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Conclusions


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Atomic/molecular layer deposition of hybrid inorganic-organic thin films

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