

LAURI AARIK

Atomic layer deposition and
characterization of thin oxide films
for application in protective coatings



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LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following publications, which will hereafter be referred to using Roman numerals.

- I. L. Aarik, T. Arroval, R. Rammula, H. Mändar, V. Sammelseg, J. Aarik, Atomic layer deposition of TiO₂ from TiCl₄ and O₃, *Thin Solid Films*, 542 (2013) 100–107.
- II. L. Aarik, T. Arroval, R. Rammula, H. Mändar, V. Sammelseg, B. Hudec, K. Hušeková, K. Fröhlich, J. Aarik, Atomic layer deposition of high-quality Al₂O₃ and Al-doped TiO₂ thin films from hydrogen-free precursors, *Thin Solid Films*, 565 (2014) 19–24.
- III. L. Aarik, J. Kozlova, H. Mändar, J. Aarik, V. Sammelseg, Chemical resistance of TiO₂ and Al₂O₃ single-layer and multilayer coatings atomic layer deposited from hydrogen-free precursors on silicon and stainless steel, Submitted to *Mater. Chem. Phys.*
- IV. V. Sammelseg, J. Kostamo, W. Bayerl, J. Aarik, L. Aarik, S. Lindfors, P. Adam, J. Poutiainen, Protecting an interior of a gas container with an ALD coating, Patent: WO 2015/132443 A1, priority date March 3, 2014.
- V. V. Sammelseg, J. Kostamo, T. Malinen, J. Aarik, L. Aarik, Protecting an interior of a hollow body with an ALD coating, Patent: WO 2015/132444 A1, priority date March 3, 2014.

AUTHOR'S CONTRIBUTION

Publication I: The author carried out the film depositions, quartz crystal microbalance (QCM), X-ray fluorescence (XRF), Raman spectroscopy and spectroscopic ellipsometry measurements, and participated in analysis of grazing incidence X-ray diffraction (GIXRD) and X-ray reflection (XRR) data, took part in the analysis of results and wrote the article.

Publication II: The author carried out the sample pretreatment, atomic layer deposition, QCM, XRF and spectroscopic ellipsometry measurements and participated in processing and analysis of GIXRD and XRR data, took part in the analysis of results and wrote the article.

Publication III: The author carried out the sample pretreatment, film depositions, XRF, GIXRD, XRR measurements and all chemical stability studies, took part in the analysis of results and wrote the article.

Publication IV: The author participated in designing the prototype reactor, which the patent is based on, constructed the reactor and proofed the concept of the invention.

Publication V: The author participated in designing the prototype reactor, which the patent is based on, constructed the reactor and proofed the concept of the invention.

AUTHOR'S OTHER PUBLICATIONS RELATED TO THE TOPIC

- V. Sammelselg, L. Aarik, M. Merisalu. Patent: Method of preparing corrosion resistant coatings. Publication number: WO 2014102758 A1. Priority date: December 31, 2012.
- V. Sammelselg, I. Netšipailo, A. Aidla, A. Tarre, L. Aarik, J. Asari, P. Ritslaid, J. Aarik, Chemical resistance of thin film materials based metal oxides grown by atomic layer deposition, *Thin Solid Films*, 542 (2013) 219–224.
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- T. Arroval, L. Aarik, R. Rammula, H. Mändar, J. Aarik, B. Hudec, K. Hušeková, and K. Fröhlich, Influence of growth temperature on the structure and electrical properties of high-permittivity TiO₂ films in TiCl₄-H₂O and TiCl₄-O₃ atomic-layer-deposition processes, *Phys. Status Solidi, A*, 211 (2014) 425–432.
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- J. Mondal, A. Marques, L. Aarik, J. Kozlova, A. Simões, V. Sammelselg, Development of thin ceramic-graphene nanolaminated coating for corrosion protection of stainless steel, *Corrosion Science*, 105 (2016) 161–169.

LIST OF ABBREVIATIONS AND SYMBOLS

AFM	Atomic force microscopy
AISI	American Iron and Steel Institute
ALD	Atomic layer deposition
ASTM	American Society for Testing and Materials
CET	Capacitance-equivalent thickness
CVD	Chemical vapor deposition
EDX	Energy dispersive X-ray spectroscopy
FWHM	Full width at half maximum
GIXRD	Grazing incidence X-ray diffraction
HR-SEM	High-resolution scanning electron microscopy
MECRALD	Microwave electron cyclotron resonance atomic layer deposition
PEALD	Plasma-enhanced atomic layer deposition
QCM	Quartz crystal microbalance
RMS	Root mean square
SE	Spectroscopic ellipsometry
SEM	Scanning electron microscopy
T_G	Growth temperature
TMA	Trimethylaluminum, $\text{Al}(\text{CH}_3)_3$
UV	Ultraviolet
XRD	X-ray diffraction
XRF	X-ray fluorescence
XRR	X-ray reflection

1. INTRODUCTION

The need for thin, conformal protective and barrier layers is continuously growing. Therefore, atomic layer deposition (ALD)—in which the gaseous precursors can travel around substrate edges and into deep trenches, and by which the film thickness can be precisely controlled—is a technique of increasing interest. Oxide thin films deposited by the ALD method have already been used in different fields, e.g., in microelectronics [1], optoelectronics [2], biomedicine [3], sensors [4, 5], energetic applications [6–10], and barrier and protective coatings [11–56].

To extend the potential of ALD, deposition chemistries and equipment are being continuously studied and optimized. In particular, reactors and precursor combinations favorable for specific applications are becoming the main targets. Having reactors that are suitable for the desired application is one of the most important requirements, especially as ALD reactors can differ in reaction chamber dimensions, design, and precursor delivery systems. All of these factors can influence the success of ALD in its intended purposes.

In addition, finding the most suitable precursor combinations may be crucial for some applications, because the physical properties and chemical stability of an ALD film may largely depend on the precursors used [14, 15]. The chemical stability is especially important in the case of protective coatings, which are exposed to different reactive environments. In these cases, it is also important to know the chemical stability as a function of the film deposition parameters.

Owing to the excellent barrier properties of aluminum oxide (Al_2O_3) and high chemical stability of titanium oxide (TiO_2), there are many studies demonstrating the use of Al_2O_3 and TiO_2 films prepared by ALD as protecting materials in different applications [11–56]. In most of these studies, Al_2O_3 and TiO_2 films were deposited using $\text{Al}(\text{CH}_3)_3\text{-H}_2\text{O}$, $\text{TiCl}_4\text{-H}_2\text{O}$, and $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4\text{-H}_2\text{O}$ ALD processes. However, previous studies have demonstrated that applying O_2 plasma and O_3 instead of H_2O has helped to decrease the impurity content [57, 58], increase the chemical resistance of the films [59], lower the film roughness [60], and limit the concentration of defects [61]. To extend the latter research, we have investigated the deposition of TiO_2 and Al_2O_3 thin films using $\text{TiCl}_4\text{-O}_3$ and $\text{AlCl}_3\text{-O}_3$ processes to develop ALD methods for depositing thin films from hydrogen-free precursors. Furthermore, an ALD reactor with a novel construction for coating the inner surfaces of hermetic containers was designed and tested, to widen the applications of the ALD technique. This Thesis summarizes the results obtained.

2. BACKGROUND

2.1 Protective and barrier coatings

The ongoing industrial evolution leads to higher demands on materials used in various applications. Development and application of protective and barrier layers prolonging the lifetime and enhance the properties of well-known materials is a way to support progress in this direction. Protective and barrier layers can shield materials against harmful environments and modify their functional properties to make the coated materials usable also in these cases. For instance, coatings may reduce the influence of the air and humidity. Moreover, coatings may reduce aroma permeability, enhance the resistance to light and temperature, and provide antibacterial properties.

The use of barrier layers on metals to slow corrosion is one of the most established applications of protective layers. This additional protection is of special importance when the metals are used in thermodynamically unfavorable environments that cause changes in the chemical composition. For example, in environments containing enough moisture, Fe can turn to $\text{Fe}(\text{OH})_3$, $\text{FeO}(\text{OH})$, or $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The most well-known coating methods for prolonging the lifetime of metals are painting, varnishing, galvanization, and spray deposition. In the cases of more sophisticated and demanding products, physical vapor deposition [62], chemical vapor deposition (CVD) [63, 64], sol-gel deposition [65, 66], magnetron sputtering [67–69], and ALD [11–56], have been used.

The main advantage of ALD compared to the other techniques listed is its ability to coat complex 3D objects with thin, conformal, and pinhole-free coatings with precisely defined thicknesses [1, 12, 70–78]. This is important if very thin barrier layers are needed. For example, Katamreddy et al. [79] demonstrated that a 1.5 nm-thick ALD Al_2O_3 layer could serve as an efficient diffusion barrier for oxygen. Moreover, Hirvikorpi et al. [80] compared the barrier properties of Al_2O_3 fabricated by different techniques and obtained the most promising results using ALD. The higher chemical stability of ALD Al_2O_3 films compared to the films grown by plasma deposition and CVD has been demonstrated in 5% HF solutions [81].

2.2 Atomic layer deposition of Al_2O_3 and TiO_2

2.2.1 Principles and specific features of ALD processes

ALD is a method based on self-terminating gas-solid reactions of two or more precursors with a solid surface [1, 12, 70–78]. The film growth takes place only via surface reactions in a stepwise manner, as the precursors are introduced alternately and the precursor pulses are separated with purge periods. The technology itself has been known for more than fifty years. The principles of this deposition method were published in 1965–1967 [78, 82] and patented in

1974–1975 [78, 83]. The first industrial applications of ALD were related to manufacturing electroluminescent displays [78]. The scaling down of microelectronic devices is considered to be the main driving force for the development and use of the method since 1990s. Concurrently, the interest in the ALD of oxides started to grow. Excellent reviews published by Leskelä and Ritala [70], Puurunen [71], Miikkulainen et al. [75], Devi [76], George et al. [74], Potts and Kessels [57], and Hatanpää et al. [77] have described the ALD of different materials, reaction mechanisms, film properties, and precursor combinations. Ritala and Niinistö [73], Niinistö et al. [1], Marin et al. [12], and Knez et al. [72] have published reviews on the possible applications of ALD. Therefore, in this Chapter, the focus will be on the deposition and key properties of TiO_2 and Al_2O_3 thin films, ALD reactors, and the applications of TiO_2 and Al_2O_3 films as protective and barrier layers. In addition, the main mechanisms and important details required to understand the results of this Thesis will be outlined.

Owing to the ability to deposit conformal coatings on 3D surfaces with atomic-level control over the material thickness and composition, ALD is a promising method for the preparation of coatings for various applications. The disadvantages of the ALD method include the need for suitable precursor combinations and the relatively slow film growth that is typical for most conventional reactors. Moreover, as the film growth takes place via chemical surface reactions, the film properties are influenced by the substrate. This complicates the deposition of homogeneous films with uniform thicknesses on heterogeneous surfaces with unknown and varying compositions.

2.2.2 ALD precursors for Al_2O_3 and TiO_2 thin films

One of the earliest approaches to ALD was the use of metal chlorides for the deposition of metal oxides. For example, AlCl_3 has been used in the ALD of Al_2O_3 [81, 84, 85] together with H_2O , a mixture of 15% He and O_2 , and several alcohols. The growth temperatures (T_G) were varied from 100 to 800°C (Table 1). The as-deposited Al_2O_3 films were mainly amorphous. On Si(100) substrates, polycrystalline films grew from AlCl_3 and H_2O at temperatures exceeding 600°C [86]. In addition, crystalline Al_2O_3 films have been obtained from AlCl_3 and the 15% He/ O_2 mixture at 450°C on single-crystal Nb and at 660°C on sapphire [87]. The solid nature and corrosive by-products complicate handling of AlCl_3 . For this reason, AlCl_3 is mostly used in ALD at high substrate temperatures or to avoid carbon and hydrogen contamination in the films [86].

Trimethylaluminum ($\text{Al}(\text{CH}_3)_3$; TMA) combined with various oxygen precursors has been most frequently applied for the ALD of Al_2O_3 [12, 71, 75], at substrate temperatures ranging from 25 to 800°C. The formation of crystalline Al_2O_3 films in TMA- H_2O_2 and TMA- N_2O processes on Si(100) substrates at 700–800 and 500°C, respectively, has been reported by Kumagai et al. [88]. In contrast, Prokes et al. [89] reported the deposition of crystalline

Al₂O₃ with TMA-H₂O ALD on Ga₂O₃, ZnO, and Si nanowires at 200°C. This result is surprising because other authors have reported that ALD Al₂O₃ films are amorphous, regardless of the substrate, when deposited at substrate temperatures of up to 600°C [75].

Although many ALD processes have known for a long time, studies on different precursor combinations—in particular those combining various organic compounds with different oxygen precursors—are still ongoing (Table 1). One reason for such studies is that the high level of residual impurities may cause problems in the applications of the films, especially when low substrate temperatures must be applied during deposition. One way to reduce the concentration of impurities and increase the film quality is to use O₂ plasma or O₃ instead of H₂O during ALD [57–61]. Unfortunately, in the case of plasma-based processes, the conformity of the films deposited on complex surfaces may be insufficient [90].

Table 1. List of processes used in ALD of Al₂O₃.

Aluminum precursors	Oxygen precursors	T_G , °C	References
Aluminumtrichloride, AlCl ₃	Water vapor	100–800	[86, 90]
	Water vapor together with a catalyst	77–327	[91]
	Mixture of helium and oxygen, 15% He in O ₂	450–660	[87]
	Methanol, CH ₃ OH	500	[92]
	Ethylene glycol, CH ₂ OHCH ₂ OH	500	[92]
	Butyl alcohol, t-C ₄ H ₉ OH	350–500	[92]
	Butyl alcohol, n-C ₄ H ₉ OH	300–500	[92]
	Aluminum isopropoxide, Al(OCH(CH ₃) ₂) ₃	150–375	[93, 94]
Trimethylaluminum (TMA), Al(CH ₃) ₃	Water vapor	33–500	[13, 95]
	Oxygen	300	[96]
	Hydrogen peroxide, H ₂ O ₂	25–800	[88, 97]
	Mixture of oxygen gas and vapor of water and hydrogen peroxide	150–250	[98]
	Nitrous oxide, N ₂ O	100–500	[88]
	Nitrogen dioxide, NO ₂	150–310	[99]
	Water vapor and nitrogen dioxide	150–310	[99]
	Ozone	25–450	[58, 100]
	Aluminum isopropoxide, Al(OCH(CH ₃) ₂) ₃	300	[93]
	Isopropyl alcohol, (CH ₃) ₂ CHOH	250	[101]
	Oxygen plasma	25–400	[102]
	Carbon dioxide (CO ₂) plasma	25–350	[103, 104]
	Nitrous oxide plasma	140–220	[105]

Aluminum precursors	Oxygen precursors	T_G , °C	References
Dimethylaluminum-chloride, $\text{Al}(\text{CH}_3)_2\text{Cl}$	Water vapor	125–500	[106]
Dimethylethylamine alane complex, $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{N}:\text{AlH}_3$	Hydrogen and oxygen plasma	100–180	[107]
Methylpyrrolidine alane complex, $\text{C}_5\text{H}_{11}\text{N}:\text{AlH}_3$	Oxygen plasma	100	[108]
Dimethylaluminumisopropoxide, $(\text{CH}_3)_2\text{Al}(\text{OC}_3\text{H}_7)$	Water vapor	100–400	[109]
	Oxygen plasma	25–400	[109]
Aluminumethoxide, $\text{Al}(\text{OC}_2\text{H}_5)_3$	Water vapor	250–500	[92]
	Oxygen	250–500	[92]
Aluminum isopropoxide, $\text{Al}(\text{OC}_3\text{H}_7)_3$	Water vapor	250–500	[92]
	Oxygen	250–500	[92]
Aluminum 1-methoxy-2-methyl-2-propoxide, $\text{Al}(\text{OC}(\text{CH}_3)_2\text{CH}_2\text{OCH}_3)_3$	Water vapor	200–450	[110]
Tris(diethylamino) Aluminum, $\text{Al}(\text{N}(\text{C}_2\text{H}_5)_2)_3$	Water vapor	200–400	[111]
	Ozone	200–275	[112]
Tris(dialkylamino) Aluminum, $\text{Al}(\text{C}_3\text{H}_8\text{N})_3$	Water vapor	250–400	[113]
Heteroleptic amidinate-containing precursor, $[\text{CH}_3\text{C}(\text{C}_3\text{H}_8\text{N})_2]\text{Al}(\text{C}_2\text{H}_5)_2$	Water vapor	125–300	[114]

TiCl_4 has been used as a precursor in the deposition of TiO_2 starting from 1960s [82]. Since then, different research groups have demonstrated the deposition of TiO_2 using various oxygen precursors, e.g., H_2O , H_2O_2 , O_2 plasma, and CH_3OH (Table 2). One of the most studied ALD processes, the TiCl_4 - H_2O process, has been thoroughly studied by many groups [82, 115, 116]. TiCl_4 is a liquid precursor with a modest vapor pressure at room temperature. Therefore, TiCl_4 is convenient to handle and hence is one of the most commonly used precursors for depositing TiO_2 [118]. However, the corrosive nature of TiCl_4 and its reaction by-products may cause problems, for example, if it is used for the deposition of multicomponent oxides that may easily form chlorides by reacting with TiCl_4 [118]. Therefore, alternative precursor systems have been studied (Table 2). Titanium isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$), titanium ethoxide ($\text{Ti}(\text{OC}_2\text{H}_5)_4$), and tetrakis(dimethylamido)titanium ($\text{Ti}(\text{N}(\text{CH}_3)_2)_4$) used together with different oxygen precursors are the most common alternatives to TiCl_4 (Table 2). Unfortunately, the thermal decomposition of these organic precursors and subsequent carbon contamination of films deposited at lower temperatures limits the application of the precursors in ALD [119].

As polycrystalline TiO₂ films can be obtained at much lower temperatures than polycrystalline Al₂O₃ films, many studies have been performed to understand how the crystallization processes correlate with T_G , film thickness, and the reactants and substrates used [75].

Table 2. List of processes used for ALD of TiO₂.

Titanium precursors	Oxygen precursors	T_G , °C	References
Titanium tetrachloride, TiCl ₄	Water vapor	25–600	[115, 120–123]
	Hydrogen peroxide, H ₂ O ₂	100–700	[122, 124, 125]
	Oxygen plasma	25–200	[126]
	Methanol, CH ₃ OH	375–420	[127, 128]
	Titanium isopropoxide, Ti[OCH(CH ₃) ₂] ₄	125–300	[129]
Titanium tetrafluoride, TiF ₄	Water vapor	300–500	[130]
Titanium tetraethoxide (TTEt), Ti(OC ₂ H ₅) ₄	Water vapor	100–350	[131–133]
Titanium tetraisopropoxide (TTIP), Ti(OC ₃ H ₇) ₄	Water vapor	35–350	[132, 134]
	Hydrogen peroxide,	100–300	[135]
	Synthetic air	100–200	[136]
	Ozone	150–380	[137–139]
	Oxygen plasma	25–400	[102]
	Nitrous oxide (N ₂ O) plasma	280	[140]
	Oxygen and nitrogen plasma	150–250	[141]
	Water vapor plasma	50–340	[142]
	Oxygen and ammonium, NH ₃	140	[143]
	Ammonium	140	[144]
	Carboxylic acid, HCOOH	50–350	[145]
Water vapor, UV assisted	260	[146]	
Titanium tetraiodide, TiI ₄	Water and hydrogen peroxide vapor	230–375	[147]
	Oxygen	230–460	[148]
	Water vapor	135–445	[149]
	Hydrogen peroxide	250–490	[150]

Titanium precursors	Oxygen precursors	T_G , °C	References
Tetrakis(dimethylamino)-titanium (TDMAT), $Ti(N(CH_3)_2)_4$	Water vapor	90–210	[151]
	Ozone	60–225	[152–154]
	Oxygen plasma	150–300	[155, 156]
	Water vapor plasma	50–340	[142]
Titanium tetramethoxide, $Ti(OCH_3)_4$	Water vapor	200–400	[118]
Titanium methylcyclopentadienyl-tris(isopropoxide), $TiC_5H_4(CH_3)(OCH(CH_3)_2)_3$	Oxygen plasma	25–400	[102]
Titanium penta-methylcyclopentadienyl-tri(methoxide), $TiC_5(CH_3)_5(OCH_3)_3$	Oxygen plasma	25–400	[102]
Titanium methyl-cyclopentadienyl-tris(dimethylamido), $TiC_5H_4CH_3(N(CH_3)_2)_3$	Oxygen plasma	100–350	[157]
Titanium di(isopropoxide)bis(N,N'-dimethyl-aminoethoxide) $Ti(OCH(CH_3))_2(OCH_2CH_2N(CH_3)_2)_2$	Water vapor	100–300	[158]
Titanium di(isopropoxide)-bis(dipivaloyl-methanate) [$Ti(IP)_2(dpm)_2$], $TiOCH(CH_3)_2(C_{11}H_{19}O_2)_2$ dissolved in ethyl-cyclohexane, $C_6H_{11}C_2H_5$	Water vapor	340–470	[159]

2.2.3 Applications of Al_2O_3 and TiO_2 thin films grown by ALD

The deposition of Al_2O_3 and TiO_2 thin films was one of the first successful applications of ALD [1, 82, 84, 85], and the number of studies demonstrating the industrial applications of ALD is still increasing. Since the first applications of ALD oxides in microelectronics, a number of studies has been published to demonstrate that Al_2O_3 can be applied as a high-permittivity (high-k) material in gate stacks of metal–oxide–semiconductor devices [1, 160] and in the capacitor structures of dynamic random access memories [1, 161, 162]. Similarly, the use of TiO_2 as a high-k dielectric material [72, 163–165] has also been investigated. The main advantages of ALD in micro- and nanoelectronic applications are the accurate control over the ultrathin film thickness and the

ability to create conformal coatings of substrates with very complex shapes. Currently, there is an increasing number of works showing that these advantages allow the thin films grown by ALD to be used in other applications too (Fig. 1).

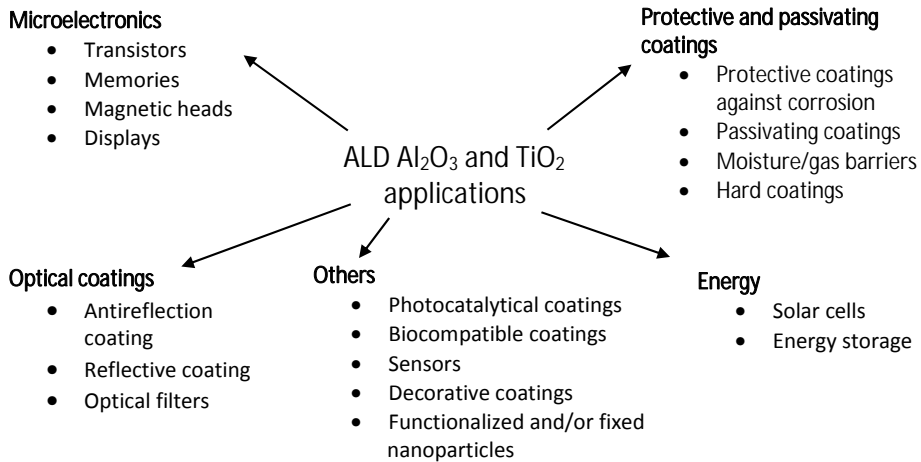


Figure 1. Available and potential applications of Al_2O_3 and TiO_2 films deposited by ALD.

The high optical transparencies and excellent diffusion barrier properties have enabled application of Al_2O_3 films in optical coatings [2, 72, 121]; medicine [72, 133, 166]; protective, barrier, and hard coatings [28, 167, 168]; and in the functionalization of nanoparticles, e.g., tubes, fibers, and powders [72, 169]. The potential applications of TiO_2 include self-cleaning surfaces [170]; biomedical sensors [5]; implantable sensor membranes and water purification membranes [171]; optical coatings [72, 121, 172]; protective and passivating coatings [11, 19, 32, 52, 54]; and several other fields. Besides their direct usage purposes in different optical, energetic, and microelectronic devices, Al_2O_3 and TiO_2 can serve as passivating and diffusion barrier coatings in these applications.

2.2.4 Previous studies on the ALD of Al_2O_3 and TiO_2 protective and barrier layers

Owing to the high chemical stability of TiO_2 and the remarkable diffusion barrier properties of Al_2O_3 thin films, the number of studies focused on their application as protective coatings is constantly growing [11–56]. The ALD of Al_2O_3 is one of the most thoroughly studied ALD processes and Al_2O_3 is one of the most frequently used materials in ALD coatings for protective and barrier purposes. For example, Schmidt et al. [33] applied Al_2O_3 coatings to a cobalt slanted columnar structure to preserve its optical properties. Hahtela et al. [21]

deposited Al_2O_3 on Ni–Cr–Cu–Al–Ge thin film resistors to improve their long-term stability. Görrn et al. [22] showed that the high reactivity of the Al_2O_3 precursor and formation of the conformal barrier layer could remove the unwanted chemisorbed oxygen from the surface of a thin film transistor, and encapsulate the surface with a moisture-resistant barrier layer. Moreover, there are studies demonstrating the ability of Al_2O_3 coatings to protect silver jewelry and collectable coins [30, 41]; encapsulate the polymers used in food packaging and organic and inorganic devices [20, 42, 48]; and protect the surfaces of solar cells, organic light-emitting diodes [9, 38], and aluminum mirrors [23]. Additionally, Al_2O_3 coatings have been used to prolong the lifetime of a NiTi alloy [43], stainless steel [28, 49], steel [31], aluminum 2024-T3 alloy [31], a magnesium–lithium alloy [12], magnesium–aluminum alloy [173], and copper [44].

The main drawback of using Al_2O_3 in protective layers is the relatively high dissolution rate of amorphous alumina films in acidic and basic solutions [174]. Moreover, there are even reports demonstrating that amorphous ALD Al_2O_3 films can dissolve in pure water because of successive hydration and dynamic dissolution processes [174]. On the other hand, Abdulagatov et al. [29] reported that the formation of polycrystalline $\gamma\text{-Al}_2\text{O}_3$ during the annealing of Al_2O_3 samples at 900°C significantly increased their stability in acidic and basic solutions. Unfortunately, annealing at these very high temperatures is energy and time intensive, and in some cases, is obstructive or even impossible in industrial applications. Therefore, if a coating with a high chemical stability is needed, Al_2O_3 should be combined or replaced with other materials, e.g., with TiO_2 .

Similarly, TiO_2 deposited by ALD has been used as a protective and barrier layer. For example, Seo et al. [37] demonstrated that TiO_2 can behave as a moisture barrier. There are also numerous works showing that TiO_2 can be used as a protective layer on stainless steel [19, 26, 49, 52], a magnesium–aluminum alloy [173], silver nanoparticles [24], carbon nanotubes [175], and different electrode materials including nickel oxide [49], CuO_2 [55], InP [50], porous ceramic foams [54], and ZnO nanorods [176].

The main drawback of using ALD TiO_2 films in protective and barrier coatings is that, depending on the precursor combination and substrate material, the as-deposited TiO_2 films tend to be polycrystalline even when grown at temperatures as low as 165°C [120]. Wang et al. [177] showed that the grain boundaries of polycrystalline films might act as preferential routes for corrosion. On the other hand, polycrystalline ALD TiO_2 films show a higher resistance to acidic environments than amorphous TiO_2 films [15, 178]. Therefore, in some cases, the relatively low crystallization temperature may be an advantage of ALD TiO_2 by increasing the durability of protective coatings containing TiO_2 .

A developing research area is combining ALD films of different compositions with nanoparticles [179, 180]. In most cases, the ALD films functionalize the nanoparticle surfaces or fix them on a substrate. Furthermore, there are

reports that the coatings can improve the resistance of the material to a destructive environment and/or increase the high-temperature durability of the nanoparticles. For instance, this has been displayed in the cases of Al_2O_3 and/or TiO_2 thin films deposited on silver [16], iron [17], copper [45], and cobalt nanoparticles [46]. The ability to increase the high-temperature durability of a material by the ALD of Al_2O_3 or TiO_2 layer on the material surface has been observed also with thin planar materials, e.g., copper plates [34], niobium coupons [18], and silver islands on planar substrates [27].

To enhance the protective properties of the coatings, combinations of different materials deposited as laminates or mixtures have been used. Abdulagatov et al. [29] suggested that including an Al_2O_3 layer under the TiO_2 will improve the adhesion/nucleation and sealing properties of the coating, and the TiO_2 will in turn confer chemical stability in acidic and basic solutions. For example, some studies have demonstrated that TiO_2 and Al_2O_3 multilayer coatings can be used to protect stainless steel [11, 32, 35], aluminum alloys [12], silver [30, 41], and organic light-emitting diodes [47].

As ALD is a very surface-sensitive and relatively slow deposition method, it is sometimes necessary to combine this method with other film fabrication techniques to achieve the best results. For instance, it has been demonstrated that anodizing the aluminum alloy surface before ALD will increase the protective properties of the coating [36]. Adding a graphene oxide layer between the stainless steel and ALD layer [51, 53], and a magnetron-sputtered Al interlayer between ALD and a Mg–Li–Zn alloy, increased the corrosion resistance of the coating [40]. Furthermore, by combining a CrN matrix, TiAlN/TiN, or TiCN deposited by physical vapor deposition and either Al_2O_3 , TiO_2 , or $\text{Al}_2\text{O}_3/\text{TiO}_2$ laminates deposited by ALD, corrosion-resistant hard coatings have been fabricated [25, 56].

2.3 Reactors for ALD

The separate supply of precursors is one of the main requirements for ALD. Therefore, ALD reactors can be roughly divided into two groups depending on how the alternate supply of precursors is ensured. For the first type, the sample that needs coating is fixed and the precursor flows – which are directed onto the sample surface – are switched on and off (Fig. 2) so that the precursor pulses are well separated in time [85, 181–183]. In the reactors of the second type, the sample moves from one continuous precursor flow into another [85, 181, 184]. In this case, the precursor flows are separated by an inert atmosphere in which no precursors are present.

Additionally, it is possible to distinguish ALD reactors based on the method of excitation of the gas-solid reactions [57]. In thermal ALD, it is important to obtain a certain temperature (sometimes in the presence of catalysts) to enable a self-limited type of deposition [71]. In the case of energy-enhanced ALD, additional energy is provided to one or all of the gaseous precursors to convert

traditional thermal reactants to species that are more reactive, or to use precursors that are otherwise not suitable for ALD. Examples of energy-enhanced ALD processes are plasma-enhanced ALD (PEALD), photo-induced (including UV-assisted) ALD, microwave electron cyclotron resonance ALD (MECRALD), and hot-wire ALD.

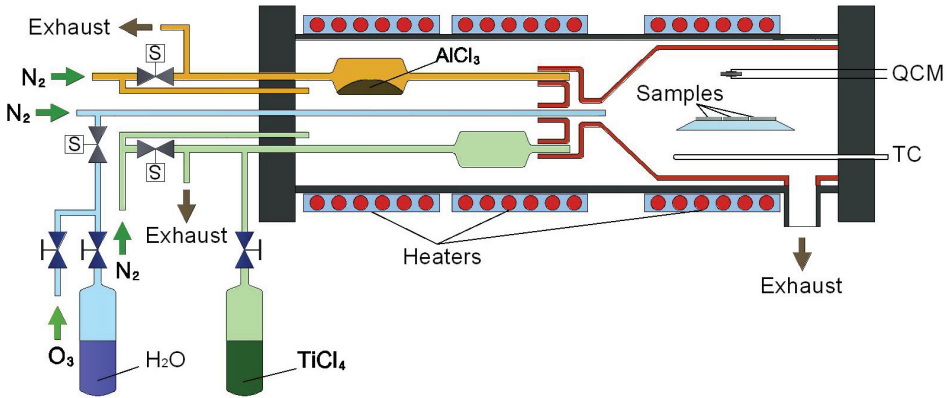


Figure 2. Schematic drawing of a flow-type ALD reactor [183]. Reprinted with permissions from Elsevier B. V. (Thin Solid Films).

In PEALD, at least one of the precursors is excited by employing plasma during the deposition process. Depending on the reactor configuration, PEALD can be divided into radical-enhanced, direct plasma, and remote plasma ALD [185]. In the first case, the plasma generation takes place relatively far from the sample surface. Therefore, the most reactive plasma species (electrons and ions) recombine via surface collisions on the way to the surface and hence only radicals are involved in the ALD reactions. In the case of direct plasma ALD, the sample is positioned between the two electrodes that are used for plasma generation. For this reason, the plasma species taking part in ALD are generated very close to and directly impact the sample surface. In the remote plasma ALD configuration, the plasma generation takes place at a significant distance from the substrate surface. In this case, the substrate does not take part in plasma generation but, unlike in radical-enhanced ALD, the electron and ion densities do not decrease to zero at the substrate location. In MECRALD, the gas/vapor is ionized as it flows through the electron cyclotron resonance zone, while in UV-assisted ALD, ultraviolet light is used to irradiate the surface after the purge steps to increase the number of chemisorption sites on the sample surface [146].

ALD reactors can be designed to deposit coatings on one substrate (single-wafer reactors) or on many samples simultaneously (batch reactors). The main differences are that batch reactor chambers are usually larger and have more complex precursor supply systems, to optimize the precursor flows and avoid increasing the times needed to supply and evacuate the precursors. It must be considered that the evacuation of excess precursors might be difficult when the

films are deposited at low temperatures or onto complex-shaped objects. For example, Groner et al. [13] used an additional carrier gas line in the reaction chamber to avoid the diffusion of the precursors inside the hollow poly(ethylene terephthalate) bottle, thereby ensuring relatively short purge periods needed for ALD of coating on the outer side of the bottle.

In addition, depending on the application, reactors with different pressures and carrier gas flow rates, precursor supply methods, and different temperatures of reactor walls compared to that of the substrates, have been described [182]. Most ALD reactors use a carrier gas to transport the precursors to the substrates, and for purging the substrate surfaces between precursor pulses. In some cases, however, no carrier gas is used, and the reactants are removed from the reaction chamber by applying only a throttled pumping. The main disadvantage of this approach is the relatively long purge periods required, which lead to a very slow deposition process. There are also differences in the supply of the precursors into the reaction area in different reactors. One possibility is to supply the precursors using a gas flow that is parallel to the sample surface (Fig. 2). Another possibility is to lead the gas flow into the reaction chamber perpendicularly to the sample surface using the so-called “showerhead” setup.

It is possible to divide ALD reactors into hot- and cold-wall systems. In the most commonly used hot-wall reactors, the reaction chamber walls, interior gas phase, and samples are heated to similar temperatures. In cold-wall reactors, only the sample holder and sample are heated to T_G , while the walls of the reaction chamber are held at much lower temperatures [186].

To use the full potential of the ALD technique, many different reactors with configurations optimized for special applications have been developed. For instance, to deposit ALD coatings on the surfaces of nanoparticles, fluidized bed reactors have been built [17]. For coating flexible materials and porous or 3D substrates, roll-to-roll reactors [187, 188] and special showerhead systems, respectively, have been designed [189].

3. RESEARCH OBJECTIVES

The first goal of this research was to design a reactor and develop processes for coating the inner walls of containers larger than the reaction chambers of conventional ALD reactors. It was also important that the reactor, which was planned to be constructed, would allow the process developers to control if the ALD-type deposition was achieved inside the container. The aim was to show that ALD could be efficiently applied to coat the inner walls of hermetic containers.

Secondly, the possibility to use hydrogen-free precursor combinations, $\text{TiCl}_4\text{-O}_3$ and $\text{AlCl}_3\text{-O}_3$, in the ALD of TiO_2 and Al_2O_3 films was investigated. The films deposited with these precursor combinations were compared, and the effects of applying O_3 instead of H_2O on the growth mechanism, structure, and morphology of the films were studied. This research was performed to demonstrate that TiO_2 and Al_2O_3 could be deposited by ALD using $\text{TiCl}_4\text{-O}_3$ and $\text{AlCl}_3\text{-O}_3$ precursor combinations, which might have advantages over other ALD processes.

Thirdly, it was of particular interest to characterize the protective and barrier performance of the Al_2O_3 and TiO_2 coatings deposited using the $\text{AlCl}_3\text{-O}_3$ and $\text{TiCl}_4\text{-O}_3$ processes, and to reveal the effects of thickness, deposition temperature, and structure on the chemical stability of the films. The aim of the investigation was to create the basis for future studies and possible applications of the films deposited by using these processes, and to demonstrate that the films can be used as barrier layers.

4. EXPERIMENTAL

4.1 Samples and pretreatment of the sample surfaces

The thin films were deposited onto quartz crystal microbalance (QCM) mass sensors and on Si(100) and AISI 310 stainless steel substrates. In the QCM studies, 6.4 MHz quartz crystal oscillators with silver electrodes were used as the mass sensors. The sizes of the Si(100) samples ranged from 10×10 to 30×30 mm². Before loading into the reactor, the samples were etched in HF and then rinsed with deionized water. The 0.9 mm-thick annealed AISI 310 stainless steel (Goodfellow Cambridge Ltd.) samples had typical sizes of 15×15 mm² and contained Ni (20%), Cr (24–26%), Mn (2%), and Si (1%), in addition to Fe [190].

For the pretreatment of the AISI 310 samples, several procedures were tested and compared. Firstly, the samples were pretreated in different organic solvents including acetone (99.5%, Sigma-Aldrich), isopropyl alcohol (99.8%, Sigma-Aldrich), and toluene (99.7%, Sigma-Aldrich). Secondly, surface pretreatments by Ar, N₂, Ar/O₂, and H₂ (all Eesti AGA AS) plasmas were tested. Thirdly, the samples were etched in different acids, i.e., HNO₃ (65%, Sigma-Aldrich), HCl (37%, Sigma-Aldrich), H₂SO₄ (95%, Sigma-Aldrich), and in mixed solutions consisting of (1) 5% HF, 10% HNO₃, and 85% H₂O (Solution A); (2) 20% H₂SO₄, 4.5% HNO₃, 14.5% HCl, and 61% H₂O (Solution B); and (3) 15% H₃PO₄ (85%, Sigma-Aldrich), 2% HNO₃, 5% HCl, 5% H₂SO₄, and 73% H₂O (Solution C), the solutions that have been previously used for steel burnishing [191]. The plasma treatments were performed using a Femto RF-UHP-PC low-pressure plasma system (Diener Electronic) at power levels of up to 100 W. Each AISI 310 sample was studied with high-resolution scanning electron microscopy (HR-SEM) using a dual-beam microscope (Helios NanoLab 600, FEI) before and after each pretreatment. The effect of the pretreatment on the film quality was evaluated by conducting etching tests with the films in Solution C at 70°C.

4.2 Thin film deposition

The deposition of TiO₂ and Al₂O₃ films using TiCl₄-O₃ and Al₂O₃-O₃ chemistries was investigated in a low-pressure flow-type hot-wall ALD reactor [183]. The vacuum chamber of the reactor (Fig. 2) has stainless steel outer walls and is surrounded by three independent heaters that allow a uniform temperature distribution over each of the three zones. Two of these zones are meant for volatilization of the solid precursors and one for deposition of the films. A quartz tube with a 50 mm inner diameter separates the stainless-steel reactor walls in the high-temperature region from the gas flowing into the deposition zone. This approach significantly reduces the influence of the stainless steel

walls on the purity of the films deposited at reactor temperatures that can reach as high as 750°C. In addition, the quartz tube can be easily removed and cleaned to ensure that the concentrations of impurities in the films are kept low.

The precursors with a low vapor pressure are volatilized in quartz evaporation cells located in the heated zones of the reactor. Using the carrier gas, the precursors are carried into the 160 mm long quartz reaction chamber, which has an inner diameter of 45 mm. The flow of the carrier gas is controlled with needle valves, and the vapor pressure of each precursor is determined by the temperature of the corresponding heating zone. To turn the injection of the precursors into the reaction zone on and off, the flow direction of the carrier gas in the evaporation cells is changed by opening and closing the solenoid valves, which are operated by a customized control system. The precursors with a high vapor pressure enter the reactor from external containers through needle and solenoid valves that control the flow and form the precursor pulses.

To optimize the deposition process parameters, a QCM system with a mass sensor that can be moved within the reaction chamber can be added for real-time studies. In this study, the QCM data were acquired by using a Q-pod quartz crystal monitor (Inficon). Based on these studies, the ALD cycle times and precursor doses were chosen for the growth of the thin films characterized in the post-growth studies. All the parameters used for the deposition of the TiO₂ and Al₂O₃ films using TiCl₄-O₃ and AlCl₃-O₃ processes are described in detail in the original publications [I–III].

To test the concept of the ALD reactor designed in this work for depositing ALD thin films onto the inner walls of hollow bodies, the well-known TiO₂ thin film deposition process using TiCl₄ (99.9%, Aldrich) and H₂O precursors was studied by QCM. In these experiments, nitrogen (99.999%, Eesti AGA AS) was used as a carrier and purge gas. The gas pressure in the reaction chamber was maintained below 10 mbar during the deposition. The vapors of TiCl₄ and deionized water were led into the reactor from external reservoirs held at room temperature (20–23°C).

According to the QCM data, the ALD cycle times that allowed self-limited deposition in a container with a diameter of 100 mm and volume of 2 dm³ were determined to be 5 s–5 s–5 s–10 s for the TiCl₄ pulse–first purge–H₂O pulse–second purge sequence. These process parameters were used for the deposition of TiO₂ films on the inner walls of the container, as well as on pieces of a Si(100) wafer that were used as test samples and placed into the reactor using a special sample holder. The TiCl₄-H₂O ALD process was also used to investigate the efficiency of different surface pretreatments for cleaning the metal substrates.

4.3 Characterization of the thin films

The compositions and mass thicknesses of the deposited films were measured with an X-ray fluorescence (XRF) spectrometer-analyzer (ZSX 400, Rigaku). Supplementary information on the film thicknesses and interfacial layers formed between the substrate and film were obtained using a spectroscopic ellipsometer (GES5E, Semilab Sopra). Spectroscopic ellipsometry (SE) was used also for characterization of the refractive indices.

Crystal structures were characterized by grazing incidence X-ray diffraction (GIXRD) using a SmartLab X-ray diffractometer (Rigaku) with Cu K_{α} radiation. The incidence angles chosen for these measurements were 0.27–0.33°. The thickness, density, and surface roughness values of each sample were evaluated by the X-ray reflection (XRR) method using the same X-ray diffractometer. Atomic force microscopy (AFM) was conducted with an Autoprobe CP-II (Veeco Instruments Inc.) equipped with Si cantilevers (typical tip radius of ≤ 10 nm) to determine the root mean square (RMS) surface roughness values.

Raman spectra were recorded with an inVia micro-Raman spectrometer (Renishaw). The power of the incident 514-nm laser beam was set to be about 10 mW at the sample, and the spectra were recorded with a resolution of 1.5 cm^{-1} . A Si reference sample was used for the calibration of the Raman shift. The Helios NanoLab 600 microscope was employed for HR-SEM studies to characterize the surface microstructure before and during the etching tests.

The etching rates of the films deposited on Si(100) were determined in an 80% solution of H_2SO_4 (95%, Sigma-Aldrich) in deionized water. The etching tests were performed in a stepwise manner, with etching steps ranging from 30 s to 5 h depending on the etching rate. Before and after each etching step, the mass thickness and structure of the film was determined with XRF and GIXRD, respectively. Other details of the testing process and measurement conditions are described in the original publication [III].

To test the barrier properties of the coatings, pitting tests of the films deposited on AISI 310 were carried out in a 6 mass% FeCl_3 solution at 22°C according to the ASTM 48G-11 standard test procedure. The other sides of the samples used in these tests were coated with a commercially available protective paint (Rust Stop 4 in 1, MOTIP DUPLI) according to the manufacturer's instructions. During these tests, the sample surfaces were investigated using optical microscopy after 1, 2, 4, 8, 26, 50, and 74 h.

The films deposited on AISI 310 were also etched at 110°C in a solution containing H_3PO_4 , HNO_3 , HCl , H_2SO_4 , and H_2O in a volume ratio of 15:2:5:5:73. Etching steps with durations of 10–70 min were used. After each step, the mass change was determined to characterize the etching rate, as described in the corresponding original publication [III]. The mass changes of the samples were determined with an analytical balance (ABS 220-4, Kern & Sohn) with an accuracy of 1 mg.

5. RESULTS AND DISCUSSION

This Chapter describes the development of an ALD reactor suitable for depositing thin films onto the interior surfaces of hollow bodies [IV, V], and summarizes the results of investigation of $\text{TiCl}_4\text{-O}_3$ and $\text{AlCl}_3\text{-O}_3$ ALD processes for the deposition of TiO_2 and Al_2O_3 films [I, II]. Additionally, the main properties of the films and, in particular, their chemical stability in wet corrosive environments are described [III].

5.1 Coating the inner surfaces of hollow bodies

5.1.1 Reactor for coating the inner walls of hollow bodies

One objective of this research was to develop an ALD apparatus capable of depositing diffusion barrier layers on the inner surfaces of hollow bodies (e.g., containers). In the equipment developed [IV, V], a hollow body connected to the vacuum and precursor supply lines is used as the reaction chamber (Fig. 3) where the thin film deposition takes place. The precursors are transported to the bottom of the interior of the body (Fig. 3) using a separate input line for each precursor to avoid any possible chemical reactions inside the gas lines. The gaseous reaction products and excess precursors are pumped out of the body through the orifice connected to the evacuation system. The evacuation system that consists of the exhaust piping, hot and sorption traps, and vacuum pump ensures the base pressure and a continuous carrier gas flow in the reaction zone. The flow levels of the carrier gas and precursors can be adjusted and controlled using needle and pneumatic valves. The pneumatic valves are operated by a control system, enabling the generation of the cycling sequence needed for the ALD-type growth.

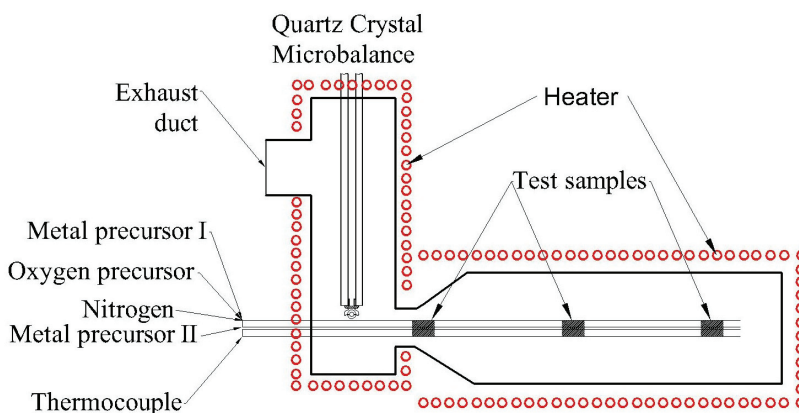


Figure 3. Schematic drawing describing the operation principle of the ALD reactor designed for coating the inner walls of hollow bodies.

The reaction chamber (i.e., the hollow body) is surrounded by a heater that ensures a temperature (distribution) suitable for ALD is achieved. The precursor supply and evacuation lines can also be heated to avoid the condensation of precursors and gaseous reaction products in these parts of the equipment. To optimize precursor delivery (precursor doses, precursor pulse durations, and purge periods) and to characterize the ALD processes in real time, a QCM mass sensor can be inserted into the evacuation line close to the reaction chamber outlet (Fig. 3). For additional evaluations of the deposition quality and thin film properties, it is possible to insert up to three test samples with maximum sizes of 15 mm × 15 mm into the interior of the hollow body by using sample holders connected to the precursor supply lines (Fig. 3).

5.1.2 Growth of TiO₂ films from TiCl₄ and H₂O on the inner walls of hollow bodies

QCM studies carried out in a prototype reactor for coating the inner walls of hollow bodies demonstrated the possibility to obtain ALD-type growth of TiO₂ films using the well-known precursor combination of TiCl₄ and H₂O (Fig. 4). During the QCM studies the container temperature was kept at 110°C. The relatively low T_G value was chosen for the test depositions because some components of the vacuum line that required heating to the deposition temperature during the QCM studies contained O-rings with a maximum working temperature of 150°C. Moreover, lower deposition temperatures require usually application of longer purge and pulse times. Therefore, the process parameters that provide the self-limited ALD-type growth at lower temperatures also give a similar growth mode at higher temperatures. Finally, at lower temperatures, the QCM signal is more stable and thus the results obtained are more reliable.

In the QCM studies, the durations of the TiCl₄ and H₂O pulses and both purge periods were varied systematically while the other time parameters were set at sufficiently high values to ensure self-limited growth. The mass increase per cycle saturated when the durations of the TiCl₄ and H₂O pulses and post-TiCl₄ purge reached 5 s (Fig. 4); this behavior is similar to that reported earlier for the TiCl₄-H₂O [117] and TiCl₄-O₃ [I] processes. A two times longer (10 s) purge duration was needed after the H₂O pulse to avoid the overlap of the two successive precursor pulses. The need for a longer purge after the H₂O pulse is, however, not surprising as water desorbs relatively slowly from solid surfaces, i.e., from the inner walls of the ALD reaction chamber and precursor supply lines [192].

To reduce the purge duration, higher nitrogen flows together with increased pumping speeds have usually been applied to ensure the faster and more efficient removal of precursors from the reaction chamber. Unfortunately, in our experiment, the gas cylinders used as reaction chambers had relatively small inlet diameters compared to the diameter of the cylinder itself. Owing to the bottleneck effect, increasing the carrier gas flow would have increased the

pressure inside of the cylinder. As shown in the case of $\text{HfCl}_4\text{-H}_2\text{O}$ and $\text{ZrCl}_4\text{-H}_2\text{O}$ processes [192], such changes in pressure might have had a detrimental influence on the ALD film growth. Therefore, to enable the comparison of these results with those obtained in previous studies, increasing the durations of the ALD cycles was the preferred choice.

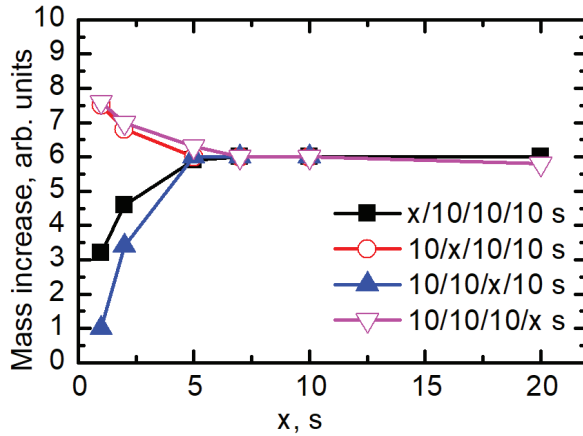


Figure 4. Mass increase per cycle determined by QCM as a function of ALD process time parameters.

According to the XRF measurements of the TiO_2 films deposited on the test samples (Fig. 3) from TiCl_4 and H_2O at 110°C by applying 500 ALD cycles, the mass thickness of the TiO_2 deposited in the main part of the reactor did not differ by more than 5% (Figs. 3 and 5). A significant decrease ($\sim 25\%$) in TiO_2 mass thickness was detected only for the reference samples positioned at the outlet of the chamber.

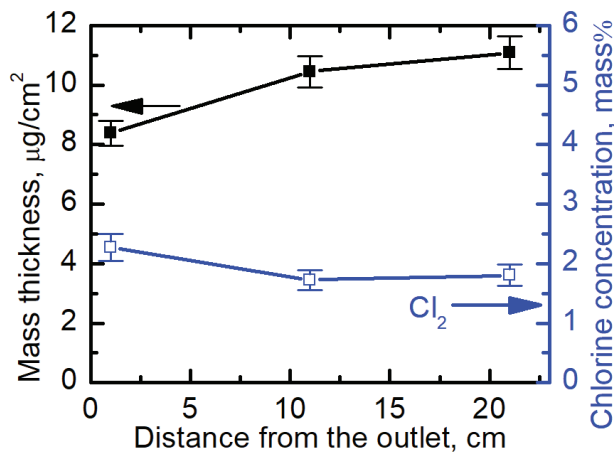


Figure 5. The dependence of the mass thickness and chlorine concentration on the position of reference samples inside the ALD reactor.

It should be mentioned that in this configuration the diameter of the reaction chamber was around four times smaller near the outlet than that of the rest of the chamber. Thus, the linear gas flow rate was more than an order of magnitude higher at the outlet. It has been demonstrated in earlier studies of $\text{HfCl}_4\text{-H}_2\text{O}$ and $\text{ZrCl}_4\text{-H}_2\text{O}$ processes that an increase in the carrier gas flow rate by 2.0–2.5 times may decrease the growth rate by up to 25–30% [192]. By correlating the growth rate with the chlorine concentration in the films, which increased from 1.8 ± 0.1 mass% in the films grown at the bottom of the container to 2.3 ± 0.1 mass% in those grown at the outlet, it can be concluded that increasing the linear gas flow rate reduces the efficiency of the chlorine replacement of surface species and therefore influences the film growth.

The growth rate of TiO_2 reached 0.05 nm per cycle at the container outlet and 0.06 nm per cycle at the bottom. For comparison, the growth per cycle of 0.07 nm at 100°C and 0.06 nm at 125°C has previously been reported for this ALD process [193]. Thus, taking into account the influence of the carrier gas flow and T_G on the growth per cycle, one can conclude that ALD of TiO_2 in the container was similar to that in a conventional ALD reactor.

5.2 Characterization of O_3 -based growth processes

5.2.1 $\text{TiCl}_4\text{-O}_3$ process

QCM studies demonstrated the possibility to deposit TiO_2 from TiCl_4 and O_3 at $\geq 225^\circ\text{C}$ [I]. At lower temperatures, no TiO_2 film growth was observed, even if pulse times of up to 60 s were used. Similar results were obtained from post-growth studies of films deposited on $\text{Si}(100)$ substrates (Fig. 6). Compared to the other processes used for the ALD of TiO_2 films (Table 2), relatively high substrate temperatures were needed for the $\text{TiCl}_4\text{-O}_3$ process. Only a few of the processes used, e.g., $\text{TiCl}_4\text{-CH}_3\text{OH}$, $\text{TiF}_4\text{-H}_2\text{O}$, and $\text{TiOCH}(\text{CH}_3)_2(\text{C}_{11}\text{H}_{19}\text{O}_2)_2\text{-H}_2\text{O}$, have required similar or higher temperatures to enable the ALD-type growth. The growth rate achieved at 225°C was still low compared to the process involving H_2O [I], but it was comparable with the growth rate obtained in the $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4\text{-H}_2\text{O}$ process (Fig. 6). With the increase of T_G from 225 to 275°C , the growth rate increased up to 0.073 nm per cycle, which is considerably higher than that in the $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4\text{-H}_2\text{O}$ process and slightly higher than that in the $\text{TiCl}_4\text{-H}_2\text{O}$ process. This difference arises from the efficient generation of TiCl_4 adsorption sites in the $\text{TiCl}_4\text{-O}_3$ process at $T_G \geq 275^\circ\text{C}$ (Fig. 6). Moreover, varying the pulse durations revealed that the pulses needed to achieve saturation in the range of $225\text{--}275^\circ\text{C}$ were markedly longer with $\text{TiCl}_4\text{-O}_3$ than with $\text{TiCl}_4\text{-H}_2\text{O}$ [I]. This occurs since the adsorption reactions in this O_3 -based process are slower at these temperatures than the corresponding reactions involving H_2O as the oxygen precursor. On increasing the temperature from 275 to 600°C , the growth rate decreased similarly in the $\text{TiCl}_4\text{-O}_3$ and $\text{TiCl}_4\text{-H}_2\text{O}$ processes (Fig. 6). However, the growth rate of the O_3 -based process remained slightly higher, especially at $500\text{--}600^\circ\text{C}$.

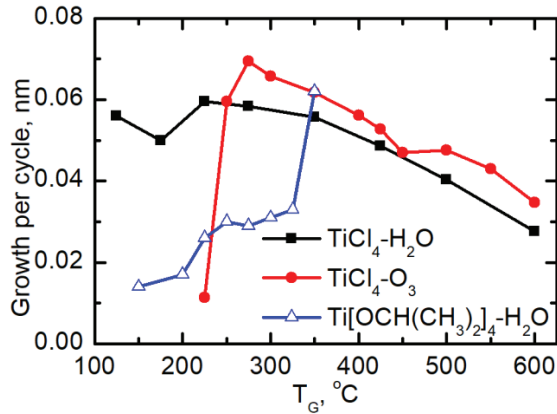


Figure 6. Influence of T_G on TiO_2 film growth per cycle for $\text{TiCl}_4\text{-H}_2\text{O}$ [1], $\text{TiCl}_4\text{-O}_3$ [1] and $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4\text{-H}_2\text{O}$ [194] processes.

Owing to the similar behaviors of the $\text{TiCl}_4\text{-O}_3$ and $\text{TiCl}_4\text{-H}_2\text{O}$ processes, the possibility that H_2O residues present in the carrier gas and/or O_2 could contribute to the deposition of TiO_2 from TiCl_4 and O_3 was checked. In these tests, O_2 was supplied through the O_3 generator that was switched off. In these experiments, however, only a 1 nm-thick TiO_2 film grew on the Si(100) substrate during 1000 ALD cycles [1]. Therefore, the contribution of H_2O residues is not notable. As the formation of TiO_2 from TiCl_4 and O_3 does not proceed via intermediate hydroxyl groups, the contribution of oxygen bridges – which are expected to participate in surface reactions at higher temperatures [195] – and the effect of excess oxygen had to be considered. Previously, Knapas et al. [196] found that the surface adsorption of excess oxygen during the O_3 pulse could, similarly to hydroxyl groups, enable the formation of intermediate oxychlorides species on the surface and enable ALD in some O_3 -based processes. A similar conclusion was reached based on thermodynamic data [197], which showed that TiCl_4 could not react with TiO_2 at the temperatures used in our experiments.

Different growth rate behaviors were observed for TiO_2 films deposited from TiCl_4 and O_3 on RuO_2 and r-sapphire ($\alpha\text{-Al}_2\text{O}_3(012)$) substrates (Fig. 7). For example, on r-sapphire, the highest growth rate (0.061 nm) was achieved at 300°C while in the range 400–600°C, the growth rate remained at 0.038–0.044 nm per cycle [198]. On RuO_2 , a relatively high growth rate (0.037 nm per cycle for 10 nm-thick films) was achieved also at 225°C [199]. However, with increasing thickness, the difference in growth rates on the Si and RuO_2 substrates decreased. Hence, the higher growth rate on RuO_2 compared to that on Si was clearly caused by the additional oxidation of RuO_2 by O_3 [200] and the contribution of this additional oxygen to the further deposition of TiO_2 [199]. The rapid increase in growth rate obtained on RuO_2 with increasing T_G values above 400°C was probably related to the decomposition of RuO_2 during the ALD of TiO_2 . This phenomenon has been employed by Jeon et al. [201] to

explain the similar growth rate increase observed when increasing the T_G above 370°C in the deposition of TiO₂ on RuO₂ from Ti[O(C₃H₇)₄]-O₃. In the latter case, however, also the decomposition of Ti[O(C₃H₇)₄] could have contributed to the growth rate increase.

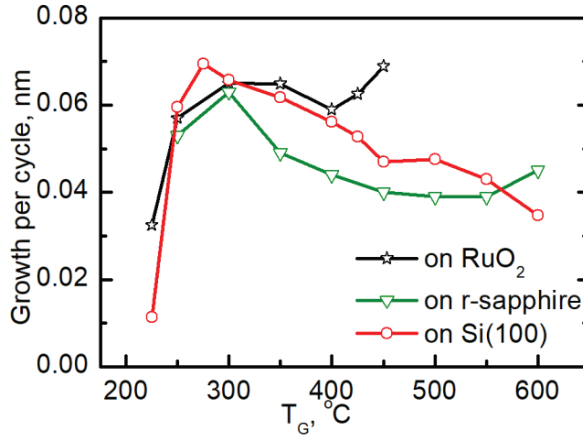


Figure 7. Influence of T_G on growth per cycle of TiO₂ films deposited in TiCl₄-O₃ process on Si(100) [I], RuO₂ [198] and r-sapphire [199].

5.2.2 AlCl₃-O₃ process

The ALD-type growth of Al₂O₃ using AlCl₃ and O₃ precursors was obtained at substrate temperatures ranging from 300 to 450°C [II]. The lower growth rate obtained using this precursor combination at 300°C (Fig. 8), and the four times higher chlorine concentration in the films (0.4 at%) compared to the corresponding values measured for films deposited in AlCl₃-H₂O process, arise from the insufficient reactivity of O₃. However, by increasing the temperature from 300 to 350°C, the growth rate increased to 0.069 nm per cycle (Fig. 8) and the chlorine concentration decreased to 0.05 at%. The latter value was even lower than that obtained with the AlCl₃-H₂O process. A similar behavior has been previously demonstrated when O₃ was used instead of water vapor together with TMA; a lower concentration of carbon impurities in the films was obtained [202]. In the TMA-based processes, Elliott et al. [203] demonstrated that the surface reactions that occur with both H₂O and O₃ oxygen sources depend on the formation of surface hydroxyl groups. As a control experiment, deposition at 350°C was performed without switching on the O₃ generator to test whether water or oxygen residues in the carrier gas influence the growth of the films in the AlCl₃-based process. No film growth was obtained in these experiments. Therefore, it could be concluded that film growth was obtained via reactions involving only AlCl₃ and O₃ as the precursors, and that O₂ was not reactive enough for ALD at these process parameters.

The lower growth rates of the Al_2O_3 films obtained with $\text{AlCl}_3\text{-O}_3$ compared to those observed for $\text{AlCl}_3\text{-H}_2\text{O}$ process, and the narrower effective T_G range of the $\text{AlCl}_3\text{-O}_3$ process compared to those of other metal chloride and O_3 processes [60, 204, I], arise from the insufficient adsorption of oxygen onto the Al_2O_3 film surface. As discussed in Section 5.2.1, excess oxygen might be required for the adsorption of the metal precursor in O_3 -based processes. The studies on the ALD of layered $\text{Al}_2\text{O}_3/\text{TiO}_2$ films with chloride- O_3 processes support this assumption. During the first ALD cycle, the growth rate of Al_2O_3 on TiO_2 was about three times higher than that on Al_2O_3 [II], while the growth rate of TiO_2 was around two times higher on TiO_2 than on Al_2O_3 . These results arise from the higher adsorption efficiency of chlorides on TiO_2 , which is most likely due to the higher concentration of excess oxygen in TiO_2 than in Al_2O_3 .

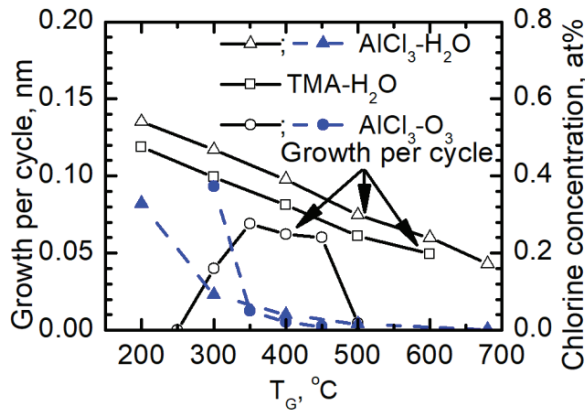


Figure 8. Effect of T_G on growth per cycle (open symbols) of Al_2O_3 films deposited in $\text{AlCl}_3\text{-O}_3$, $\text{AlCl}_3\text{-H}_2\text{O}$, and $\text{TMA-H}_2\text{O}$ processes and on chlorine concentration (closed symbols) of films deposited in $\text{AlCl}_3\text{-O}_3$ and $\text{AlCl}_3\text{-H}_2\text{O}$ processes [I]. Reprinted with permissions from Elsevier B. V. (Thin Solid Films).

5.3 Physical properties of thin films deposited in $\text{TiCl}_4\text{-O}_3$ and $\text{AlCl}_3\text{-O}_3$ processes

The substrate material, T_G , and film thickness markedly influenced the structure and therefore also other properties, e.g., roughness and density of the TiO_2 films deposited from TiCl_4 and O_3 [198, 199, I]. The deposition of amorphous films with densities of $3.7\text{--}3.8\text{ g/cm}^3$ (Fig. 9) was attained on $\text{Si}(100)$ surfaces at $225\text{--}400^\circ\text{C}$, provided that the film thickness did not exceed 7 nm [I]. In the thicker films, the formation of anatase-phase TiO_2 on $\text{Si}(100)$ was detected at $\geq 250^\circ\text{C}$; correspondingly, the density increased to 3.9 g/cm^3 . The presence of the rutile phase on $\text{Si}(100)$ was confirmed only in the films deposited at 600°C [I]. However, the concentration of the rutile phase was lower than in films deposited using $\text{TiCl}_4\text{-H}_2\text{O}$ at the same temperature [I].

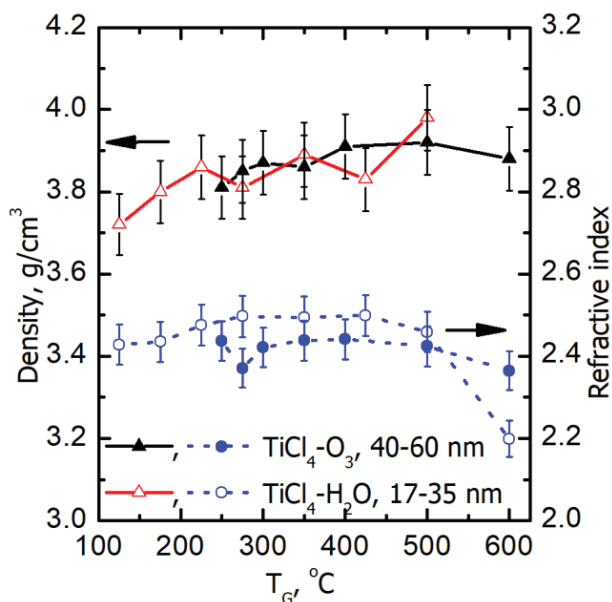


Figure 9. Effect of T_G on density and refractive index of TiO₂ films deposited in TiCl₄-O₃ and TiCl₄-H₂O ALD processes by applying 1000 and 600 ALD cycles, respectively [1]. The densities were measured by XRR and refractive indices were determined by SE at a wavelength of 633 nm.

On RuO₂ [199] and r-sapphire [198], however, the growth of the rutile phase was obtained with the TiCl₄-O₃ process at temperatures as low as 225 and 300°C, respectively. In addition, on c-sapphire (α -Al₂O₃ (001)), a mixture of (100)-oriented rutile and TiO₂-II grew from TiCl₄-O₃ at 400–600°C [198].

The ability to deposit rutile-phase TiO₂ films on RuO₂ at low temperatures enabled us to obtain dielectrics with relative permittivity values as high as 106–122, and prepare Pt/TiO₂/RuO₂ structures with leakage current densities below 10⁻⁷ A/cm² at capacitance equivalent thickness (CET) values of 0.41–0.45 nm [199]. The latter result is of particular importance in the development of capacitor structures for memory devices and several other components at nanoelectronics. The investigation of electrical characteristics demonstrated that replacing H₂O with an O₃ oxygen precursor had a positive effect, and allowed the preparation of capacitor structures with a leakage current density as low as 6.6 × 10⁻⁸ A/cm² at 0.8 V and CET of 0.41 nm [205].

In addition to the changes in phase composition of the films deposited on Si(100) substrates, the crystal orientations in polycrystalline anatase films changed with increasing T_G . The increase of the T_G from 350 to 450°C reduced the intensity of the 101 anatase reflection that was the strongest one according to the powder diffraction pattern database (ICSD, FIZ Karlsruhe, collection code 202242) and dominated in the GIXRD patterns of the films deposited at 250–350°C (Fig. 10a). At the same time the intensity of the 004 anatase reflection increased significantly. For comparison, no significant changes in the

intensity of the main anatase Raman band ($142\text{--}143\text{ cm}^{-1}$) was detected (Fig. 10b). Consequently, the decrease in the intensity of the GIXRD 101 reflection was due to changes in the crystallite orientations rather than in the phase composition, as Raman spectroscopy – which is less sensitive to crystallite orientation than X-ray diffraction (XRD) – showed no considerable decrease in the amounts of anatase in the films.

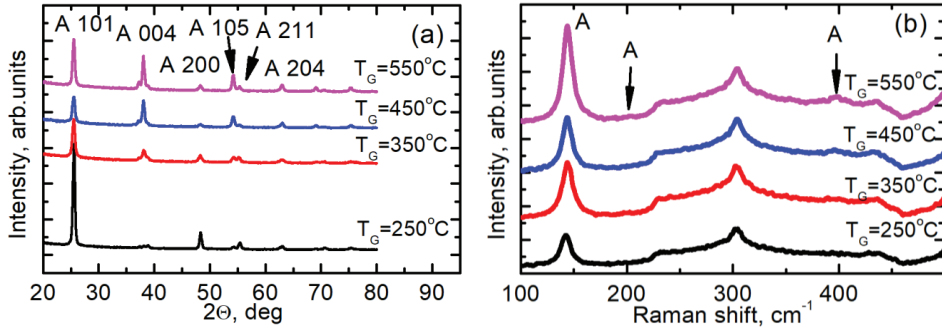


Figure 10. (a) GIXRD patterns and (b) RAMAN spectra of 26–44 nm-thick TiO_2 films deposited by $\text{TiCl}_4\text{-O}_3$ at different T_G values.

The HR-SEM studies of TiO_2 films deposited at different temperatures demonstrated the marked dependence of grain size on T_G [III]. The lateral sizes of the grains formed in a 26 nm-thick film deposited at 250°C were about 10 times larger than the film thickness (Fig. 11a). Puurunen et al. [206] observed a similar phenomenon, and explained this in terms of the laterally spreading crystallization that occurs in amorphous films after the formation of crystalline nuclei that are located sufficiently far from each other.

With the increase of T_G from 250 to 450°C , the lateral grain sizes decreased by around six times, i.e., to 30–40 nm for the 35 nm-thick films (Figs. 11b, 11c). The further increase in T_G from 450 to 550°C increased the grain size to 50–80 nm for the 45 nm-thick TiO_2 films (Fig. 11d).

An interesting result is that the large differences in grain sizes had only a minor influence on the surface roughness, determined to be 2.3, 2.5, and 2.8 nm for the 26, 36, and 35 nm-thick TiO_2 films deposited at 250, 350, and 450°C , respectively (Fig. 12). A slightly different behavior was observed when the 56 and 57 nm-thick films (deposited at 250°C and 400°C , respectively) were investigated. The surface roughness decreased from 3.6 to 1.9 nm with the increase of T_G from 250 to 400°C [I]. However, in both cases, the further increase of T_G to $550\text{--}600^\circ\text{C}$ increased the surface roughness to 5–6 nm.

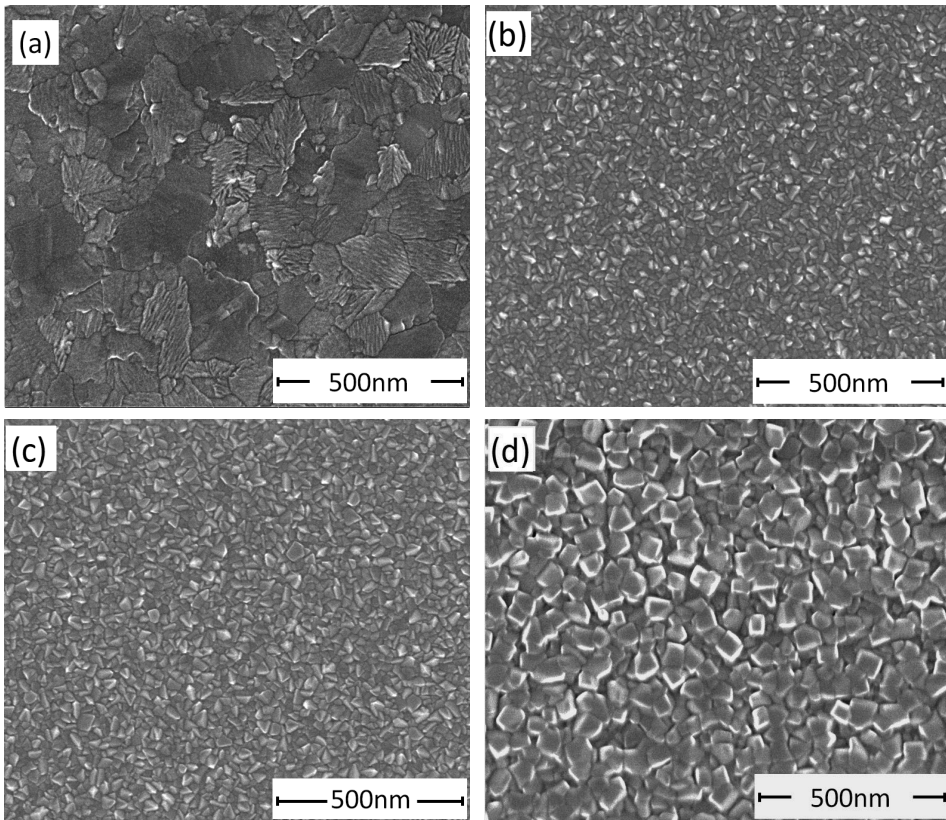


Figure 11. HR-SEM images of TiO₂ films deposited at (a) 250, (b) 350, (c) 450, and (d) 550°C. The mass thicknesses of the films were (a) 26, (b) 36, (c) 35, and (d) 45 nm, respectively. Printed with permissions from Elsevier B.V, (Mater. Chem. Phys) [III].

The refractive indices determined at a wavelength of 633 nm for TiO₂ films deposited from TiCl₄ and O₃ [I] were comparable to the corresponding values obtained for the films deposited using TiCl₄ and H₂O, with values lying between 2.37 and 2.45 (Fig. 9). The lowest refractive indices obtained for the films deposited at 275 and 600°C were probably related to optical inhomogeneities caused by the transition from an amorphous to a randomly oriented polycrystalline structure at 275°C, and the high surface roughness of the films grown at 600°C [I].

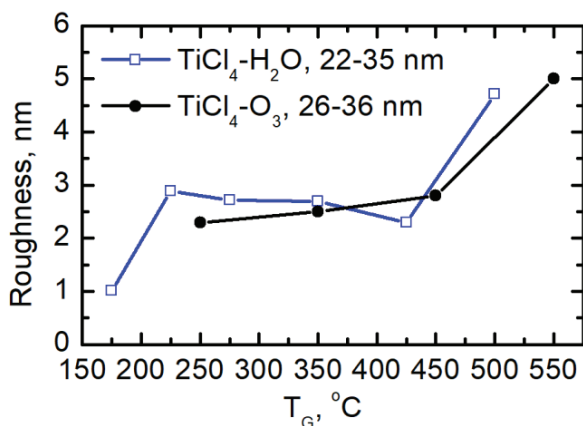


Figure 12. Effect of T_G on surface roughness of TiO_2 films deposited in $\text{TiCl}_4\text{-O}_3$ and $\text{TiCl}_4\text{-H}_2\text{O}$ [I] ALD processes. The surface roughness was measured by XRR.

The Al_2O_3 films deposited on Si(100) using AlCl_3 and O_3 were amorphous, and had roughness values of 0.5–1.1 nm, similar to the films deposited by other Al_2O_3 ALD processes at these temperatures [II]. The film densities varied from 3.0 to 3.2 g/cm^3 . Markedly higher Al_2O_3 densities (up to 3.7 g/cm^3) have been obtained in ALD processes only for crystalline films deposited at temperatures exceeding 600°C [86].

The refractive indices of the films deposited from AlCl_3 and O_3 were comparable to the corresponding values of Al_2O_3 deposited from $\text{AlCl}_3\text{-H}_2\text{O}$ and TMA- H_2O at 300–600°C, and were 1.67–1.69 at a wavelength of 633 nm [II].

5.4 Chemical stability of Al_2O_3 and TiO_2 films deposited in $\text{TiCl}_4\text{-O}_3$ and $\text{AlCl}_3\text{-O}_3$ processes on Si substrates

Before applying materials in protective and barrier coatings, it is important to know their performance in aggressive environments, even if the primary role of the coatings is not protection against corrosion. For this reason, chemical tests were conducted on Al_2O_3 and TiO_2 films deposited on Si(100) at different temperatures.

The chemical stability tests performed in hot H_2SO_4 for Al_2O_3 deposited on Si(100) from AlCl_3 and O_3 demonstrated the significant dependence of the etching rate on T_G . With the increase of T_G from 300 to 450°C, the etching rate determined for the first 30 s of etching decreased from ≥ 0.9 nm/s to 0.085–0.095 nm/s (Fig. 13). This decrease correlated with the changes in concentration of the chlorine impurities from (0.4 at% at $T_G = 300^\circ\text{C}$ to < 0.02 at% at $T_G = 450^\circ\text{C}$) [III]. A similar dependence of the etching rate on T_G and the concentration of impurities (Fig. 13) has been previously reported for films deposited using AlCl_3 and H_2O and tested in the same solution [15], and for

films deposited with TMA-H₂O and TiCl₄-H₂O processes and tested in various etchants [178]. The etching rates of the Al₂O₃ films deposited from AlCl₃ and O₃ increased to 0.16–0.21 nm/s when etched for 120 s (Fig. 13). A possible reason for this increase in etching rate could be the increased surface roughness. For instance, Gorrea et al. [207] demonstrated that the surface roughness of Al₂O₃ deposited from TMA and H₂O increased by two orders of magnitude during chemical stability tests in 1 M KCl. Surface roughness correlates with specific surface area and therefore should influence the contact area between Al₂O₃ and the etchant. Consequently, this should have a direct effect on the etching process.

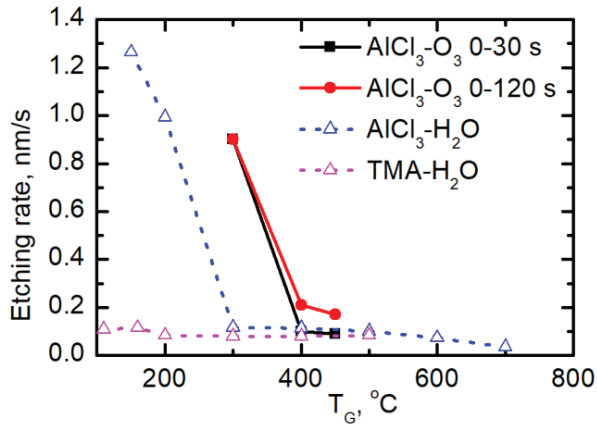


Figure 13. Dependence of the etching rate on T_G of Al₂O₃ films deposited in AlCl₃-O₃ [III], AlCl₃-H₂O [15] and TMA-H₂O [15] processes.

In our etching experiments, however, the surface roughness remained between 0.6 and 1.2 nm for the 6–34 nm-thick Al₂O₃ films deposited from AlCl₃ and O₃. During the 120 s etching of a 34 nm-thick film deposited at 450°C, the surface roughness increased only from 1.2 ± 0.1 to 1.4 ± 0.1 nm, while the etching rate increased by a factor of two. Therefore, the changes in surface roughness were small and could not be the main reason for the increased etching rate in this case.

The etching rate of the TiO₂ films deposited on Si(100) from TiCl₄ and O₃ decreased with increasing T_G from 0.53–0.62 pm/s at 250°C to 0.22–0.49 pm/s at 450°C (Fig. 14). These etching rates were up to 1000 times lower than those measured for Al₂O₃ and comparable to or slightly lower than those of the TiO₂ films deposited in the TiCl₄-H₂O process [15].

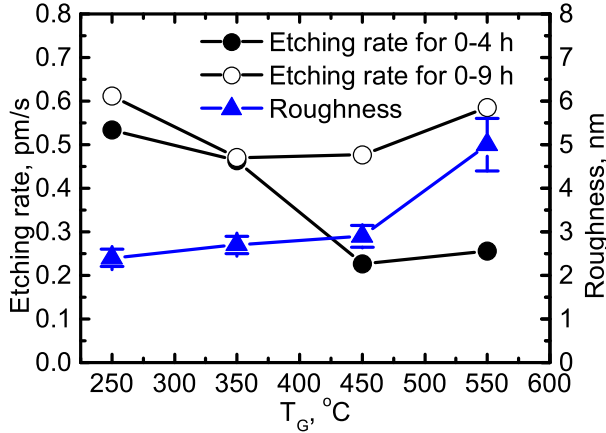


Figure 14. Etching rates and initial surface roughness values of 26–37 nm-thick TiO₂ films deposited at different temperatures [III]. Printed with permissions from Elsevier B. V. (Mater. Chem. Phys.).

The decrease in the etching rate of TiO₂ film correlated, similarly to that of the Al₂O₃ films, with the concentration of chlorine impurities in the films. However, the chlorine concentration was as low as 0.12 at% in the films deposited from TiCl₄ and O₃ at 250°C, and ≤ 0.06 at% in the films deposited at 300°C and higher temperatures. It is hence unlikely that such a low chlorine concentration was the main factor influencing the etching rate of these films. Therefore, the correlation between the etching rate and film thickness, roughness, density, and structure was studied [III]. The etching rate was found to correlate significantly with the surface roughness only for films deposited at 450–550°C (Fig. 14). In this temperature range, the film density decreased from 3.9 ± 0.1 to 3.7 ± 0.1 g/cm³ with the increase of T_G from 450 to 550°C. The lowered density can be related to the less perfect packing of crystallites in the films deposited at 550°C, and therefore is one potential reason for the increased etching rate.

It is worth mentioning that Puurunen et al. [178] reported the reduced chemical resistance for TiO₂ films containing crystallites with a “peculiar nature,” like those obtained in the TiO₂ films deposited from TiCl₄ and O₃ at 550°C (Fig. 11d). This result indicates that the etching rate might depend on the sizes as well as orientations of the crystallites in a film. As the TiO₂ films studied in our wet-chemistry tests were polycrystalline (Fig. 10), the different crystallite (grain) sizes and orientations obtained at different temperatures were considered as possible reasons for the different etching rates. The grain sizes were evaluated from HR-SEM images (Fig. 11) while the crystallite sizes were estimated from the full width at half maximum (FWHM) values of the GIXRD reflections. The HR-SEM images enabled the characterization of the lateral grain sizes, though the possibility that each grain could contain several crystallites had to be accounted for. In contrast, GIXRD allowed the determination of crystallite sizes only in the out-of-plane directions. No obvious

relationship between the etching rates and grain sizes of the as-deposited films could be detected [III], although some films with smaller lateral grain sizes and larger out-of-plane crystallite sizes showed lower etching rates.

Comparing the GIXRD patterns and etching data demonstrated that the decrease of etching rate with increasing T_G correlated with changes in the preferred orientation of the crystallites. In films with randomly orientated crystallites, the intensity ratio of the 004 and 101 anatase reflections was expected to be 0.22 (ICSD, FIZ Karlsruhe, collection code 202242). However, for the 26–37 nm-thick films, this ratio increased from 0.06 to 0.82 with the increase of T_G from 250 to 450°C. In addition, with the increase of the film thickness from 9 to 67 nm, the ratio determined for the films deposited at 450°C increased from 0.3 to 1.1. In both cases, the chemical resistance of the film increased, allowing us to conclude that crystallite orientation had an influence on this property.

5.5 Protective properties of TiO₂ and Al₂O₃ coatings deposited in TiCl₄-O₃ and AlCl₃-O₃ processes on AISI 310

Prolonging the lifetime of the AISI 310 alloy could be one possible application of the TiO₂ and Al₂O₃ thin coatings deposited using the TiO₂-O₃ and AlCl₃-O₃ processes. As such, the barrier properties of these coatings deposited at different temperatures and with various thicknesses will be described in this Chapter. It should be noted that the coating thicknesses reported in this Section were measured for the films grown on Si(100) substrates that were in the reactor simultaneously with the AISI 310 samples. Therefore, the coatings should have similar thicknesses on Si(100) and AISI310, but, according to cross-sectional HR-SEM studies, the thicknesses of ALD Al₂O₃ coatings, can differ by up to 10% owing to the somewhat different nucleation conditions on the different substrates.

5.5.1 Pretreatment of the AISI 310 substrate surfaces before ALD

ALD is a result of successive chemical reactions on a solid surface; therefore, the film growth and resulting properties of coatings are affected by the substrate [208, 209]. Hence, different methods for pretreating the AISI 310 samples were tested, and the best method was selected for the following studies.

In these experiments, a well-known TiCl₄-H₂O ALD process was used to deposit TiO₂ coatings by applying 1000 ALD cycles on samples with different surface pretreatments. Then, the chemical stability of each coating in Solution C (see Section 4.1) at 70°C was investigated. When the pretreatment involved an organic solution such as acetone, isopropyl alcohol, and toluene with or without a following Ar, N₂, Ar/O₂, or H₂ plasma clean, the TiO₂ coatings caused no considerable increase of the acid resistance. Scanning electron microscopy (SEM)

showed that some surface areas staid still contaminated after the treatment (Fig. 15, darker area). According to the energy-dispersive X-ray (EDX) studies, these areas contained different carbon compounds. The surface contamination obviously caused the non-uniform nucleation and growth of the films, and so reduced the adhesion of the coating to the substrate. However, that the plasma treatment did not increase the quality of the TiO₂ coatings is surprising, as there are reports about employing plasma for cleaning stainless steel surfaces before deposition of coatings [210–212]. For instance, Härkönen et al. [212] concluded that the plasma pretreatment increased the corrosion protection properties of the ALD Al₂O₃ coatings deposited on the top of a AISI 52100 low alloy steel sample. Nevertheless, similar problems with carbon contamination were encountered in their work [212]. Moreover, they demonstrated that the plasma cleaning results may vary significantly.

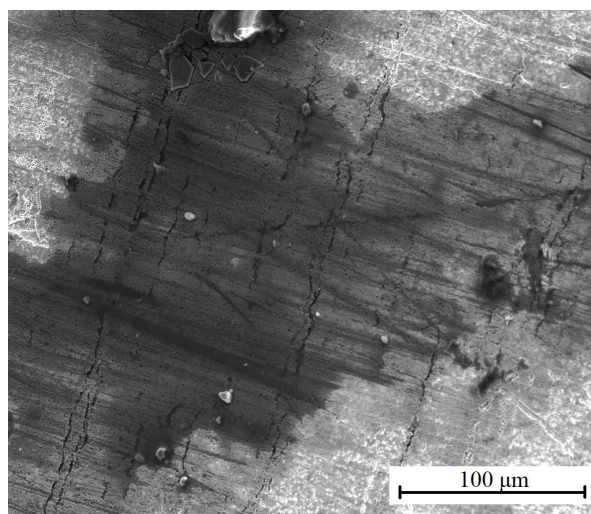


Figure 15. SEM image of the AISI 310 surface after pretreatment in toluene, acetone and isopropyl alcohol followed by treatment in Ar/O₂ plasma for 10 minutes.

In our experiments, the quality and barrier properties of the TiO₂ coatings deposited on AISI 310 samples increased when different acids, i.e., HNO₃, HCl, H₂SO₄, and Solutions A, B, and C (see Section 4.1) were used for the pretreatment. The chemical resistance increased most significantly, when Solution C (15% H₃PO₄, 2% HNO₃, 5% HCl, 5% H₂SO₄, and 73% water) was used for the surface pretreatment at 70°C. This treatment more than doubled the lifetime of the AISI 310 samples. SEM images (Fig. 16) showed that the porous top layer of AISI 310 was removed only during the pretreatment with Solution C. This appeared to be crucially important for releasing the carbon residues from the surface, reducing the surface porosity, and removing the contamination that may be present in the pores.

As demonstrated in Sections 5.3 and 5.4, the growth process and physical properties of the ALD coatings can depend on the material, composition, and

even crystal orientation of the substrate. Therefore, the results obtained for films deposited on other materials and even on other stainless steel alloys could differ. For this reason, treatment in Solution C at 70°C may not be the best choice for other materials. In the present work, however, this pretreatment preceded ALD on AISI 310 in all the experiments performed to test the barrier properties described in the following Sections.

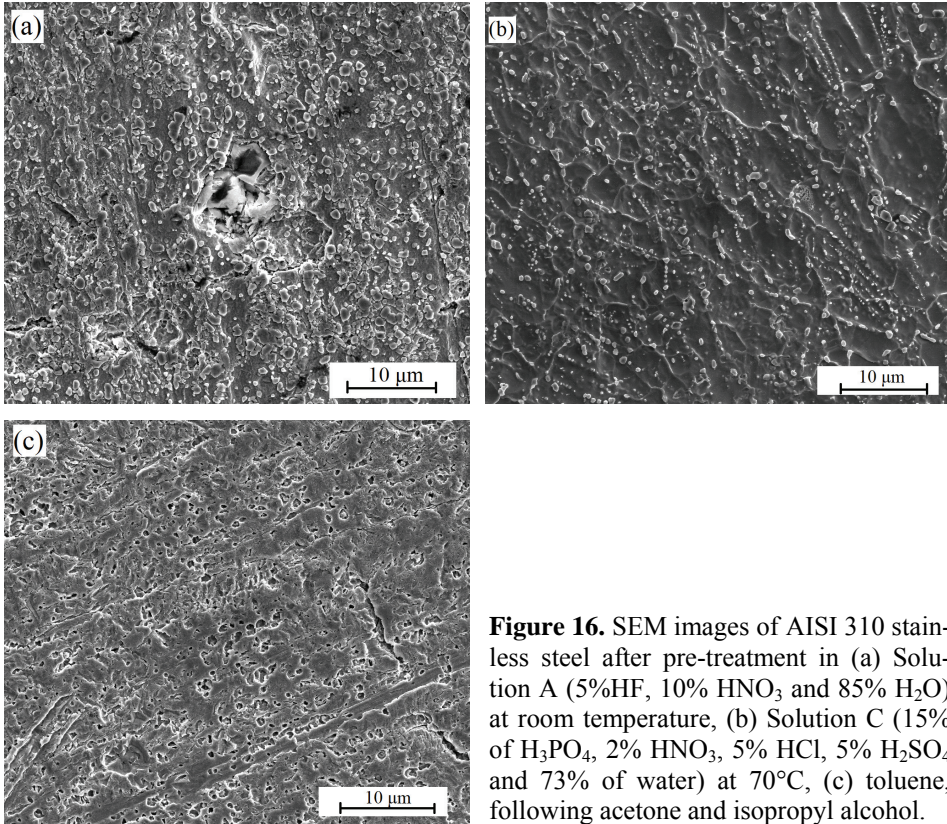


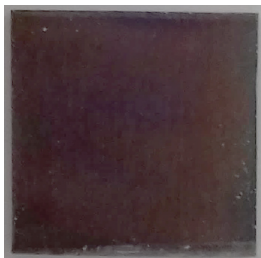
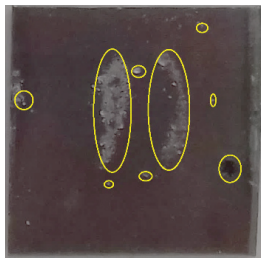
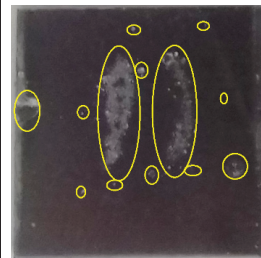

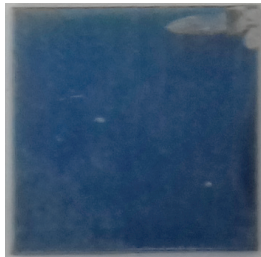
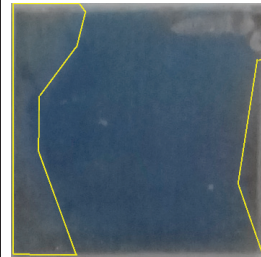


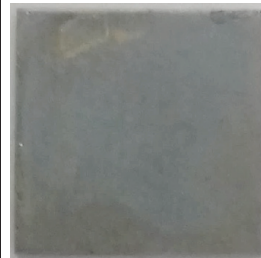
Figure 16. SEM images of AISI 310 stainless steel after pre-treatment in (a) Solution A (5%HF, 10% HNO₃ and 85% H₂O) at room temperature, (b) Solution C (15% of H₃PO₄, 2% HNO₃, 5% HCl, 5% H₂SO₄ and 73% of water) at 70°C, (c) toluene, following acetone and isopropyl alcohol.

5.5.2 ASTM G48-11 pitting tests of AISI 310 samples coated with Al₂O₃ and TiO₂

The pitting corrosion resistance of the materials was evaluated by ASTM G48-11 tests [213]. This test imitates the material performance in seawater and strongly oxidizing chlorine-containing environments with a low pH [213]. In this work, the ASTM G48-11 tests (performance of coatings in 6 mass% FeCl₃ solution) were performed to investigate the influence of T_G and thickness on the protective properties of the coatings deposited on AISI 310 using the TiCl₄-O₃ and AlCl₃-O₃ processes.

Tests lasting 74 h were performed on 27–44 nm-thick TiO₂ coatings deposited at different temperatures. No signs of pitting corrosion appeared when the AISI 310 surface was coated with the 37 nm and 36 nm-thick films deposited at 350°C and 450°C, respectively (Table 4).

Table 4. Results of pitting tests for 26, 36 and 35 nm-thick TiO₂ coatings deposited at 250, 350 and 450°C, respectively, on AISI 310 from TiCl₄ and O₃.

Time T_G , °C	Before	After 26 h	After 74 h
250			
350			
450			

Although the coating deposited at 350°C started to delaminate from one side of the sample after 74 h of testing, this was due to sample handling rather than the lower quality of the coating. The lowest resistance to the 6 mass% FeCl₃ solution was detected for the 44 nm-thick TiO₂ coating deposited at 550°C. In this film, pinhole-type defects appeared during the first hour of testing. After the following 4 h of testing, no TiO₂ coating remained on the surface (image not presented in this work). As for the 27 nm-thick TiO₂ coatings deposited at 250°C, signs of pitting appeared after 26 h (Table 4). These results agree with those of the chemical resistance tests on Si(100) in 80% H₂SO₄ (Section 5.4). In the latter tests, the highest etching rates during the first 4 h were obtained also

for TiO₂ coatings deposited at 250 and 550°C (Fig. 14). A possible explanation for the lower barrier properties obtained for TiO₂ coatings deposited at 250°C on both AISI 310 and Si(100) could be the higher concentration of impurities and unfavorable crystal structure of the coatings compared to those deposited at 350 or 450°C. The higher structural inhomogeneity of the TiO₂ coatings deposited at 550°C (Sections 5.2 and 5.3) could enhance the possibility that the grain boundaries of polycrystalline coatings act as preferential routes for corrosive media and cause the formation of pinholes. It is worth noting that penetration of the etchant into the coating might increase the etching rate, as described in Section 5.4 for the coatings deposited at 550°C on Si(100) (Fig. 14). Similarly, once the 6 mass% FeCl₃ solution has sufficient access to the AISI 310 substrate through the already generated pinholes, the lift-off of the remaining protective layer can occur, as can be seen in Table 4 (after 74 h testing of TiO₂ coatings deposited at 350°C).

To evaluate the effect of coating thickness on the barrier properties of the TiO₂ coatings, the ASTM G48-11 test was conducted on the 9, 19, 36, and 67 nm-thick films deposited on AISI 310 at 450°C (Table 5). The samples coated with 36 and 67 nm-thick TiO₂ layers showed no signs of defect formation during the 74 h tests. However, in the coatings with thicknesses of 9 and 19 nm, pitting corrosion occurred after 26 h (Table 5). In the H₂SO₄ etching tests of the coatings deposited on Si(100) (Section 5.4), the etching rate significantly decreased (from 3.5 to 0.8 pg/mm²/s) with the increase of the coating thickness from 9 to 19 nm, and only slightly increased (from 0.8 to 0.6 pg/mm²/s) with the following increase of the thickness to 67 nm [III]. The somewhat different barrier behavior on AISI 310 is probably due to differences in the thicknesses and structures of the coatings deposited on different substrates.

For the AISI 310 samples with the 31 and 23 nm-thick Al₂O₃ coatings deposited from AlCl₃ and O₃ at 300 and 450°C, respectively, the first traces of corrosion were detected after 4 h of testing. (Table 6). However, the pinhole density was markedly higher in the coatings deposited at 450°C than 300°C. The highest resistance of Al₂O₃ observed in the ASTM G48-11 tests was obtained for a 41 nm-thick coating deposited on the AISI 310 surface at 400°C (Table 6). Nevertheless, the durability of the coating (< 26 h) was more than three times shorter than that of the TiO₂ coatings deposited at T_G values of 300–450°C from TiCl₄ and O₃. The higher resistance of TiO₂ was not surprising, considering the etching rates in H₂SO₄ solution (Section 5.4) and the results reported by Puurunen et al. [178] for performance of Al₂O₃ and TiO₂ in various corrosive environments.

Table 5. Results of ASTM G48-11 pitting tests for TiO₂ coatings deposited on AISI 310 at 450°C from TiCl₄ and O₃ to different thicknesses.

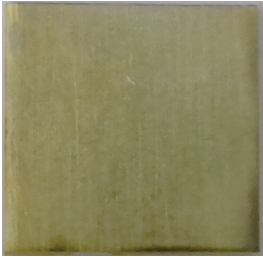
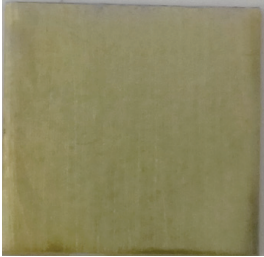



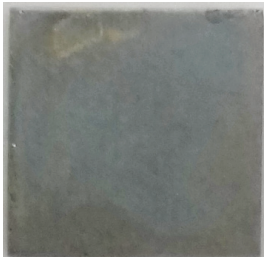
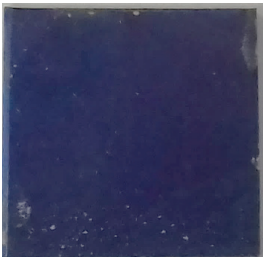
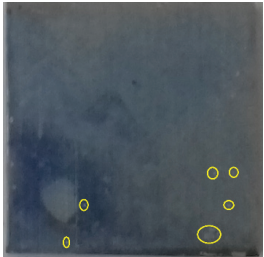
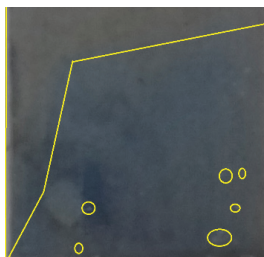

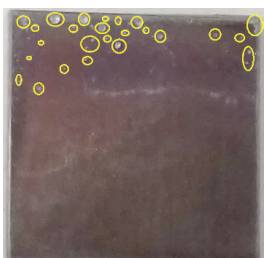
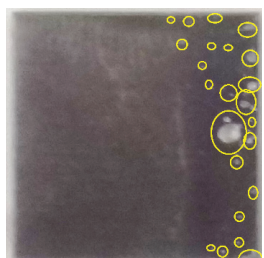
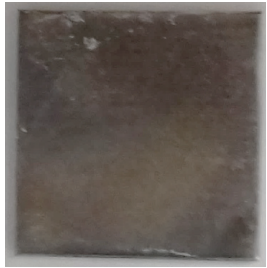
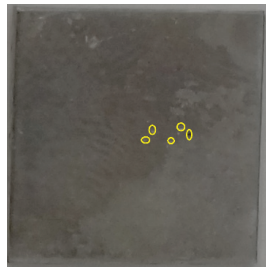
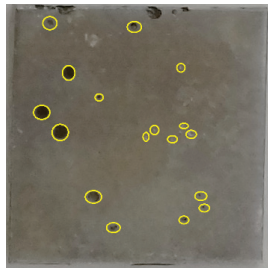
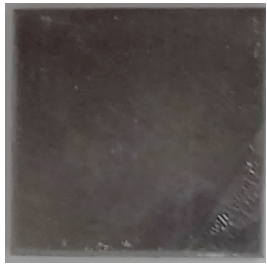
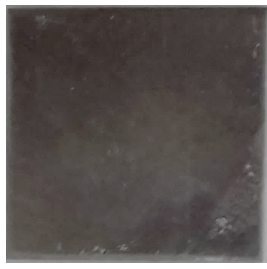
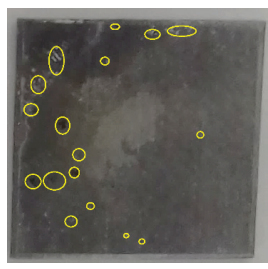

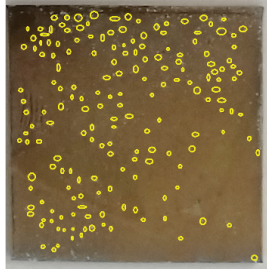
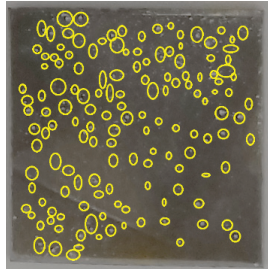
Time Thick- ness	Before testing	After 26 h testing	After 74 h testing
67 nm			
36 nm			
19 nm			
9 nm			

Table 6. Results of ASTM G48-11 pitting tests for 31, 41 and 23 nm-thick Al_2O_3 coatings deposited on AISI 310 from AlCl_3 and O_3 at 300, 400 and 450°C, respectively.

Time T_G , °C	Before testing	After 4 h testing	After 26 h testing
300			
400			
450			

5.5.3 Protective properties of TiO_2 coatings on stainless steel in a wet low-pH environment

To evaluate how the TiO_2 coatings influence the lifetime of the AISI 310 stainless steel samples in a corrosive environment, the mass losses of coated and uncoated samples were measured. The tests were carried out at 110°C in Solution C, which was also chosen for the sample pretreatment, as described in Sections 4.1 and 5.5.1.

During 20 min, the uncoated samples lost about 34% of their mass. For comparison, the mass loss was only 8% for a sample with a 36 nm-thick TiO_2 coating deposited at 450°C; 10% for a sample with a 37 nm-thick TiO_2 coating deposited at 350°C; and 11% for a sample with a 27 nm-thick TiO_2 coating deposited at 250°C [III]. Furthermore, even if the coatings started to fail at weak points during the early stages of etching (Fig. 17), the coatings continued to

protect the samples even after the etchant could access the metal through the defects. Therefore, these films markedly prolonged the possible functional lifetime of the material [III].

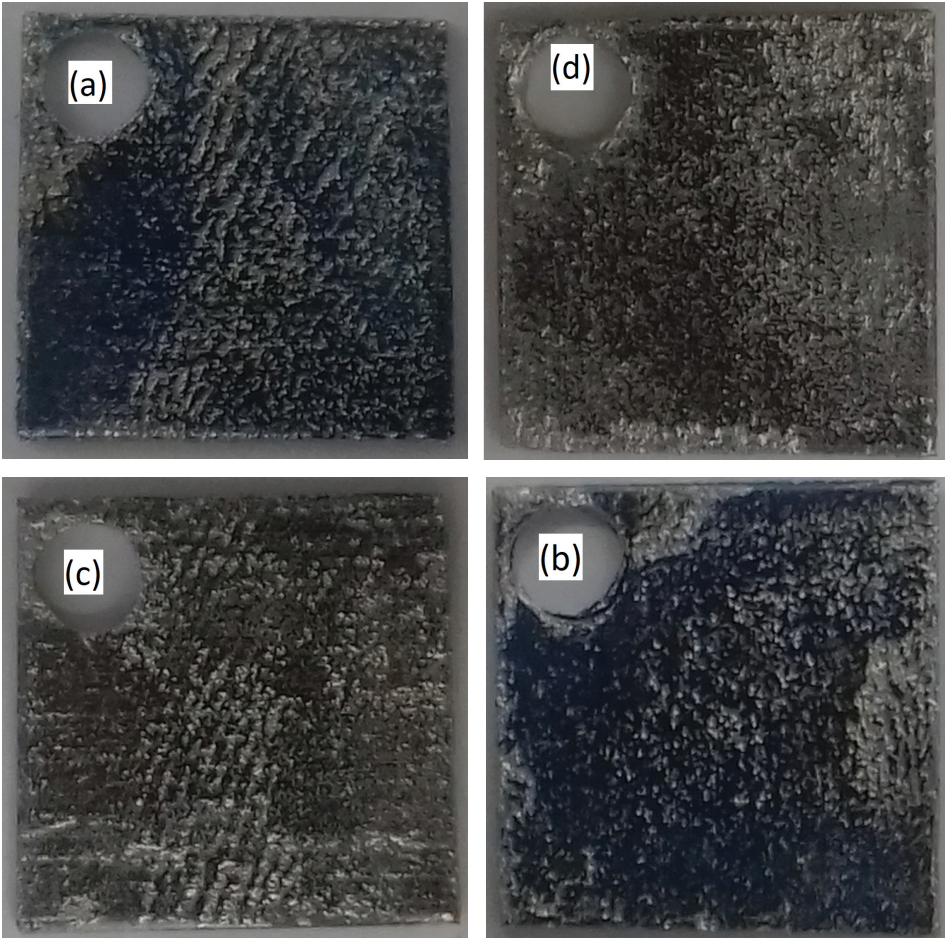


Figure 17. Photographs (a and b) of 36 nm-thick TiO_2 coating deposited at 450°C and (c and d) 37 nm-thick TiO_2 coating deposited at 350°C simultaneously on the both sides of the AISI 310 samples. Images of front sides (a and c) and back sides (b and d) of the coated samples were recorded after 20 min etching in solution C at 110°C .

Similar to the chemical resistance tests of the coatings deposited on Si(100) and ASTM G48-11 pitting tests of the coatings on AISI 310, these tests demonstrated that the highest acid resistance and best barrier properties were achieved with TiO_2 coatings deposited from TiCl_4 and O_3 at 450°C [III]. Furthermore, our studies confirmed that ALD allows the conformal deposition of protective coatings on 3D samples, as no marked differences in performance of coatings on different sides of samples were observed (Fig. 17). The studies also confirmed that the lifetime of coatings deposited on AISI 310 depended on the concentration of weak points. The latter depends on the surface cleanliness, composition, and morphology, as discussed in previous publications [44, 214].

SUMMARY AND CONCLUSIONS

To extend applications of ALD a special reactor for the deposition of thin films on the inner surfaces of hermetic containers was designed and constructed. The reactor was equipped with a QCM for the real-time characterization of the deposition. Also, it contained substrate holders that allowed test samples to be placed at different positions inside the container to study the film properties according to the sample location. Based on the QCM data recorded, it was demonstrated that by using the constructed reactor, the self-limited growth of TiO_2 from TiCl_4 and H_2O was achieved inside the containers. The growth rates of the TiO_2 films deposited at 110°C on Si(100) test samples placed at three positions in the reactor remained between 0.05 and 0.06 nm per cycle, while the growth rate variations were mainly due to differences in the linear speed of the gas flow in the container.

The deposition of TiO_2 films using TiCl_4 and O_3 was demonstrated at substrate temperatures of $225\text{--}600^\circ\text{C}$. Growth rates of up to 0.07 nm per cycle at 275°C were obtained on Si(100) substrates. This growth rate was higher than the corresponding value of 0.06 nm per cycle obtained for the H_2O -based process at the same temperature in the same reactor. The structure of the TiO_2 films depended on the deposition temperature and substrates. Films containing amorphous, anatase, rutile, and/or TiO_2 -II phases were obtained in the TiCl_4 - O_3 ALD process. The ALD of Al_2O_3 films from AlCl_3 and O_3 was also demonstrated at temperatures ranging from 300 to 450°C . All the Al_2O_3 films deposited were amorphous, with lower growth rates than those obtained in the AlCl_3 - H_2O process at the same temperatures. The highest growth rate of 0.07 nm per cycle was observed for the AlCl_3 - O_3 process at a substrate temperature of 350°C .

The chemical stabilities of the TiO_2 and Al_2O_3 films deposited on Si(100) using TiCl_4 - O_3 and AlCl_3 - O_3 precursor combinations were tested in hot H_2SO_4 . According to these tests, the chemical stability depended on the deposition temperature, composition, and structure of the film. The lowest etching rate of 0.2 pm/s (6.3 μm /per year) was obtained for TiO_2 films containing the anatase phase deposited at 450°C . The etching rate of the Al_2O_3 films depended mainly on the amount of chlorine residues in the film, with the lowest values ranging from 0.09 to 0.10 nm/s (2.8–3.2 mm/per year) for films deposited at 450°C .

The protective properties of the TiO_2 and Al_2O_3 films deposited in the TiCl_4 - O_3 and AlCl_3 - O_3 ALD processes on AISI 310 stainless steel were evaluated using the ASTM G48-11 pitting test. In addition, the TiO_2 films were tested by etching in a solution containing 15% H_3PO_4 , 2% HNO_3 , 5% HCl , 5% H_2SO_4 , and 73% H_2O . According to both tests, most of the films deposited on the AISI 310 surface prolonged the lifetime of the material. The best protection was achieved with TiO_2 films with thicknesses of ≥ 36 nm deposited at 450°C . The results allowed us to conclude that the TiO_2 and Al_2O_3 films deposited using the TiCl_4 - O_3 and AlCl_3 - O_3 ALD processes have marked potential to be applied as protective coatings in the future.

SUMMARY IN ESTONIAN

Õhukeste kilede aatomkihtsadestamine, karakteriseerimine ja rakendamine kaitsekattedena

Eesmärgiga avardada aatomkihtsadestamise rakendusvõimalusi konstrueeriti uurimistöö käigus spetsiaalne reaktor, mis võimaldab sadestada kaitsekatteid hermeetiliste anumate sisepindadele. Loodud reaktor varustati sadestamisprotsessi reaallajalist jälgimist võimaldava kvartsresonantskaalumise süsteemiga. Selleks, et koguda infot sadestatud kilede omaduste kohta, varustati reaktor objektihoidjatega, mis võimaldasid paigutada testobjekte erinevatesse kohtadesse anuma sisemusse. Kvartsresonantskaaluga 110°C juures läbi viidud mõõtmiste tulemustest oli võimalik järeldada, et valminud reaktoris saab sadestada kilesid iseküllastuvas, aatomkihtsadestamisele omases režiimis. Proovisadestused, milles lähteainetena olid kasutusel TiCl_4 ja H_2O , näitasid, et TiO_2 kasvukiirus Si(100) katseobjektide pinnal jäi selles seadmes vahemikku 0,05–0,06 nm tsüklis ja tulenevalt erinevast gaasivoo kiirusest anuma sees sõltus objekti asukohast.

Uurimistöös demonstreeriti võimalust TiO_2 aatomkihtsadestamiseks temperatuuridel 225–600°C protsessis, milles lähteaineteks olid TiCl_4 ja O_3 . Suurim kasvukiirus rüni pinnal, 0,07 nm tsüklis, saavutati 275°C juures. See kasvukiirus oli suurem, kui samal temperatuuril TiCl_4 ja H_2O protsessis saadud kasvukiirus, 0,06 nm tsüklis. TiCl_4 - O_3 protsessis sadestatud TiO_2 struktuur sõltus sadestamise temperatuurist ja alusmaterjalist. Erinevatel alustel oli võimalik saada kas amorfseid või kristallilisi anataasi, rutiili ja/või TiO_2 II faasi sisaldavaid kilesid.

Lisaks näidati uurimistöös, et kasvutemperatuuride vahemikus 300–450°C on võimalik sadestada Al_2O_3 kilesid aatomikihtsadestamise protsessis, milles lähteaineteks olid AlCl_3 ja O_3 . Kõik sadestatud Al_2O_3 kiled olid amorfsed ja nende sadestamise kiirused olid veidi väiksemad kui AlCl_3 - H_2O protsessile tüüpilised kasvukiirused samadel aluse temperatuuridel. Suurim Al_2O_3 kasvukiirus, 0,07 nm tsüklis, mõõdeti AlCl_3 - O_3 protsessis aluse temperatuuril 350°C.

Uurimistöös testiti TiCl_4 - O_3 ja AlCl_3 - O_3 protsessides Si(100) pinnale sadestatud TiO_2 ja Al_2O_3 kilede keemilist vastupidavust kuumas 80% väävelhappe lahuses. Saadud tulemuste järgi sõltus keemiline vastupidavus kile sadestamise temperatuurist, koostisest ja struktuurist. Madalaim söövituskiirus, 0,2 pm/s (6,3 µm aastas), mõõdeti TiO_2 kiledel, mis sisaldasid anataasi faasi ja olid sadestatud 450°C juures. Al_2O_3 kilede söövituskiirus sõltus peamiselt kloori jääkide sisaldusest ja oli madalaim, s.o 0,09–0,10 nm/s (2,8–3,2 mm aastas), 450°C juures sadestatud kiledel.

TiCl_4 - O_3 ja AlCl_3 - O_3 protsessides AISI 310 roostevabale terasele sadestatud TiO_2 ja Al_2O_3 katete kaitsvaid omadusi hinnati ASTM G48-11 punktkorrosiooni testides. Lisaks sellele testiti ka TiO_2 katete vastupidavust lahuses, mis sisaldas 15% H_3PO_4 , 2% HNO_3 , 5% HCl , H_2SO_4 ja 73% H_2O . Mõlema eelmainitud testi tulemuste järgi enamuse AISI 310-le sadestatud katetest pikendas roostevaba

terase eluiga. Parim kaitse saadi siis, kui kasutati ≥ 36 nm paksuseid TiO_2 katteid, mis sadestati 450°C juures. Töös kogutud tulemuste järgi on võimalik järeldada, et $\text{TiCl}_4\text{-O}_3$ ja $\text{AlCl}_3\text{-O}_3$ aatomkihtsadestamise protsesside abil valmistatud TiO_2 and Al_2O_3 õhukesed katted omavad suurt rakenduspotentsiaali kaitsekatetes.

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Conference presentation

1. **L. Aarik**, J. Kozlova, M. Merisalu, R. Rammula, I. Netšipailo, J. Aarik, V. Sammelselg, High-Temperature Corrosion Resistive ALD Coatings for Nickel Alloys. Poster presentation at European Materials Research Society (E-MRS) Spring meeting (2011) Nice, France
2. **L. Aarik**, J. Asari, K. Kukli, H. Mändar, A. Tamm, J. Aarik, V. Sammelselg, Properties of ZrO_2 thin films grown in $C_5H_5Zr[N(CH_3)_2]_3-H_2O$ and $ZrCl_4-H_2O$ atomic layer deposition processes. Poster presentation at AVS-ALD & Baltic ALD 2012 - 12th International Conference on Atomic Layer Deposition (2012), Dresden, Germany
3. **L. Aarik**, T. Arroval, V. Sammelselg, J. Aarik, Atomic layer deposition of high-quality nanostructured TiO_2 and Al_2O_3 thin films in hydroxyl-free chloride-based processes. Poster presentation at the 8th International Conference on Surfaces, Coatings and Nanostructured Materials (NANOSMAT-2013) 2013, Granada, Spain.
4. **L. Aarik**, T. Arroval, R. Rammula, H. Mändar, V. Sammelselg, J. Aarik, Titanium dioxide thin films grown from titanium chloride and ozone by Atomic layer deposition. Poster presentation at 8th International conference Functional Materials and Nanotechnologies, (FM&NT) 2013, Tartu, Estonia.

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9. **L. Aarik**, V. Sammelseg, J. Aarik, Using the TiO_2 , Al_2O_3 one layer and multilayer coatings for protecting stainless steel (grade 310). Poster presentation at the 16th International Conference on Atomic Layer Deposition (ALD 2016), 2016, Dublin, Ireland.

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Keelteoskus

Eesti keel, emakeel
Inglise keel, hea
Vene keel, hea
Saksa keel, rahuldav

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