Atomic Layer Deposition of Groups 4 and 5 Transition Metal Oxide Thin Films: Focus on Heteroleptic Precursors.

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Academic Dissertation
To be presented with the permission of the Faculty of Science of the University of Helsinki for public criticism in Auditorium A110 of the Department of Chemistry, A.I. Virtasen aukio 1, on 23.05.2013 at 12 o'clock noon
Helsinki 2013
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Preface

This thesis is based on the experimental work carried out during the year 2010-2012 in the Laboratory of Inorganic Chemistry, University of Helsinki.

I am very grateful to my supervisors Jaakko Niinistö, Mikko Ritala and Markku Leskelä for their help, guidance, as well as their amazing responsiveness and knowledgeability. It was certainly a privilege to learn about ALD within such an exceptional stronghold of knowledge.

I wish to thank my co-workers at the laboratory of inorganic chemistry who have helped me during my thesis: Dr Jani Päiväsaari for his ever kindness and availability in assisting me with technical issue. Dr Kaupo Kukli, for his more than diligent assistance with the electron beam evaporator and electrical characterization. Mikko Heikkilä and Dr. Esa putkonen for their helpfulness and the time they spent teaching me about X-ray diffraction and AFM, respectively.

The research leading to this thesis was funded by the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement number ENHANCE-238409. I wish to thanks the different actors who gave life to this European project. Especially Dr. Harish Parala and Prof. Anjana Devi who spend a tremendous amount of their time making sure ENHANCE was a success. Also, Prof. WMM Kessell, Dr. Susanne Hoffmann-Eifert and Prof. H.D. Wanzenboeck are thanks for welcoming me for short stay at their research facility.

Finally, I would like to thanks the other EHNANCE research fellows for fruitful discussions and collaborations. Among them: Valentino Longo, Matthieu Weber, Yoann Tomczack, Marco Gavagnin, Dr. Daniela Beckermann, Dr. Quentin Simon, Bruno Gouat, Nabeel Aslam, Manish Banerjee and Babu Srinivasan.

Helsinki, May 2013

Timothee Blanquart
Table of Contents

Abstract .............................................................................................................................. 7
List of publications ............................................................................................................. 9
List of abbreviations ......................................................................................................... 10
1. Introduction ................................................................................................................... 12
  1.1 Atomic layer deposition of thin films ........................................................................ 12
  1.2 Groups 4 and 5 transition metal oxide thin films .................................................... 14
  1.3 ALD of groups 4 and 5 oxides thin films ................................................................. 14
    1.3.1 Precursor requirements and oxygen sources .................................................... 14
    1.3.2 ALD of groups 4 and 5 oxides thin films from homoleptic precursors .......... 19
      1.3.2.1 Halides ....................................................................................................... 19
      1.3.2.2 Alkoxides .................................................................................................. 20
      1.3.2.3 Alkylamides ............................................................................................. 21
      1.3.2.4 Amidinates ............................................................................................... 23
      1.3.2.5 Donor functionalized alkoxides ................................................................. 24
      1.3.2.6 ß–diketonates .......................................................................................... 24
    1.3.3 ALD of groups 4 and 5 oxides thin films from heteroleptic precursors ........ 25
      1.3.3.1 Synthesis of heteroleptic precursors ....................................................... 28
      1.3.3.2 Heteroleptic alkoxides .............................................................................. 31
      1.3.3.3 Heteroleptic cyclopentadienyls ............................................................... 33
      1.3.3.4 Heteroleptic alkylamides ........................................................................ 37
      1.3.3.5 Heteroleptic oxo compounds ................................................................... 38
      1.3.3.6 Imide-pyrazolate and halide-silylamide .................................................... 39
      1.3.3.7 Heteroleptic compounds with three ligands ............................................ 39
2. Experimental ................................................................................................................. 42
  2.1 Precursors and film growth ....................................................................................... 42
  2.2 Film characterization ............................................................................................... 43
3. Results and discussion ................................................................. 45

3.1 ALD of group 4 metal oxide thin films ...................................... 45

3.1.1 ALD of titanium oxide from mixed alkylamide-alkoxide and amidinate-alkoxide precursors ......................................................... 45

3.1.2 ALD of zirconium oxide thin films from an alkylamide-guanidinate compound ........................................................................ 47

3.2 ALD of group 5 metal oxide thin films ...................................... 50

3.2.1 ALD of vanadium oxide thin films from a tetraethylmethylamide vanadium precursor .................................................................................. 50

3.2.2 ALD of niobium and tantalum oxide thin films from mixed imides-alkylamides precursors .................................................................. 53

3.2.3 Growth of niobium oxide thin films from mixed imide-alkoxide precursors ................................................................................. 56

4. Conclusions .................................................................................. 57

5. References .................................................................................... 60
Abstract

The atomic layer deposition process (ALD) is an alternative to the chemical vapour deposition (CVD) method that is universally appreciated for its unique advantages such as excellent repeatability, conformity and thickness control at the atomic level. ALD precursor chemistry has mainly been based on homoleptic compounds such as, but not limited to, metal halides, alkylamides or alkoxides. However, these precursors have drawbacks such as possible halide contamination and low thermal stabilities with respect to the alkylamides and alkoxides. Consequently, heteroleptic precursors were investigated as alternatives to the existing homoleptic counterparts, which have led to the development of several advantageous processes. Nevertheless, no thematic review dedicated to heteroleptic precursor and their properties exists and it seems that no coherent strategy has been adopted for the development of heteroleptic precursors.

This thesis gives a brief description of ALD and presents studies on the deposition of thin films of groups 4 and 5 metal oxide films using ALD. A description of the general ALD properties of homoleptic precursors in addition to a review on the thermal ALD of groups 4 and 5 metal oxides from heteroleptic precursors is provided. Trends in the properties of heteroleptic ALD precursors based on a literature review and new experimental data are discussed. Several novel heteroleptic compounds were evaluated for the ALD of thin films of TiO$_2$, ZrO$_2$, Nb$_2$O$_5$ and Ta$_2$O$_5$. The characteristics of these processes were evaluated and the film properties of these oxides were investigated by means of various characterization approaches. The effects of oxygen source, water or ozone, on the film growth characteristics and properties of ZrO$_2$, Nb$_2$O$_5$, and Ta$_2$O$_5$, were also investigated.

Mixed alkoxide-alkylamide and alkoxide-amidinate titanium compounds are liquid at room temperature. They are highly volatile, have excellent reactivity towards water and have high thermal stability. The deposited films exhibit high purity and conformability on high aspect ratio substrates. The growth of thin films of ZrO$_2$ from a heteroleptic alkylamide-guanidinate zirconium precursor was notable in that the films grew in the high permittivity cubic phase and the ozone-based process had a high growth rate. Thin films of VO$_x$ were deposited from the homoleptic vanadium alkylamide precursor, vanadium tetraethylmethylamide. It was found that the structure and oxidation state of the films could be tuned from an amorphous mixture of VO$_2$ and V$_2$O$_5$ to crystalline VO$_2$ or V$_2$O$_5$. This was accomplished by simply exposing the films to heat treatment in different atmospheres, namely air or N$_2$. Finally, alkylamide-imide precursors were investigated for the ALD of Nb$_2$O$_5$ and Ta$_2$O$_5$ thin films.
These precursors are liquid at room temperature, and exhibited high thermal stabilities compared with the earlier known niobium and tantalum ALD precursors. The alkylamide-imide precursors studied had high volatility and excellent reactivity towards both water and ozone. The deposited films were smooth, uniform, and contained only low amounts of impurities.
List of publications

In addition to the present review, this thesis includes the following publications, which are referred to in this text by their corresponding Roman numerals (I-VI).


### List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>acac</td>
<td>Acetylacetonate, $\text{CH}_3\text{C(O)CH}_2\text{C(O)CH}_3$</td>
</tr>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope/microscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>amd</td>
<td>Amidinate, $\text{NR(CR}^\prime\text{)NR}$</td>
</tr>
<tr>
<td>Amyl</td>
<td>1,1-dimethylpropyl, $\text{C(CH}_3\text{)}_3\text{CH}_3$</td>
</tr>
<tr>
<td>CHT</td>
<td>Cycloheptiene, $\text{C}<em>7\text{H}</em>{14}$</td>
</tr>
<tr>
<td>Cp</td>
<td>Cyclopentadienyl, $\text{C}_5\text{H}_5$</td>
</tr>
<tr>
<td>C-V</td>
<td>Capacitance-voltage</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary metal–oxide–semiconductor</td>
</tr>
<tr>
<td>dmae</td>
<td>Dimethylaminoethoxide, $\text{OC}_2\text{H}_5\text{N(CH}_3\text{)}_2$</td>
</tr>
<tr>
<td>DRAM</td>
<td>Dynamic random access memory</td>
</tr>
<tr>
<td>DL</td>
<td>Detection limit</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl, $\text{C}_2\text{H}_5$</td>
</tr>
<tr>
<td>GI</td>
<td>Grazing incidence</td>
</tr>
<tr>
<td>GR</td>
<td>Growth rate</td>
</tr>
<tr>
<td>guan</td>
<td>Guanidinate, $\text{NR(CNR}^\prime\text{R}^\prime\prime\text{)NR}$</td>
</tr>
<tr>
<td>HTXRD</td>
<td>High temperature X-ray diffraction</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-voltage</td>
</tr>
<tr>
<td>iPr</td>
<td>Isopropyl, $-\text{CH(CH}_3\text{)}_2$</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl, $-\text{CH}_3$</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
</tr>
<tr>
<td>MIM</td>
<td>Metal-insulator-metal</td>
</tr>
<tr>
<td>mmp</td>
<td>1-methoxy-2-methyl-2-propanolate, $\text{OCMe}_2\text{CH}_2\text{OMe}$</td>
</tr>
<tr>
<td>MOSFET</td>
<td>Metal oxide semiconductor field effect transistor</td>
</tr>
<tr>
<td>mp</td>
<td>Methyl pentoxide, $\text{C}<em>5\text{H}</em>{10}(\text{CH}_3)$</td>
</tr>
<tr>
<td>PEALD</td>
<td>Plasma enhanced ALD</td>
</tr>
<tr>
<td>Py</td>
<td>Pyridine, $\text{C}_3\text{H}_5\text{N}$</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz crystal microbalance</td>
</tr>
<tr>
<td>QMS</td>
<td>Quadrupole mass spectrometry</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford backscattering spectrometry</td>
</tr>
<tr>
<td>rms</td>
<td>Root mean square</td>
</tr>
<tr>
<td>SE</td>
<td>Spectroscopic ellipsometry</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>tBu</td>
<td>Tert-butyl, C(CH$_3$)$_3$</td>
</tr>
<tr>
<td>thd</td>
<td>2,2,6,6-tetramethyl-3,5-heptanedione, C$<em>{11}$H$</em>{20}$O$_2$</td>
</tr>
<tr>
<td>ToF-ERDA</td>
<td>Time-of-flight elastic recoil detection analysis</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary ion mass spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRR</td>
<td>X-ray reflectivity</td>
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</table>
1. Introduction

1.1 Atomic layer deposition of thin films

Thin films are material layers that typically range in thickness from one monolayer of atoms or molecules to several micrometres. Thin films are extremely important in modern technology. All electronic devices rely on thin film technologies. For example, thin films are essential for the fabrication of integrated circuits in which a large number of transistors and other devices are simultaneously prepared on a single silicon wafer. Moreover, thin films are needed in the fields of optoelectronics, optics and nanotechnology.

There are many different methods used for the deposition of thin films, physical methods such as sputtering, pulsed laser deposition, and e-beam evaporation. There are also chemical methods for thin film deposition such as sol-gel and chemical vapour deposition (CVD). A particularly suitable method for making uniform conformal layers is atomic layer deposition (ALD). The ALD process typically deposits thin layers of solid materials by using two or more different vapour-phase reactants. The different reactants are sequentially pulsed onto the substrate surface while being kept separate by purging with an inert gas. Gas phase reactions are prevented by the removal of the excess of the reactants and their reaction by-products. In the case of metal oxide film growth, the complete ALD growth cycle comprises: the metal precursor exposure phase, the first purging period, oxygen source exposure (ozone or water), and the second purging phase.

The precursor molecules chemisorb or react with the surface groups until saturated, and thus after the formation of the chemisorbed layer no further adsorption takes place. Therefore, the growth proceeds in a self-limiting manner. The ALD reactions produce coatings with very uniform thickness due to this self-limiting characteristic even into demanding high aspect ratio 3D structures. Other advantages of the step-wise deposition growth are high reproducibility and good thickness control, which are achieved by simply varying the number of cycles.

Additionally to the traditional thermally driven ALD, plasma enhanced ALD (PEALD) is an energy-enhanced method that has been recently investigated. In PEALD, the surface is exposed to the species generated by a plasma discharge during the reactant step. PEALD allows typically lower deposition temperature as compared to thermal ALD. Moreover, plasma assisted ALD has been employed successfully to the deposition of several metal thin films that cannot be deposited by thermal ALD. However, PEALD also faces certain challenges such as the development of suitable equipment for the industrial scale-up of the
processes, plasma-induced damage to the surface and often lower conformality on nonplanar substrates.\textsuperscript{8}

Although one full cycle in ALD ideally deposits a monolayer of material, many factors affect the overall growth rate (GR). Adsorption and desorption equilibria in addition to reaction kinetics play an important role in the net deposition rates. Moreover, the size and number of ligands in the metal precursor often limit the maximum possible adsorption density during the deposition phase through steric effects. Therefore, the GR observed in ALD is generally only a fraction of a monolayer. On the other hand, thermal decomposition or condensation of the precursor can increase the GR but should be avoided because the growth would lose its self-limiting characteristic.

An ALD process must operate within a temperature range so that the film growth is self-limiting, viz., with large enough precursor doses the GR becomes saturated to a constant value may or may not be temperature independent.\textsuperscript{2} An ALD process’s quality and versatility is largely based on the width of such a temperature range which in turn depends on the surface chemistry taking place during the growth.

Dense and pure films usually require high deposition temperatures and therefore high thermal stabilities of their respective precursors. However, certain applications such as coating on polymers and biomaterials require low deposition temperatures and therefore the lower end of the ALD process temperature range is also an important criterion. Of course, high GR, and consequently high throughput, is very important for industrial applications. Furthermore, the development of a preferential phase and/or oxidation state might be an important characteristic of a given process that is desired and sought for a certain application. For example, the rutile and anatase phase of TiO\textsubscript{2} for microelectronic\textsuperscript{9} and catalysis applications,\textsuperscript{10} respectively. Another example is the preferable formation of the high permittivity of cubic and tetragonal phases of ZrO\textsubscript{2} and HfO\textsubscript{2} for dynamic random access memory (DRAM) capacitors.

Given the importance of thin films, intense effort has been devoted to develop more efficient precursors for new ALD processes. The development and evaluation of new precursors with high thermal stabilities that allow wide temperature ranges of self-limiting growth and ensures the rapid deposition of high quality films is a key factor for further industrial applications of ALD.
1.2 Groups 4 and 5 transition metal oxide thin films

The oxides of group 4 metals (Ti, Zr, Hf) exist as either binary oxides or mixed with other oxides, have been of great interest in the development of high permittivity (high-k) insulators for microelectronics. The uses of these oxides in particular include dielectrics in complementary metal oxide semiconductor (CMOS) transistors and in DRAM capacitors. Currently, Zr- and Hf-based oxide materials are used in high volume manufacturing. Hitherto, they have achieved the objective of continuously shrinking semiconductor devices. In addition, TiO$_2$ thin films are of considerable interest for microelectronic applications, and thus strontium titanate (SrTiO$_3$) and the rutile phase of TiO$_2$ are amongst the most promising dielectric materials for the next generation of DRAMs. Additionally, TiO$_2$ thin films have applications as self-cleaning and antimicrobial surfaces due to their photocatalytic activity.

The metallic oxides Nb$_2$O$_5$ and Ta$_2$O$_5$ are high-k materials with high band gaps and have applications as antireflective coatings, solid-state ion sensors and electrochromic devices. They have also been studied for their use as diffusion barriers and dielectric layers. The properties of vanadium oxide thin films largely depend on their stoichiometry, structure and morphology. However, vanadium oxide exists in many stable oxidation states and in several polymorphic forms. Therefore, depositing thin films of vanadium oxide with a specific oxidation state/structure is an important objective. When investigating vanadium oxide thin films, particular attention has been focused on +4 and +5 oxidation states. Vanadium pentoxide (V$_2$O$_5$) has applications as an electrode in lithium ion batteries and as a catalyst support material. An interesting feature of vanadium dioxide (VO$_2$) is the well-known semiconductor-to-metal phase transition that occurs close to 67 °C and this transition is accompanied by an abrupt change in its resistivity and near-infrared transmission. This property makes VO$_2$ of interest for smart windows, resistive memories and switches in microelectronics.

1.3 ALD of groups 4 and 5 oxides thin films

1.3.1 Precurso requirements and oxygen sources

Precursors used for ALD need to satisfy several requirements, especially those of having sufficient volatility and thermal stability and high reactivity. ALD precursors may be solid,
liquid or gaseous. However, solid precursors have certain disadvantages as they have low volatility and unwanted particles might be transported and incorporated into the films by the carrier gas with detrimental effects on the film properties. Therefore, either liquid or gas precursors are preferred, if these are available.

ALD-precursors should be sufficiently volatile. Although, the required vapour pressure varies greatly with reactor’s operating pressure and geometry, a vapour pressure of 0.1 Torr in the source condition can be considered as minimum requirement. Evaporation should also occur in a single step without any thermal decomposition.\textsuperscript{2,4}

Self-limiting growth can generally take place only when the precursor does not decompose, which is in contrast to CVD-type growth. Decomposition is thermally activated and increases exponentially with increasing temperature.\textsuperscript{2} Therefore, thermal stability of a precursor is a crucial constraint that determines the higher end of the ALD process window. As long as the self-decomposition proceeds at only a modest rate it is likely to be a surface reaction limited process rather than diffusion limited activity, thus it maintains film uniformity and conformality. Consequently, the extent to which precursor self-decomposition can be tolerated is highly application dependent.\textsuperscript{4}

Aggressive and also complete reactions are desired. Aggressive reactions ensure rapid completion of the surface reaction, and therefore short cycle times, whereas complete reactions should ensure that no impurities are left in the films.\textsuperscript{2}

The growth reaction must not result in the formation of reactive by-products. In the most severe cases reactive by-products can etch the film material and thereby provoke non-uniformity and low GR.\textsuperscript{30,31} Moreover, reactive by-products may reabsorb on the surface and occupy reactive sites leading to surface passivation.\textsuperscript{4}

Some ALD processes may exhibit a so-called “ALD-window”.\textsuperscript{32} An ALD-window is a temperature range with a constant GR. However, the presence of an ALD-window in a process does not guarantee that self-limiting growth will take place within this temperature range. Although the linearity of the thickness as a function of the number of cycles is a typical feature of self-limiting growth process, it does not necessarily predict that self-limiting growth will take place. Only the study of the GR as a function of the precursor pulse or \textit{in situ} monitoring of the growth may confirm whether self-limiting ALD growth has actually occurred.
Unfortunately, many studies reported ALD processes and claimed that self-limiting growth had indeed occurred, solely based on the observation of an ALD-window and/or the linearity of the thickness versus the number of cycles. This assumption is incorrect and complicates a literature review because many of these studies probably actually reported on CVD processes. The processes for which self-limiting growth was not proved by the study of the GR as a function of the precursor pulse, and/or in situ study, or failed to report it, are all denoted with \( n \) in the following tables. These table(s) summarise the reporting of the basic ALD properties of groups 4 and 5 metal precursors in the literature relevant to this thesis.

Figure 1 shows a list of the different ligands used as ALD precursors. The following section will describe their uses as ALD precursors for the thermal ALD of groups 4 and 5 metal oxides and describe the respective precursor’s general properties.

Several oxygen sources, such as \( \text{H}_2\text{O} \), \( \text{O}_3 \), \( \text{O}_2 \), \( \text{N}_2\text{O} \), \( \text{H}_2\text{O}_2 \), oxygen radicals, and metal alkoxides, have been used in the ALD of metal oxide thin films.\(^7\) However, water and ozone have been by far the most common oxygen precursors for ALD. The choice of the oxygen source should be made according to the targeted application. For example, when considering high-k materials, the oxidative power of the oxygen source towards the bare Si surface is an important parameter. Additional growth of low permittivity layers, such as the \( \text{SiO}_x \) interfacial layer, should be minimized when attempting to obtain high permittivity dielectric layer. It has been reported that ozone, can cause the formation of an interfacial layer on H-terminated silicon substrate because of its strong oxidizing power.\(^{33,34}\) For this reason, ozone as a strong oxidizer may not be the most suitable oxygen source for the ALD of high k-oxides for CMOS applications. However, ozone efficiently burns the ligands during the process.\(^{35-37}\) This in turn often leaves lower amounts of impurities that produces cleaner and denser films with improved electrical properties than those films that had been deposited with water as the oxygen source.\(^{38,39}\) Another reason to prefer ozone instead of water as the oxygen source is the long purging required with water due to the strong interaction between the polar water molecule and oxide surface, in particular at low deposition temperature and with high aspect ratio structure.\(^4\)

Water-based processes rely upon the presence of hydroxyl groups on the surface and also the high reactivity of the chemisorbed metal precursor towards water. When water is used as the oxygen source, the ligand-exchange involves the breaking of the metal-ligand bonds of the precursor and also the breaking of an O-H bond, which forms both an M-O bond and an L-H bond.\(^{40}\) Such ligand exchanges are common in the ALD of high-k dielectric products.
The strengths of the bonds that dissociate and form during the ALD reactions directly determine the thermodynamics of the reaction and, less directly, influence the rate of reaction per se.\textsuperscript{50} If the metal precursor is not reactive enough towards the oxygen source, a stronger oxygen source such as ozone must be used to deposit a good quality film.

The growth properties of a given precursor are often different depending on whether ozone or water is used as the oxygen source. Unfortunately, only a few studies report the investigation of the growth mechanism of ozone-based processes as compared to the number of reports on the water-based process.\textsuperscript{40} Moreover, the surface chemistry is much more complex with ozone and involves combustion of the ligands during the ozone pulse.
Figure 1. Overview of the classes of ligands used as precursors for the ALD of groups 4 and 5 metal oxides (mmp: 1-methoxy-2-methyl-2-propanolate, dmae: dimethylaminoethoxide M: metal atom).
1.3.2 ALD of groups 4 and 5 oxides thin films from homoleptic precursors

1.3.2.1 Halides

The metal halides consist of a metal atom that is directly bonded to halogen atoms (F, Cl, Br or I). Table 1 presents a list of selected halide precursors for the ALD of groups 4 and 5 metal oxides and summarizes their basic ALD properties. The beneficial characteristics of many metal halides include their high thermal stability over a wide temperature range and good reactivity. Furthermore, they are readily available and/or can be easily synthesized. Unfortunately, metal halides are usually solids with low volatilities and their use can lead to possible halide incorporation into the films. However, TiCl₄ is liquid at room temperature and it has a relatively low evaporation temperature. In the presence of water as the oxygen source, TiCl₄ is a rather successful precursor for the ALD of TiO₂.⁴¹

Metal chlorides produce HCl as a by-product that can etch the film and cause non-uniform film thicknesses. Similarly, the HCl by-product also corrodes reactors. In the ALD of Ta₂O₅ and of Nb₂O₅, thin films the failure of the metal chloride precursors and water processes was reportedly due to the formation of volatile MOCl₃.³⁰,³¹

\[\text{M}_2\text{O}_5 + \text{MCl}_5 (g) \rightarrow 5 \text{MOCl}_3 (g). \text{ (M= Nb, Ta)} \]  

Fluorides were also investigated but they usually have very low volatilities, and HF is a corrosive and hazardous by-product.⁴²-⁴⁴ Transition metal iodides do not offer significant advantages over the chlorides.⁴⁵-⁴⁷ In the ALD of TiI₄ and of ZrI₄, in which a solution of H₂O-H₂O₂ was used as the oxygen source, an entirely self-limiting growth mode could not be achieved, supposedly because of the decomposition of the metal iodide on the oxide surface.⁴⁶,⁴⁷
Table 1. Selected published processes for the thermal ALD of groups 4 and 5 metal oxides from halide precursors.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>O source</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>GR at $T_{\text{max}}$</th>
<th>Impurities (at.%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiF$_4$</td>
<td>H$_2$O</td>
<td>400</td>
<td>0.80 borosilicate</td>
<td>NR</td>
<td>42</td>
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<tr>
<td>TiCl$_4$</td>
<td>H$_2$O</td>
<td>500</td>
<td>0.5</td>
<td>Cl&lt;0.5, H=0.1</td>
<td>41</td>
</tr>
<tr>
<td>ZrCl$_4$</td>
<td>H$_2$O</td>
<td>500</td>
<td>0.53</td>
<td>Cl&lt;0.5, H&lt;0.4</td>
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</tr>
<tr>
<td>HfI$_4$</td>
<td>H$_2$O</td>
<td>500</td>
<td>0.50</td>
<td>Cl&lt;DL, (RBS)</td>
<td>45</td>
</tr>
<tr>
<td>ZrI$_4$</td>
<td>H$_2$O+H$_2$O$_2$</td>
<td>CVD-growth</td>
<td>46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiI$_4$</td>
<td>H$_2$O+H$_2$O$_2$</td>
<td>CVD-growth</td>
<td>47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HfCl$_4$</td>
<td>H$_2$O</td>
<td>500</td>
<td>0.50</td>
<td>Cl&lt;1.0, H&lt;0.4</td>
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<tr>
<td>NbCl$_5$</td>
<td>H$_2$O</td>
<td>CVD-growth</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NbF$_5$</td>
<td>H$_2$O</td>
<td>225$^a$</td>
<td>1.33</td>
<td>NR</td>
<td>44</td>
</tr>
<tr>
<td>TaF$_5$</td>
<td>H$_2$O</td>
<td>450$^a$</td>
<td>1.25</td>
<td>F&lt;4.0</td>
<td>42</td>
</tr>
<tr>
<td>TaCl$_5$</td>
<td>H$_2$O</td>
<td>250</td>
<td>0.70</td>
<td>Cl&lt;0.1</td>
<td>31</td>
</tr>
</tbody>
</table>

NR: not reported  
$T_{\text{max}}$: maximum deposition temperature at which self-limiting growth was reported  
GR: growth rate reported in Å/cycle  
RBS: Rutherford backscattering spectrometry  
$^a$: no evidence of self-limiting growth reported

1.3.2.2 Alkoxides

Table 2 presents a list of selected alkoxide precursors for the ALD of groups 4 and 5 metal oxides and summarizes their fundamental ALD properties. Alkoxide precursors already possess M-O bonds and consequently the growth mechanism relies upon ligand exchange reactions with water to maintain the same number of M-O and O-H bonds. Thus these reactions have small enthalpic driving forces.\(^{50}\)

Alkoxide ligands must be relatively bulky to achieve sufficient volatilities and have low melting points; although a bulky ligand may actually hinder the film growth due to steric hindrance effects. Moreover, the bulkier the ligands, the lower the thermal stability of the precursor, as demonstrated by the in-situ decomposition study on titanium alkoxide precursors (Figure 2).\(^{51}\) Therefore, precursors with bulky alkoxide ligands are usually associated with high carbon contamination. For example, a carbon content as high as 8 at.% was reported in the case of the Hf(OtBu)$_2$/O$_3$ process.\(^{52}\) In general, the self-limiting growth using alkoxides has been limited to well below 300 °C.\(^{52-57}\)

20
Table 2. Selected published processes for the thermal ALD of groups 4 and 5 metal oxides from alkoxide precursors.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Oxygen source</th>
<th>$T_{\text{max}}$ ($^\circ$C)</th>
<th>GR at $T_{\text{max}}$</th>
<th>Impurities (at.%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(O'Pr)$_4$</td>
<td>H$_2$O</td>
<td>250</td>
<td>0.30</td>
<td>H&lt;0.4</td>
<td>53</td>
</tr>
<tr>
<td>Ti(OEt)$_4$</td>
<td>H$_2$O</td>
<td>250</td>
<td>0.35</td>
<td>C&lt;DL (XPS, 300$^\circ$C) H&lt;0.3</td>
<td>54</td>
</tr>
<tr>
<td>Zr(O'Pr)$_4$</td>
<td>H$_2$O</td>
<td>CVD-growth</td>
<td></td>
<td></td>
<td>55</td>
</tr>
<tr>
<td>Hf(mp)$_4$</td>
<td>H$_2$O</td>
<td>250</td>
<td>0.80</td>
<td>4.0&lt;C&lt;5.0, 14&lt;H&lt;18</td>
<td>56</td>
</tr>
<tr>
<td>Hf(O'Bu)$_4$</td>
<td>O$_3$</td>
<td>250$^n$</td>
<td>0.24</td>
<td>C=8.0, H=5.5</td>
<td>52</td>
</tr>
<tr>
<td>Nb(OEt)$_5$</td>
<td>H$_2$O</td>
<td>230</td>
<td>0.28</td>
<td>C&lt;0.1</td>
<td>57</td>
</tr>
<tr>
<td>Ta(OEt)$_5$</td>
<td>H$_2$O</td>
<td>250</td>
<td>0.40</td>
<td>H=4.0, C=3.0</td>
<td>58</td>
</tr>
</tbody>
</table>

NR: not reported  
$T_{\text{max}}$: maximum deposition temperature at which self-limiting growth was reported  
GR: growth rate reported in Å/cycle  
mp: methyl pentoxide  
n: no evidence of self-limiting growth reported

Figure 2. QMS study on the thermal decomposition of Ti(OCH$_3$)$_4$, Ti(OC$_2$H$_5$)$_4$, Ti(OCH(CH$_3$)$_2$)$_4$ and Ti(OC(CH$_3$)$_3$)$_4$ as a function of the deposition temperature.$^{51}$ (reproduced with the permission of Dr. Antti Rahtu)

1.3.2.3 Alkylamides

Alkylamide precursors have relatively weak M-N bonds and their by-products have strong N-H bonds. Therefore, they can be used in low temperature oxide processes when required.$^{50}$ Unfortunately, another consequence of the weakness of the M-N bond is the limitation of their low thermal stabilities. Table 3 presents a list of selected alkylamide precursors for the ALD of groups 4 and 5 metal oxides and summarizes their fundamental ALD properties.
Alkylamides have good reactivity towards both water and ozone. Alkylamides are generally found as liquids that have high volatilities and low melting points. Moreover, carbon contamination in the alkylamide ALD processes has been reportedly low due to the absence of metal-carbon bond.\textsuperscript{59-63} Similarly, nitrogen contamination was also reported to be low in the alkylamide ALD process.\textsuperscript{64-68} Surprisingly, the hafnium compounds Hf(NEtMe)\textsubscript{4} and Hf(NMe\textsubscript{2})\textsubscript{4} did cause notable carbon contamination, between 2 and 6 at.\%, when used with water as the oxygen source.\textsuperscript{44,69,70}

The titanium alkylamides had lower growth rates, 0.25–0.65 Å/cycle,\textsuperscript{71} compared to the other alkylamides of groups 4 and 5. Otherwise, the reported growth rates of ZrO\textsubscript{2}, HfO\textsubscript{2}, VO\textsubscript{x} and Ta\textsubscript{2}O\textsubscript{5} from their alkylamide precursors were rather high, typically between 0.6 and 0.9 Å/cycle.\textsuperscript{52,64-70} Interestingly, the ALD of ZrO\textsubscript{2} from alkylamides led to the growth of the high permittivity cubic phase of ZrO\textsubscript{2}.\textsuperscript{64} Unfortunately, HfO\textsubscript{2} thin films deposited from hafnium alkylamide precursors do not have the same tendency to form the cubic phase; instead they form the monoclinic phase.\textsuperscript{69,70}

If a given targeted application, such as coating on polymers and biomaterials, requires a low deposition temperature, alkylamide compounds are certainly a very advantageous class of precursors.
Table 3. Selected published processes for the thermal ALD of groups 4 and 5 metal oxides from alkylamide precursors.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Oxygen source</th>
<th>( T_{\text{max}} ) (°C)</th>
<th>GR at ( T_{\text{max}} )</th>
<th>Impurities (at.%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(NMe(_2))(_4)</td>
<td>H(_2)O</td>
<td>200(^{\text{a}})</td>
<td>0.60</td>
<td>NR</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>O(_3)</td>
<td>225(^{\text{a}})</td>
<td>0.65</td>
<td>NR</td>
<td>71</td>
</tr>
<tr>
<td>Ti(NEt(_2))(_4)</td>
<td>H(_2)O</td>
<td>250(^{\text{a}})</td>
<td>0.25</td>
<td>NR</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>O(_3)</td>
<td>225(^{\text{a}})</td>
<td>0.40</td>
<td>NR</td>
<td>71</td>
</tr>
<tr>
<td>Ti(NEtMe)(_4)</td>
<td>H(_2)O</td>
<td>225(^{\text{a}})</td>
<td>0.40</td>
<td>NR</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>O(_3)</td>
<td>225(^{\text{a}})</td>
<td>0.55</td>
<td>NR</td>
<td>71</td>
</tr>
<tr>
<td>Zr(NMe(_2))(_4)</td>
<td>H(_2)O</td>
<td>250(^{\text{a}})</td>
<td>0.96</td>
<td>C&lt;1.0, N&lt;0.2</td>
<td>64</td>
</tr>
<tr>
<td>Zr(NEt(_2))(_4)</td>
<td>H(_2)O</td>
<td>350(^{\text{a}})</td>
<td>0.96</td>
<td>C&lt;1.0, N&lt;0.2</td>
<td>64</td>
</tr>
<tr>
<td>Zr(NEtMe)(_4)</td>
<td>H(_2)O</td>
<td>300</td>
<td>0.90</td>
<td>C&lt;1.0, N&lt;0.2</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>O(_3)</td>
<td>&lt;300</td>
<td>1</td>
<td>C&lt;1 at 300 °C</td>
<td>65</td>
</tr>
<tr>
<td>Hf(NMe(_2))(_4)</td>
<td>H(_2)O</td>
<td>250</td>
<td>0.80</td>
<td>C=1.5, N=0.7, H=6</td>
<td>69</td>
</tr>
<tr>
<td>Hf(NEt)(_4)</td>
<td>O(_3)</td>
<td>300</td>
<td>1.4</td>
<td>C=0.6</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>H(_2)O</td>
<td>250</td>
<td>0.93</td>
<td>C=6.0, N=0.7, H=1.5</td>
<td>70</td>
</tr>
<tr>
<td>Hf(NEtMe)(_4)</td>
<td>O(_3)</td>
<td>300</td>
<td>0.86</td>
<td>C=2.5, N=0.8, H=2.8</td>
<td>52</td>
</tr>
<tr>
<td>V(NEtMe)(_4)</td>
<td>H(_2)O</td>
<td>175</td>
<td>0.80</td>
<td>C=3.8, N=2.8</td>
<td>III</td>
</tr>
<tr>
<td></td>
<td>O(_3)</td>
<td>175</td>
<td>0.45</td>
<td>C,N&lt;DL (XPS)</td>
<td>72</td>
</tr>
<tr>
<td>Ta(NMe)(_5)</td>
<td>H(_2)O</td>
<td>250</td>
<td>0.85</td>
<td>C,N&lt;1.0</td>
<td>68</td>
</tr>
<tr>
<td>Ta(NEt)(_5)</td>
<td>H(_2)O</td>
<td>250</td>
<td>0.65</td>
<td>C,N&lt;0.2</td>
<td>67</td>
</tr>
</tbody>
</table>

NR: not reported

\( T_{\text{max}} \): maximum deposition temperature at which self-limiting growth was reported
GR: growth rate reported in Å/cycle

\(^{\text{a}}\): no evidence of self-limiting growth reported

1.3.2.4 Amidinates

The chelating effect of the amidinate ligands usually contributes to the high thermal stability properties of these compounds.\(^{50}\) Amidinate complexes also have good reactivity with ozone and with water. Their high reactivity results in the efficient removal of the ligands, and low impurity levels of the deposited films. However, these compounds are solids. Despite that, the synthesis of numerous amidinate compounds have been published,\(^{73-75}\) only a few processes have been reported for the ALD of metal oxides from these precursors as yet. Only the growth of ZrO\(_2\) from tetrakis(N,N\(^{\prime}\)-dimethylacetamidinate) zirconium, (Zr(amd)\(_4\)) and water was reported for the ALD of groups 4 and 5 metal oxides, (Table 4).\(^{79}\) In that same study, self-limiting growth could be achieved at 300 °C but with a low GR (0.24 Å/cycle). Unfortunately, the study did not contain any compositional analysis.
### 1.3.2.5 Donor functionalized alkoxides

Donor functionalized alkoxide precursors were investigated as potential ALD precursors for the growth of ZrO$_2$ and HfO$_2$ thin films (Table 4). The functionalization of an alkoxide by the incorporation of an additional neutral donor favour the chelating bonding mode over the general bridging mode of the alkoxide complexes.$^{76}$ The expected benefits would be an increase in the thermal stability, because of the chelating effect, and also the formation of monomeric complexes.$^{76}$ Unfortunately, the ALD precursor properties of donor functionalized alkoxides were disappointing. No saturation/self-limiting was observed when growing HfO$_2$ and ZrO$_2$ using Hf(mmp)$_4$ and Zr(dmae)$_4$ with water: even at a deposition temperature as low as 240 °C decomposition of the precursor was observed.$^{80,81}$

### 1.3.2.6 β–diketonates

Metal β–diketonates are common precursors that are used in CVD and they form a very versatile group of precursors that can be found for nearly every metal.$^{77}$ Metal β–diketonates possess two M-O bonds per ligand, thus these precursors have low reactivity with water. Instead strong oxidizers, such as ozone, are required to break the resilient C–O bonds. Unfortunately, carbon tends to remain in the film with detrimental effects on the film properties. The carbon contamination detected in the films deposited from β–diketonate precursors was due to carbonate-type impurities.$^{78}$ For the most part, β-diketonates are solids and therefore possess low volatilities and slow vaporisation kinetics. In addition, the large size of the ligands, results in low GRs (<0.2 Å/cycle) due to the high steric hindrance of the ligands.$^{50}$ However, β–diketonates usually have excellent thermal stability, which typically is well above 300 °C. Only one homoleptic β–diketonate process namely, Zr(thd)$_4$ with ozone,was reported for the ALD of groups 4 and 5 oxides (Table 4).$^{82}$ As expected, Zr(thd)$_4$ possessed very high thermal stability, achieved self-limiting growth that was confirmed at 375 °C, but a rather low GR of 0.24 Å/cycle. More surprisingly, the films also had good purity with respective carbon and hydrogen contents of 0.2 and 0.3 at.%. 
Table 4. Published processes for the thermal ALD of groups 4 and 5 metal oxides from amidinate, donor functionalized alkoxide and β-diketonates precursors.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Oxygen Source</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>GR at $T_{\text{max}}$</th>
<th>Impurities (at.%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>amidinate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr(amd)$_4$</td>
<td>H$_2$O</td>
<td>300</td>
<td>0.24</td>
<td>NR</td>
<td>79</td>
</tr>
<tr>
<td>Donor functionalized alkoxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr(dmae)$_4$</td>
<td>H$_2$O</td>
<td>CVD-growth</td>
<td></td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>Hf(mmp)$_4$</td>
<td>H$_2$O</td>
<td>CVD-growth</td>
<td></td>
<td></td>
<td>81</td>
</tr>
<tr>
<td>β–diketonate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr(thd)$_4$</td>
<td>O$_3$</td>
<td>375</td>
<td>0.24</td>
<td>C=0.2, H=0.3</td>
<td>82</td>
</tr>
</tbody>
</table>

NR: not reported  
$T_{\text{max}}$: maximum deposition temperature at which self-limiting growth was reported  
GR: growth rate reported in Å/cycle  
n: no evidence of self-limiting growth reported  
mmp: 1-methoxy-2-methyl-2-propanolate  
dmae: dimethylaminoethoxide

1.3.3 ALD of groups 4 and 5 oxides thin films from heteroleptic precursors

Recently, interest has been focused on the synthesis and evaluation of heteroleptic precursors. Heteroleptic precursors consist of a metal atom bonded to two or more different ligands. The purpose behind such an approach is that by combining different ligands, the resulting precursor should possess a combination of the best properties of the respective parent homoleptic compounds. For example, with a hypothetical alkylamide-halide heteroleptic precursor, the high thermal stability of the halides might be combined with the good volatility of the alkylamides.

Although based on a rather naïve principle, the results obtained from various heteroleptic precursors have demonstrated that it is not so straightforward to predict the ALD precursor properties of heteroleptic compounds. For example, a heteroleptic precursor might also exhibit undesired properties of the corresponding homoleptic precursors. The same hypothetical halide-alkylamide precursor cited above could also manifest the low thermal stability characteristic of the alkylamides and halide contamination, or even worse, etching of the deposited layers due to the formation of HCl or HF. Moreover, the possible outcomes are not limited to the simple sum of the advantages or drawbacks of the homoleptic compounds. Indeed, some heteroleptic precursors have exhibited better (or lower) thermal stability as compared to the individual homoleptic precursors. Table 5 presents a list of the heteroleptic
precursors which have been evaluated as precursors for the thermal ALD of groups 4 and 5 oxides (heteroleptic precursors with three different ligands are not listed in Table 5: instead they are discussed later in this thesis). It can be seen that many candidate precursors have not yet been explored, though some specific ligand combinations have been extensively studied.

Until now, there has been no systematic literature survey of the ALD properties of heteroleptic compounds. A case study of the ALD of groups 4 and 5 metal oxides is presented in the following section to attempt to determine trends in the properties of heteroleptic compounds that depend on their constituent ligands. For the clarity of the discussion the different heteroleptic precursors were classified into five categories: mixed alkoxides, cyclopentadienyls (Cp’s), alkylamides, oxo heteroleptic compounds and precursors with three different ligands.
Table 5. Heteroleptic precursors used for the thermal ALD of groups 4 and 5 metal oxides (precursors with three different ligands are described in section 1.3.3.7).

<table>
<thead>
<tr>
<th></th>
<th>Alkoxides</th>
<th>Cp’s</th>
<th>Alkylamides</th>
<th>Oxos</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkoxides</strong></td>
<td>(CpMe)_3Ti(OMe)_3</td>
<td>(CpMe)_3Ti(OMe)_3</td>
<td></td>
<td>VO(O'Pr)_3</td>
</tr>
<tr>
<td></td>
<td>(CpMe)Ti(OMe)_3</td>
<td>Cp_Hf(OMe)_2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CpMe)_2Hf(OMe)_2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cp’s</strong></td>
<td>(CpMe)_3Ti(OMe)_3</td>
<td>(CpMe)_3Ti(OMe)_3</td>
<td>CpZr(NMe)_3</td>
<td>NR</td>
</tr>
<tr>
<td></td>
<td>Cp_Hf(OMe)_2</td>
<td>Cp_Hf(OMe)_2</td>
<td>CpZr(NMe)_3</td>
<td>NR</td>
</tr>
<tr>
<td></td>
<td>(CpMe)_2Hf(OMe)_2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Alkylamides</strong></td>
<td>(tBuO)_2Ti(NMe)_3</td>
<td>(tBuO)_2Ti(NMe)_3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CpMe)_3Ti(NMe)_3</td>
<td>(CpMe)_3Ti(NMe)_3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CpMe)_2ZrMe_2</td>
<td>(CpMe)_2ZrMe_2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CpMe)_2HfMe_2</td>
<td>(CpMe)_2HfMe_2</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Alkyls</strong></td>
<td>NR</td>
<td>(CpMe)_2ZrMe_2</td>
<td>(CpMe)_2HfMe_2</td>
<td>NR</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(CpMe)_2HfMe_2</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Halides</strong></td>
<td>NR</td>
<td>Cp_ZrCl_2</td>
<td>(EtMeN)_2Nb=NEt</td>
<td>NR</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(EtMeN)_2Ta=NEt</td>
<td></td>
</tr>
<tr>
<td><strong>β–diketonates</strong></td>
<td>(tPrO)_2Ti(thd)_2</td>
<td>(tPrO)_2Ti(thd)_2</td>
<td>(MeEtN)_3Nb=N'Bu</td>
<td>NR</td>
</tr>
<tr>
<td></td>
<td>(t'amylO)_2Ti(thd)_2</td>
<td>(t'amylO)_2Ti(thd)_2</td>
<td>(Et_2N)_3Ta=N'Bu</td>
<td></td>
</tr>
<tr>
<td><strong>Imides</strong></td>
<td>(tBuO)_3Nb=Namyl</td>
<td>NR</td>
<td>(Et_2N)_3Ta=NEt</td>
<td>NR</td>
</tr>
<tr>
<td><strong>Amidinates</strong></td>
<td>(tPrO)_3Ti(NPr-Me- amd)</td>
<td>NR</td>
<td>(EtMeN)_2Nb=NEt</td>
<td>NR</td>
</tr>
<tr>
<td><strong>Guanidinates</strong></td>
<td>NR</td>
<td></td>
<td>(EtMeN)_2Zr(guan-NEtMe)_2</td>
<td>NR</td>
</tr>
<tr>
<td><strong>Donor functionalized alkoxides</strong></td>
<td>(tPrO)_2Ti(dmae)_2</td>
<td>(tBuO)_2Zr(dmae)_2</td>
<td>(EtO)_2Ta(dmae)</td>
<td>NR</td>
</tr>
<tr>
<td></td>
<td>(PrO)_2Zr(dmae)_2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(BuO)_2Hf(mmp)_2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>CHT’s</strong></td>
<td>NR</td>
<td>CpTiCHT</td>
<td>(CpMe)_2ZrCHT</td>
<td>NR</td>
</tr>
</tbody>
</table>

NR: not reported
1.3.3.1 Synthesis of heteroleptic precursors

This section briefly describes the strategy adopted for the synthesis of heteroleptic precursors for the thermal ALD of groups 4 and 5 metal oxides.

Heteroleptic alkylamides: In the case of alkylamide-alkoxides, alkylamide-Cp’s, and alkylamide-guanidinates, the homeoleptic alkylamide is used as the starting material. Then, to form alkylamide-Cp’s and alkylamide-guanidinates, carbodiimide or Cp ligands are added and ligand exchange reactions produce the desired alkylamide-Cp’s or alkylamide-guanidinates:

\[
M(N\text{Me}_2)_4 + HCpR_n \rightarrow (CpR)M(N\text{Me})_3 + NHMe_2 \quad (\text{refs. 83,84})
\]

\[M = \text{Ti, Zr, Hf} ; R = H, \text{Me, Et} ; n = 1\]

\[
M(NR_2)_4 + n (\text{NHR}´-\text{guan}) \rightarrow (NR_2)_{4-n}M(NR´-\text{guan})_n + (4-n) \text{NHR}_2 \quad (\text{refs. 85,86})
\]

\[n = 1, 2 ; \quad M = \text{Ti, Zr, Hf} ; \quad R, R´= \text{Me, Et, EtMe}\]

Alkylamide-alkoxides are prepared by reacting homeoleptic alkylamide and homeoleptic alkoxide, the rearrangement reaction proceeds as follows:

\[
\text{Ti(NR}_2)_4 + n \text{Ti(OR}_4 \rightarrow (n+1) (\text{R}_2\text{N})_{4-n} \text{Ti(OR}´)_n \quad \text{(ref. 87)}
\]

\[n = 1, 2, 3 ; \quad M = \text{Ti, Hf} ; \quad R = \text{Me, EtMe} ; \quad R´= ^1\text{Pr, }^1\text{Bu}\]

In the synthesis of the alkylamide-imides of niobium and tantalum, the respective metal chloride is used as the starting material. The imide ligand is first added by reacting the homoleptic chloride with R(Me_3Si)NH and pyridine (Py), then the alkylamide ligands are added with the appropriate amino lithium:

\[
\text{MCls} + 2 \text{R(Me}_3\text{Si)NH} + 2 \text{Py} \rightarrow \text{RN=MClsPy}_2 + \text{H}_2\text{NR} + 2 \text{Me}_3\text{SiCl}_3 \quad (4)
\]

\[
\text{RN=MClsPy}_2 + 3 \text{LiNR}_2 \rightarrow (\text{R}_2\text{N})_3\text{M=NR} + 3 \text{LiCl} + 2 \text{Py} \quad \text{(refs. 88-90)}
\]

\[M = \text{Nb, Ta} ; \quad R = \text{Et, }^1\text{Bu} ; \quad R´= \text{Et, EtMe}\]

Heteroleptic Cp’s: Heteroleptic Cp-halides are synthesized by salt metathesis using the metal chlorides as starting materials and substituting the chloride ligands with Cp’s:

\[
\text{MCls} + 2 \text{NaCp} \rightarrow \text{Cp}_2\text{MCls} + 2 \text{NaCl} \quad (\text{refs. 91,92})
\]
M = Zr, Hf

Cp-alkyls can be easily prepared by a salt metathesis reaction from the Cp-halides and alkyllithium (7). The ansa-metallocenes are also prepared by the appropriate ligand exchange reaction. However, metal chloride is used as the starting material (8):

\[
\text{Cp}_2\text{MCl}_2 + 2 \text{LiMe} \rightarrow \text{Cp}_2\text{MMe}_2 + 2 \text{LiCl} \quad \text{(ref. 92-95)}
\]

\[
\text{H}_2\text{Cp}_2\text{CMe}_2 + 4 \text{MeLi} + \text{MCl}_4 \rightarrow (\text{Cp}_2\text{CMe}_2)\text{MMe}_2 + 4\text{LiCl} \quad \text{(ref. 96)}
\]

Heteroleptic alkoxides:

Alkoxide-amidinates, alkoxide-donor functionalized alkoxides and alkoxide-ß-diketonates are prepared using the homoleptic alkoxides as starting material. Then, the amidinate, donor functionalized alkoxide or ß-diketonate ligands were added and the resulting ligand exchange reaction leads to the desired heteroleptic compounds:

\[
\text{Hf(O}^\text{tBu})_4 + 2 \text{mmpH} \rightarrow (\text{O}^\text{tBu})_2\text{M(mmp)}_2 + 2 ^\text{tBuOH}
\]

\[
\text{M(OR)}_4 + 2 \text{dmaeH} \rightarrow (\text{OR})_2\text{M(dmae)}_2 + 2 \text{ROH} \quad \text{(ref. 80)}
\]

\[
\text{Ti(OR)}_4 + 2 \text{Hthd} \rightarrow (\text{OR})_2\text{Ti(thd)}_2 + 2 \text{ROH} \quad \text{(ref. 97)}
\]

\[
\text{Ti(O}^\text{Pr})_4 + \text{HN}^\text{Pr}^+\text{-amd} \rightarrow (\text{O}^\text{Pr})_3\text{Ti(N}^\text{Pr}^-\text{-amd}) + ^\text{tPrOH} \quad \text{(ref. 98)}
\]

Titanium alkoxide-monocyclopentadienyls are prepared from cyclopentadienyltitanium trichloride and alcohol. The chlorides are substituted with alkoxide ligands:

\[
\text{CpR}_n\text{TiCl}_3 + 3 \text{MeOH} \rightarrow \text{CpTi(OMe)}_3 + 3 \text{HCl} \quad \text{(ref. 99)}
\]

\[
\text{R} = \text{H, Me}; \quad n = 1, 5
\]

Alkoxide-bicyclopentadienyls hafnium is prepared by reacting Cp-alkyl and the appropriate alcohol, and the alkyls are substituted by alkoxide groups:
\[(\text{CpR})_2\text{HfMe}_2 + 2 \text{MeOH} \rightarrow (\text{CpR})_2\text{Hf(OMe)}_2 + 2 \text{MeOH} \text{ (ref. } 84)\] (14)

\[R = \text{H, Me}\]

**Vanadium oxo compounds:**

Vanadium pentoxide is used as the starting material for the synthesis of \(\text{VOCl}_2\), \(\text{VO(acac)}_2\) and \(\text{VO(O}^\text{iPr})_3\). Acid-base reaction with isopropanol produces \(\text{VO(O}^\text{iPr})_3\), whereas a redox reaction with acetylacetone and vanadium trichloride produces \(\text{VO(acac)}_2\) and \(\text{VOCl}_2\), respectively.

\[\text{V}_2\text{O}_5 + 3 \text{VCl}_3 + \text{VOCl}_3 \rightarrow 6 \text{VOCl}_2 \text{ (ref. } 100)\] (15)

\[2 \text{V}_2\text{O}_5 + 9 \text{Hacac} \rightarrow 4 \text{VO(acac)}_2 + (\text{acac})_2\text{CO} + 5 \text{H}_2\text{O} \text{ (ref. } 101)\] (16)

\[\text{V}_2\text{O}_5 + 6 \text{iPrOH} \rightarrow 2 \text{VO(O}^\text{iPr})_3 + 3 \text{H}_2\text{O} \text{ (ref. } 102)\] (17)

**Three ligands:**

Cp-alkyl-alkoxides and donor functionalized alkoxide were prepared by ligand exchange reactions that use Cp-alkyls with the appropriate alcohol. The reactions proceed as follows:

\[(\text{CpR})_2\text{MMe}_2 + R´\text{OH} \rightarrow (\text{CpR})_2\text{MROR´} + \text{CH}_4\] (18)

\[M = \text{Zr, Hf}; \quad R = \text{H, Me}; \quad R´ = \text{Me, }^3\text{Bu}\]

\[(\text{MeCp})_2\text{HfMe}_2 + \text{Hmmp} \rightarrow (\text{MeCp})_2\text{HfMe(mmp)} + \text{HMe} \text{ (ref. } 103)\] (19)

The alkylamide-imide-amidinate tantalum compound was also prepared by a ligand exchange reaction. The starting material was \(\text{Ta(N}^\text{tBu})\text{Cl}_3(\text{py})_2\) the synthesis of which is described earlier (4).

\[(\text{N}^\text{tBu})\text{TaCl}_3(\text{py})_2 + 2 \text{Li(PrNMeN}^\text{Pr}) \rightarrow (\text{N}^\text{tBu})\text{Ta(PrNMeN}^\text{Pr})_2\text{Cl} + 2 \text{py} + 2 \text{LiCl}\] (20)

\[(\text{N}^\text{tBu})\text{Ta(PrNMeN}^\text{Pr})_2\text{Cl} + \text{LiNMe}_2 \rightarrow (\text{N}^\text{tBu})\text{Ta(}^3\text{BuNMeN}^\text{Bu})_2(\text{NMe}_2) + \text{LiCl} \text{ (ref. } 104)\] (21)

In summary, heteroleptic compounds are mostly prepared by ligand exchange reactions that start with the appropriate homoleptic compound and substitute, with the appropriate
ligand(s). On the other hand, the vanadium oxo compound synthesis is based on redox or acid/base reactions.

### 1.3.3.2 Heteroleptic alkoxides

Table 6 summarizes the published ALD processes that use alkoxide heteroleptic compounds. The heteroleptic approach appeared to be rather beneficial, compared to the otherwise poorly thermally stable homoleptic alkoxides, as many heteroleptic compounds had thermal stabilities above 300 °C.

**Alkoxide-β-diketonates**: Alkoxide-β-diketonate titanium compounds have high thermal stability properties, and self-limiting growth can be achieved above 360 °C, which is characteristic for the homoleptic β-diketonates. Additionally, the alkoxide ligands had added reactivity towards water as compared to homoleptic β-diketonates. With (’PrO)₂Ti(thd)₂ and O₃ as the oxygen source it was even possible to grow rutile TiO₂ on ruthenium substrate with the appreciable GR, of 0.43 Å/cycle. Otherwise, the use of these precursors was associated with the low GR characteristic of homoleptic β-diketonates.

**Alkoxide-alkylamides**: The alkoxide-alkylamide compounds, (O’Pr)₂Ti(NMe₂)₂ (described in publication IV, and in chapter 3) and (’BuO)Hf(NEtMe)₃ were used successfully for the ALD of TiO₂ and HfO₂. Although alkoxide and alkylamide compounds usually have thermal stabilities well below 300 °C, the resulting heteroleptic compounds exhibit self-limiting growth above 300 °C. Interestingly, both processes exhibit high GR and the oxide films had excellent purity.

The use of alkoxide-imide and alkoxide-amidinate as alkoxide-imide and alkoxide-amidinate precursors for the ALD of groups 4 and 5 metal oxides are described in this thesis. The results are presented in chapter 3 and in the publications I and IV.

**Alkoxide-donor functionalized alkoxides**: Several alkoxide-donor functionalized alkoxide precursors have been reported in the literature. (’BuO)₂Zr(dmae)₂ and (’PrO)₂Zr(dmae)₂, together with water as the oxygen source, do not undergo self-limiting growth and were reported to decompose at temperatures as low as 240 °C. Only the studies on the growth of HfO₂ and TiO₂ thin films that used water and (’BuO)₂Hf(mmp)₂ or (’PrO)₂Ti(dmae)₂, reported self-limiting growth. However, high carbon and hydrogen contamination was found in the films grown from (’BuO)₂Hf(mmp)₂. The self-limited growth of
(\textit{iPrO})_2\text{Ti(dmae)}_2 was demonstrated at the low temperature of 100 °C but no compositional data were reported. The ALD growth of Ta_2O_5 thin films from (EtO)_4Ta(dmae) and ozone was reported at 400 °C.\textsuperscript{109} However, no data on self-limiting growth or compositional data were reported and the growth was most likely to be of the CVD-type. In summary, it seems that donor functionalized alkoxides are not suitable ALD precursors, either in homoleptic or heteroleptic compounds, because of their low thermal stabilities and/or the high amounts of impurities found in their deposited films.

**Table 6.** Published processes for the thermal ALD of groups 4 and 5 metal oxides from heteroleptic alkoxide compounds.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>O source</th>
<th>T\textsubscript{max} (°C)</th>
<th>GR at T\textsubscript{max}</th>
<th>Impurities (at.%%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Alkoxide</em>-\textit{β}-diketonates</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\textit{iPrO})\textsubscript{2}\text{Ti(thd)}\textsubscript{2}</td>
<td>H\textsubscript{2}O, O\textsubscript{3}</td>
<td>370, 370</td>
<td>0.25, 0.43</td>
<td>Negligible, Negligible</td>
<td>105</td>
</tr>
<tr>
<td>(\textit{amylo})\textsubscript{2}\text{Ti(thd)}\textsubscript{2}</td>
<td>H\textsubscript{2}O, O\textsubscript{3}</td>
<td>380, 300</td>
<td>0.10</td>
<td>NR</td>
<td>106</td>
</tr>
<tr>
<td><em>Alkoxide</em>-alkylamides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\textit{iPrO})\textsubscript{2}\text{Ti(NMe}\textsubscript{2})\textsubscript{2}</td>
<td>H\textsubscript{2}O</td>
<td>325</td>
<td>0.75</td>
<td>C=0.6</td>
<td>I</td>
</tr>
<tr>
<td>(\textit{tBuO})Hf(NEtMe)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>300</td>
<td>1.6</td>
<td>C, N&lt; AES DL</td>
<td>107</td>
</tr>
<tr>
<td><em>Alkoxide</em>-imide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\textit{tBuO})\textsubscript{2}\text{Nb=Namyl}</td>
<td>H\textsubscript{2}O</td>
<td>CVD-growth</td>
<td></td>
<td>IV</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O\textsubscript{3}</td>
<td>CVD-growth</td>
<td></td>
<td>IV</td>
<td></td>
</tr>
<tr>
<td><em>Alkoxide</em>-amidinate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\textit{iPrO})\textsubscript{3}\text{Ti(NPr-Me-amd)}</td>
<td>H\textsubscript{2}O</td>
<td>325</td>
<td>0.45</td>
<td>0.6</td>
<td>I</td>
</tr>
<tr>
<td></td>
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<tr>
<td><em>Alkoxide</em>-donor functionalized alkoxides</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(\textit{iPrO})\textsubscript{2}\text{Ti(dmae)}\textsubscript{2}</td>
<td>H\textsubscript{2}O</td>
<td>300, 100</td>
<td>0.30</td>
<td>NR</td>
<td>108</td>
</tr>
<tr>
<td>(EtO)\textsubscript{4}\text{Ta(dmae)}</td>
<td>O\textsubscript{3}</td>
<td>400</td>
<td>NR</td>
<td>NR</td>
<td>109</td>
</tr>
<tr>
<td>(\textit{BuO})\textsubscript{2}\text{Zr(dmae)}\textsubscript{2}</td>
<td>H\textsubscript{2}O</td>
<td>CVD-growth</td>
<td></td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>(\textit{PrO})\textsubscript{2}\text{Zr(dmae)}\textsubscript{2}</td>
<td>H\textsubscript{2}O</td>
<td>CVD-growth</td>
<td></td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>(\textit{BuO})\textsubscript{2}\text{Hf(mmp)}\textsubscript{2}</td>
<td>H\textsubscript{2}O</td>
<td>300</td>
<td>0.6</td>
<td>H=18.0, C=8.0 at 275 °C</td>
<td>110</td>
</tr>
</tbody>
</table>

\textit{NR}: not reported

T\textsubscript{max}: maximum deposition temperature at which self-limiting growth was reported

GR: growth rate reported in Å/cycle

n: no evidence of self-limiting growth reported

AES: Auger electron spectroscopy
1.3.3.3 Heteroleptic cyclopentadienyls

Table 7 summarizes the published ALD processes that use heteroleptic Cp compounds. Cyclopentadienyl ligands are good electron donors and the bonds they form with metals as electron acceptors are relatively stable. Therefore, these compounds possess good thermal stabilities. Cp’s also offer interesting opportunities to tune the properties of the precursor by varying the degree of substitution and the nature of the substituents. Figure 3 illustrates the opportunity to tune the volatility of neodymium Cp’s by varying the nature of the substituent. The synthesis of homoleptic tetrakiscyclopentadienyl metal complexes of group 4 was also reported. These compounds seem stable and the zirconium and hafnium compounds have suitable evaporation temperatures. However, there have been no reports on their evaluation as ALD precursors.

![Image of substituents and their boiling points](reproduced by permission of John Wiley and Sons)

Figure 3. Effect of substituents on the boiling point of NdCp3 complexes. (reproduced by permission of John Wiley and Sons)

Cp-alkyls: ALD is impractical for many alkyl compounds because metal alkyl compounds are vulnerable to decomposition into metal hydrides and metal alkenes. However, alkyl compounds have been utilized successfully for the ALD of other metal oxides. For example, the ALD of Al2O3 from Al(CH3)3 and water is often considered as the “ideal ALD process”. Alkyl compounds usually possess reasonably high volatility and reactivity, and also are often found as liquids. Cp-alkyls perform well as ALD precursors and they also have high thermal stabilities (Table 7), up to 400 °C in the case of (CpMe)2HfMe2. They also lead to the growth of high purity films with carbon contents typically below 0.2 at.%.

The main drawback of these precursors is their moderate GR, which lie typically between 0.45 and...
0.55 Å/cycle. Ansa-metallocene compounds, \((\text{Cp}_2\text{CMe}_2)\text{ZrMe}_2\) and \((\text{Cp}_2\text{CMe}_2)\text{HfMe}_2\), together with ozone as the oxygen source, were also investigated for the ALD of \(\text{ZrO}_2\) and \(\text{HfO}_2\), respectively.\(^{96}\) The study concluded that these complexes deposit oxide films at higher substrate temperatures than unbridged metallocenes. However, the TG experiment indicated very large amounts of residue after evaporation, about 60% for the zirconium and 10% for hafnium complexes. Moreover, no evidence of self-limiting growth that would sustain the claim of high thermal stability were provided. Moreover, while studying the growth per cycle as a function of the \(((\text{Cp})_2\text{CMe}_2)\text{HfMe}_2\) dose at 350 °C, it was clearly demonstrated that this precursor severely decomposes at this temperature.\(^{96}\)

\textit{Cp-halides:} \(\text{Cp}_2\text{HfCl}_2\)\(^{121}\) and \(\text{Cp}_2\text{ZrCl}_2\)\(^{82}\) have been investigated for the ALD of \(\text{HfO}_2\) and \(\text{ZrO}_2\). These precursors have good thermal stability as self-limiting growth was confirmed at 350 and 300 °C, for \(\text{Cp}_2\text{HfCl}_2\)\(^{121}\) and \(\text{Cp}_2\text{ZrCl}_2\)\(^{82}\) respectively. The \(\text{Cp}_2\text{HfCl}_2/\text{water}\) process caused some Cl contamination (0.4 at.%) and produced only a modest growth rate (0.35 Å/cycle). However, the ozone processes of both \(\text{Cp}_2\text{HfCl}_2\) and \(\text{Cp}_2\text{ZrCl}_2\) did not show signs of chlorine contamination and had higher growth rates (0.65 for \(\text{Cp}_2\text{HfCl}_2\) and 0.53 for \(\text{Cp}_2\text{ZrCl}_2\) Å/cycle) compared to the water processes (Table 7).

\textit{Cp-alkylamides:} zirconium and hafnium \(\text{Cp}\)-alkylamide compounds resulted in rather high GRs that ranged between 0.8-0.9 Å/cycle when ozone was used as the oxygen source. The films typically contained low levels of carbon and nitrogen contamination,\(^{65,119}\) when using homoleptic and heteroleptic alkylamide precursor. With the exception of \((\text{CpMe}_5)\text{Ti(NMe}_2\text{)}_3\)\(^{71}\) the \(\text{Cp}\)-alkylamides studied in the literature are less thermally stable (\(T_{\text{max}}<300\) °C, Table 7), than the other heteroleptic \(\text{Cp}\)-containing compounds. One reason for the exceptionally high thermal stability of \((\text{CpMe}_5)\text{Ti(NMe}_2\text{)}_3\) is the high degree of substitution on its \(\text{Cp}\) ring, the addition of electron donor groups to the \(\text{Cp}\) ring contributes to the further strengthening of the \(\text{Cp}\)-metal bond. Interestingly, the \(\text{ZrO}_2\) thin films deposited from the heteroleptic \(\text{Cp}\)-alkylamide zirconium precursor were also crystallized into the high permittivity cubic phase in the as-deposited state, which was similar to that found for the homoleptic alkylamides.\(^{65}\)

It is also worth noting that the investigated heteroleptic \(\text{Cp}\)-alkylamide compounds had only one \(\text{Cp}\) ligand\(^{65,71,119}\) and somehow have lower thermal stabilities than heteroleptic bисcyclopentadienyl-alkyls, -halides and -alkoxides. Therefore, it seems that \(\text{Cp}\)-alkylamide compounds with a high degree of substitution and/or two \(\text{Cp}\) ligands are highly performing precursors. \(\text{Cp}_2\text{Zr(NMe}_2\text{)}_2\), \((\text{CpMe}_2)\text{Zr(NMe}_2\text{)}_2\) and \((\text{CpMe}_2)\text{Zr(NEt}_2\text{)}_2\) are stable compounds but they have only been evaluated for the PE-ALD of zirconium carbide. However, the study showed that a rather large residual mass remains after evaporation (30–58%).\(^{120}\)
Furthermore, Cp$_2$Hf(NEt$_2$)$_2$ is stable and has a suitable evaporation temperature but was only evaluated for the MOCVD of HfO$_2$.$^{121}$

*Cp-alkoxides:* Cp-alkoxides were used for the ALD of TiO$_2$ and HfO$_2$ thin films with ozone as the oxygen source. The bicsyclopentadienyl-alkoxide hafnium compounds Cp$_2$Hf(OMe)$_2$ and (CpMe$_2$)Hf(OMe)$_2$ were thermally stable up to 350 °C and had high growth rates. The HfO$_2$ thin films deposited from these precursors were very pure.$^{115}$ TiO$_2$ thin films were deposited from the monocyclopentadienyl-alkoxide titanium precursors (MeCp)Ti(OMe)$_3$, (Me$_5$Cp)Ti(OMe)$_3$, and CpTi(OMe)$_3$. These processes had low growth rates (0.24–0.27 Å/cycle). However, (Me$_5$Cp)Ti(OMe)$_3$, with a highly substituted Cp ring, is significantly more thermally stable than (MeCp)Ti(OMe)$_3$ and CpTi(OMe)$_3$ (Table 7). This observation concurs with the previous remarks about the benefits of a high degree of substitution for the Cp precursors mentioned above.

*Cp-CHT:* In a recent study, Niinistö *et al.* introduced CHT ligands in novel solid Cp-CHT compounds for the ALD of TiO$_2$ and ZrO$_2$ (Table 7). These precursors do not react with water but they do require ozone as the oxygen source.$^{124}$ The zirconium compound appeared to perform well with self-limiting growth that occurred up to 350 °C and also a high GR of 0.8 Å/cycles. The titanium compound was significantly less thermally stable ($T_{\text{max}}=300$ °C) than the zirconium precursor and had only a modest GR (0.35 Å/cycle). Interestingly, CpTiCHT had a strong tendency to form the high permittivity rutile phase upon annealing at rather low temperatures.
Table 7. Published processes for the thermal ALD of group 4 and 5 metal oxides from heteroleptic Cp’s compounds.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>O source</th>
<th>T&lt;sub&gt;max&lt;/sub&gt; (°C)</th>
<th>GR at T&lt;sub&gt;max&lt;/sub&gt;</th>
<th>Impurities (at.%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cp-alkyls</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CpMe)&lt;sub&gt;2&lt;/sub&gt;ZrMe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>350</td>
<td>0.50</td>
<td>C&lt;0.5, H=0.38</td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>350</td>
<td>0.55</td>
<td>NR</td>
<td>94</td>
</tr>
<tr>
<td>Cp&lt;sub&gt;2&lt;/sub&gt;Zr(Alk)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>350</td>
<td>0.43</td>
<td>C&lt;0.1, H&lt;0.1</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>350</td>
<td>0.55</td>
<td>C=0.16, H=0.1</td>
<td>82</td>
</tr>
<tr>
<td>(CpMe)&lt;sub&gt;2&lt;/sub&gt;HfMe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>350</td>
<td>0.40</td>
<td>C&lt;0.5, H=0.6</td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>400</td>
<td>0.50</td>
<td>0.1&lt;C,H,N</td>
<td>115</td>
</tr>
<tr>
<td>Cp&lt;sub&gt;2&lt;/sub&gt;HfMe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>350</td>
<td>0.44</td>
<td>C=0.2, H=0.4</td>
<td>118</td>
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<td></td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>350</td>
<td>0.54</td>
<td>C&lt;0.1, H&lt;0.1</td>
<td>118</td>
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<tr>
<td>(Cp&lt;sub&gt;2&lt;/sub&gt;CMe)&lt;sub&gt;2&lt;/sub&gt;ZrMe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>350</td>
<td>NR</td>
<td>C=2.8 (250°C)</td>
<td>96</td>
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<tr>
<td>(Cp&lt;sub&gt;2&lt;/sub&gt;CMe)&lt;sub&gt;2&lt;/sub&gt;HfMe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>CVD-growth</td>
<td></td>
<td>C=2.7 (250°C)</td>
<td>96</td>
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<tr>
<td><strong>Cp-halides</strong></td>
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</tr>
<tr>
<td>Cp&lt;sub&gt;2&lt;/sub&gt;HfCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>350</td>
<td>0.35</td>
<td>C=1.2, H=0.5, Cl=0.4</td>
<td>118</td>
</tr>
<tr>
<td></td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>350</td>
<td>0.65</td>
<td>C&lt;0.3, H&lt;0.3, Cl&lt;0.1</td>
<td>118</td>
</tr>
<tr>
<td>Cp&lt;sub&gt;2&lt;/sub&gt;ZrCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>300</td>
<td>0.53</td>
<td>C=0.54, H=0.5</td>
<td>82</td>
</tr>
<tr>
<td><strong>Cp-alkylamides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp(Ti(NMe&lt;sub&gt;2&lt;/sub&gt;))&lt;sub&gt;3&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>275</td>
<td>0.41</td>
<td>NR</td>
<td>71</td>
</tr>
<tr>
<td>(CpMe)&lt;sub&gt;2&lt;/sub&gt;Ti(NMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>350</td>
<td>0.31</td>
<td>NR</td>
<td>71</td>
</tr>
<tr>
<td>CpZr(NMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>300</td>
<td>0.90</td>
<td>C&lt;1.0</td>
<td>65</td>
</tr>
<tr>
<td>(MeCp)&lt;sub&gt;2&lt;/sub&gt;Zr(NMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>300</td>
<td>0.90</td>
<td>C&lt;1.0</td>
<td>65</td>
</tr>
<tr>
<td>(EtCp)&lt;sub&gt;2&lt;/sub&gt;Zr(NMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>300</td>
<td>0.90</td>
<td>C=1.0</td>
<td>65</td>
</tr>
<tr>
<td>(CpMe)&lt;sub&gt;2&lt;/sub&gt;Hf(NMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>300</td>
<td>0.80</td>
<td>C&lt;0.3, H=0.5, N=0.2</td>
<td>119</td>
</tr>
<tr>
<td>(Cp)&lt;sub&gt;2&lt;/sub&gt;Hf(NMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>300</td>
<td>0.80</td>
<td>C&lt;0.3, H=0.7, N&lt;0.1</td>
<td>119</td>
</tr>
<tr>
<td><strong>Cp-alkoxides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Me&lt;sub&gt;2&lt;/sub&gt;Cp)Ti(OMe)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>350</td>
<td>0.25</td>
<td>C=0.6, H=0.2</td>
<td>122</td>
</tr>
<tr>
<td>(MeCp)Ti(OMe)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>325&lt;sup&gt;n&lt;/sup&gt;, 250</td>
<td>0.27</td>
<td>NR</td>
<td>71</td>
</tr>
<tr>
<td>CpTi(OMe)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>280</td>
<td>0.24</td>
<td>Low (ToF-SIMS)</td>
<td>123</td>
</tr>
<tr>
<td>Cp&lt;sub&gt;2&lt;/sub&gt;HF(OMe)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>&lt;350&lt;sup&gt;n&lt;/sup&gt;</td>
<td>0.70</td>
<td>0.1&lt;C,H,N</td>
<td>115</td>
</tr>
<tr>
<td>(CpMe)&lt;sub&gt;2&lt;/sub&gt;HF(OMe)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>&lt;350&lt;sup&gt;n&lt;/sup&gt;</td>
<td>0.60</td>
<td>0.1&lt;C,H,N</td>
<td>115</td>
</tr>
<tr>
<td><strong>Cp-CHT’s</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CpMe)&lt;sub&gt;2&lt;/sub&gt;ZrCHT</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>350</td>
<td>0.80</td>
<td>NR</td>
<td>124</td>
</tr>
<tr>
<td>CpTiCHT</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>300</td>
<td>0.35</td>
<td>Low</td>
<td>124</td>
</tr>
</tbody>
</table>

NR: not reported

T<sub>max</sub>: maximum deposition temperature at which self-limiting growth was reported

GR: growth rate reported in Å/cycle

ToF-SIMS: Time-of-Flight Secondary Ion Mass Spectrometry

<sup>n</sup>: no evidence of self-limiting growth reported

ToF-SIMS:
1.3.3.4 Heteroleptic alkylamides

Table 8 summarizes the published ALD processes that use the heteroleptic alkylamide compounds. Alkylamide-alkoxides and alkylamide-Cp’s have been described in the previous sections.

Alkylamide-guanidinates:
A novel alternative chemistry for ALD and CVD precursors has recently been introduced using guanidine ligands.\textsuperscript{125,126} The flexibility of the guanidine structure with respect to the modification of its steric and electronic properties makes it an interesting ligand and its well-known decomposition pathways allow the control of its thermal chemistry.\textsuperscript{85} Only a few studies are currently available that report the performances of guanidine compounds as ALD precursors and more research is necessary for a better understanding of their properties. However, the first reports on Dy\textsubscript{2}O\textsubscript{3}\textsuperscript{127} and Gd\textsubscript{2}O\textsubscript{3}\textsuperscript{127,128} are promising.

The ALD growth of ZrO\textsubscript{2} from (EtMeN)\textsubscript{2}Zr(guan-NEtMe\textsubscript{2}) with either ozone or water as the oxygen source are described in chapter 3.1.2 and publication II. The precursor (Me\textsubscript{2}N)\textsubscript{2}Hf(guan-NMe\textsubscript{2})\textsubscript{2} was evaluated for the ALD of HfO\textsubscript{2} thin films with water as the oxygen source. Self-limiting growth was achieved at 200 °C with a high GR of 1.2 Å/cycle.\textsuperscript{129}

Alkylamide-imides: The ALD of Nb\textsubscript{2}O\textsubscript{5} and Ta\textsubscript{2}O\textsubscript{5} from (MeEtN)\textsubscript{3}Nb=N\textsuperscript{t}Bu, (Et\textsubscript{2}N)\textsubscript{3}Nb=N\textsuperscript{t}Bu and (Et\textsubscript{2}N)\textsubscript{3}Ta=N\textsuperscript{t}Bu is described in chapter 3 and publications IV and VI. Prior to this present research series, only one study has investigated alkylamide-imide precursors for the ALD of group 5 metal oxides. That study reported the growth of Ta\textsubscript{2}O\textsubscript{5} thin films from (Et\textsubscript{2}N)\textsubscript{3}Ta=NEt\textsubscript{2} and water.\textsuperscript{68} The alkylamide-imide precursor was found to have thermal stability as self-limiting growth of Ta\textsubscript{2}O\textsubscript{5} thin films was achieved at 350 °C. The process had the relatively high growth rate of 0.65 Å/cycle and high conformity of the films as 100% step coverage was obtained when the Ta\textsubscript{2}O\textsubscript{5} film was grown on 1:30 high aspect ratio substrates. The carbon and nitrogen contents were below the detection limit of RBS.\textsuperscript{68}
Table 8. Published processes for the thermal ALD of group 4 and 5 metal oxides from alkylamide heteroleptic compounds.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>O source</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>GR at $T_{\text{max}}$</th>
<th>Impurities (at.%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkylamide-guanidinates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Me$_2$N)Hf(guan-NMe$_2$)$_2$</td>
<td>H$_2$O</td>
<td>200</td>
<td>1.10</td>
<td>C=2.0</td>
<td>129</td>
</tr>
<tr>
<td>(EtMMe)$_2$Zr(guan-NEtMe$_2$)</td>
<td>H$_2$O</td>
<td>300</td>
<td>0.90</td>
<td>C=3.5, N=1.5</td>
<td>II</td>
</tr>
<tr>
<td></td>
<td>O$_3$</td>
<td>300</td>
<td>1.15</td>
<td>C=1.1, N&lt;DL</td>
<td>II</td>
</tr>
<tr>
<td><strong>Alkylamide-imides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(MeEtN)$_3$Nb=N*Bu</td>
<td>H$_2$O</td>
<td>275*</td>
<td>0.40</td>
<td>H=1.0, C=0.1, N=0.9</td>
<td>IV</td>
</tr>
<tr>
<td></td>
<td>O$_3$</td>
<td>275</td>
<td>0.40</td>
<td>H=0.6, C=2.4, N=0.3</td>
<td>IV</td>
</tr>
<tr>
<td>(Et$_2$N)$_3$Nb=N*Bu</td>
<td>H$_2$O</td>
<td>275</td>
<td>0.45</td>
<td>H=6.0, C=1.2, N=1.1</td>
<td>IV</td>
</tr>
<tr>
<td></td>
<td>O$_3$</td>
<td>275</td>
<td>0.45</td>
<td>H=0.7, C &lt;0.1, N=0.3</td>
<td>IV</td>
</tr>
<tr>
<td>(Et$_2$N)$_3$Ta=N*Bu</td>
<td>H$_2$O</td>
<td>325</td>
<td>0.60</td>
<td>C&lt;0.1</td>
<td>VI</td>
</tr>
<tr>
<td></td>
<td>O$_3$</td>
<td>325</td>
<td>0.50</td>
<td>C&lt;0.1</td>
<td>VI</td>
</tr>
<tr>
<td>(Et$_2$N)$_3$Ta=NEt$_2$</td>
<td>H$_2$O</td>
<td>350</td>
<td>0.65</td>
<td>C,N&lt;0.2</td>
<td>68</td>
</tr>
</tbody>
</table>

NR: not reported
$T_{\text{max}}$: maximum deposition temperature at which self-limiting growth was reported
GR: growth rate reported in Å/cycle
n: no evidence of self-limiting growth reported

1.3.3.5 Heteroleptic oxo compounds

Amongst the heteroleptic precursors reported for the ALD growth of groups 4 and 5 oxides, heteroleptic oxo compounds were only reported for vanadium oxide film growth. With the exception of V(NEtMe)$_4$, they actually represent the only precursors available for the growth of vanadium oxide thin films. VO(OPr)$_3$ is the standard precursor for the ALD of vanadium oxide and the deposition process is well characterized. However, VO(OPr)$_3$ has very limited thermal stability, below 170 °C, and only a low GR. The studies on VOCl$_2$ and VO(acac)$_2$ were focused on the properties of the films rather than on the ALD growth of the films per se and thus there are few data to discuss (Table 9).
Table 9. Published processes for the thermal ALD of group 4 and 5 metal oxides from oxo heteroleptic compounds.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>O source</th>
<th>$T_{\text{max}}$ ($^\circ$C)</th>
<th>GR at $T_{\text{max}}$</th>
<th>Impurities (at.%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O xo-alkyl VO(O'Pr)$_3$</td>
<td>H$_2$O O$_3$</td>
<td>150 170</td>
<td>0.23 0.20</td>
<td>C contamination Negligible</td>
<td>131 25</td>
</tr>
<tr>
<td>O xo-halide VOCl$_2$</td>
<td>H$_2$O</td>
<td>470$^n$</td>
<td>NR</td>
<td>heavily contaminated</td>
<td>132</td>
</tr>
<tr>
<td>O xo-$\beta$–diketonate VO(acac)$_2$</td>
<td>O$_2$</td>
<td>475$^n$</td>
<td>2.40</td>
<td>NR</td>
<td>133</td>
</tr>
</tbody>
</table>

NR: not reported

$T_{\text{max}}$: maximum deposition temperature at which self-limiting growth was reported

GR: growth rate reported in Å/cycle

$n$: no evidence of self-limiting growth reported

1.3.3.6 Imide-pyrazolate and halide-silylamide

The pyrazolate group can be considered as rather exotic ligands to be used in ALD precursors. Nevertheless, Ta(N'Bu)-(3,5-di-tert-butylpyrazolate) is highly thermally stable as the self-limiting growth was confirmed at 325 °C and when ozone was used as the oxygen source.$^{134}$ In addition, low amounts of impurities were found in the films. However, the GR remains somewhat rather low (0.3 Å/cycle). Similarly, the silylamide ligand has rarely been investigated for metal oxide precursor chemistry. One study reported the ALD growth of ZrO$_2$ from a halide-silylamide precursor, Cl$_2$Zr(N(SiMe$_3$_2)$_2$)$_2$ with water as the oxygen source.$^{135}$ As could be expected, significant amounts of silicon were detected in the films (1.10–5.40 at.%). According to ToF-SIMS analysis, the silicon was found to be distributed uniformly throughout the film. However, self-limiting growth was demonstrated at 175 °C with a very high growth rate of 1.6 Å/cycle.

1.3.3.7 Heteroleptic compounds with three ligands

The next logical step for further tuning the properties of precursors for ALD is the development of heteroleptic compounds with three different ligands. Most of the efforts in this respect have been devoted to the Cp-alkyl-alkoxide compounds. An alkylamide-imide-amidinate compound, (N'Bu)Ta(PrNC(Me)N'Pr)$_2$(NMe$_2$) was investigated for the ALD of
\( \text{Ta}_2\text{O}_5 \), together with water as the oxygen source \(^{136}\) but it did not have any significant advantages over those of the corresponding imido-amido precursor.\(^{\text{VI}}\)

The best performing Cp-alkyl-alkoxide precursors for the ALD growth of \( \text{HfO}_2 \) and \( \text{ZrO}_2 \) thin films were \((\text{CpMe})_2\text{Hf}(\text{OMe})\text{Me}\)\(^{115,116}\) and \((\text{CpMe})_2\text{Zr}(\text{OMe})\text{Me}\).\(^{94,116}\) Using ozone as the oxygen source, both precursors had high thermal stability with sel-limiting growth confirmed at 400 °C and also high GRs (0.60-0.75 Å/cycle) (Table 10).\(^{94,115,116}\) Using water as the oxygen source, saturation growth was confirmed at 350 °C with a growth rate of 0.5 Å/cycle. These results represent a clear improvement for the Cp-alkyl-alkoxide compounds over the properties exhibited by the Cp-alkyl or the Cp-alkoxide compounds. Compared to the less thermally stable \((\text{CpMe})_2\text{Hf}(\text{OPr})\text{Me}\)^\(^{103}\) and \((\text{CpMe})_2\text{Zr}(\text{O}^\text{Bu})\text{Me}\)^\(^{138}\) it seems that, for this class of Cp-alkyl-alkoxide precursors, short alkoxide chains are preferable to achieve better thermal stability.

The similar ansa-metallocenes \((\text{Cp}_2\text{CMe}_2)\text{Hf}(\text{OMe})\text{Me}\) and \((\text{Cp}_2\text{CMe}_2)\text{Zr}(\text{OMe})\text{Me}\) with ozone as the oxygen source showed no improvement and actually exhibited lower thermal stability (<350 °C) than the similar Cp-alkyl-alkoxides. In the TG study it was observed that a very large amount of residue remained after evaporation, which amounted to about 40 and 25% for the zirconium and hafnium complexes, respectively.\(^{96}\)

Finally, the Cp-alkyl-donor functionalized alkoxide compound \((\text{MeCp})_2\text{HfMe(mmp)}\) with water was investigated. It had self-limited growth at 400 °C and relatively high GR (0.6 Å/cycle). However, carbon contamination of 3.1 at.% was detected in the films.\(^{103}\)
Table 10. Published processes for the thermal ALD of group 4 and 5 metal oxides from heteroleptic precursors with three different ligands.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>O source</th>
<th>$T_{\text{max}}$ ($^\circ$C)</th>
<th>GR at $T_{\text{max}}$</th>
<th>Impurities (at.%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkylamide-imide-amidinate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(N\text{Bu})Ta(PrNC(Me)N\text{Pr})$_2$(NMe$_2$)</td>
<td>H$_2$O</td>
<td>325</td>
<td>0.28</td>
<td>C,N&lt;DL</td>
<td>136</td>
</tr>
<tr>
<td>Cp-alkyl-alkoxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CpMe)$_3$Hf(OPr)Me</td>
<td>H$_2$O</td>
<td>CVD-growth</td>
<td></td>
<td></td>
<td>103</td>
</tr>
<tr>
<td>(CpMe)$_3$Hf(OMe)Me</td>
<td>O$_3$</td>
<td>450$^n$, 400</td>
<td>0.60</td>
<td>C,H,N&lt;0.1</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>350</td>
<td>0.5</td>
<td>C&lt;0.5, H=0.8</td>
<td>116</td>
</tr>
<tr>
<td>(CpMe)$_2$Zr(OMe)Me</td>
<td>O$_3$</td>
<td>400</td>
<td>0.75</td>
<td>NR</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>350</td>
<td>0.5</td>
<td>C&lt;0.5, H=0.4</td>
<td>116</td>
</tr>
<tr>
<td>Cp$_2$ZrMe(OMe)</td>
<td>O$_3$</td>
<td>300$^n$</td>
<td>NR</td>
<td>NR</td>
<td>137</td>
</tr>
<tr>
<td>(CpMe)$_2$Zr(OR\text{Bu})Me</td>
<td>H$_2$O</td>
<td>350$^n$</td>
<td>NR</td>
<td>C=1.4</td>
<td>138</td>
</tr>
<tr>
<td>(Cp$_2$CMe$_2$)Hf(OMe)Me</td>
<td>O$_3$</td>
<td>250</td>
<td>0.55</td>
<td>C=1.9 (250 °C)</td>
<td>96</td>
</tr>
<tr>
<td>(Cp$_2$CMe$_2$)Zr(OMe)Me</td>
<td>O$_3$</td>
<td>350$^n$</td>
<td>2.50</td>
<td>C=1.8 (250 °C)</td>
<td>96</td>
</tr>
<tr>
<td>Cp-alkyl-donor functionalized alkoxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CpMe)$_3$HfMe(mmp)</td>
<td>H$_2$O</td>
<td>400</td>
<td>0.60</td>
<td>C=3.1</td>
<td>103</td>
</tr>
</tbody>
</table>

NR: not reported
$T_{\text{max}}$: maximum deposition temperature at which self-limiting growth was reported
GR: growth rate reported in Å/cycle
$n$: no evidence of self-limiting growth reported
2. Experimental

This chapter describes the methods used for the deposition and characterization of some groups 4 and 5 metal oxide thin films. Further details, of the electrical characterization and mechanistic studies can be found in the publications I-VI in appendix.\textsuperscript{1-VI}

2.1 Precursors and film growth

Groups 4 and 5 metal oxide thin films were deposited in a commercial flow-type hot-wall ALD reactor (ASM Microchemistry F-120). The reactor pressure was maintained between 5-10 mbar during the deposition phase of the process. Either O\textsubscript{3}, ozone concentration 100 g/m\textsuperscript{3}, or water were used as the oxygen source. Ozone was produced from >99.999% O\textsubscript{2} in an ozone generator (Wedeco Ozomatic modular 4 HC Lab Ozone. Nitrogen (>99.999%) was generated from Nitrox UHPN 3000-1 nitrogen generator and used as a carrier and also as a purging gas. All the studied metal precursors are air and moisture sensitive and were consequently handled in a glove box and transferred in sealed boats into the reactor. As deposition substrates, p- or n-type Si(100) (Okmetic, Finland) was used. The precursors were evaporated from open boats inside the reactor. The GRs of thin films were studied as a function of the deposition temperatures. The self-limited growth of the films was determined by studying the GR as a function of the metal precursor pulse length. The precursors used in this study are listed in Table 11, along with their respective origins and evaporation temperatures.
Table 11. Summary of the ALD experiments carried out with various group 4 and 5 metal precursors.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Oxygen sources</th>
<th>Subl./evap temperature (°C) at 5–8 mbar</th>
<th>Deposition temperatures tested (°C)</th>
<th>Precursor sources</th>
<th>Publication</th>
</tr>
</thead>
<tbody>
<tr>
<td>(iPrO)₂Ti(NMe₂)_2</td>
<td>H₂O</td>
<td>35 (liquid)</td>
<td>250-375</td>
<td>Air Liquide</td>
<td>I</td>
</tr>
<tr>
<td>(iPrO)₃Ti(NPr-amd)</td>
<td>H₂O</td>
<td>55 (liquid)</td>
<td>275-425</td>
<td>Air Liquide</td>
<td>I</td>
</tr>
<tr>
<td>(EtMeN)₂Zr(guan-NEtMe₂)</td>
<td>H₂O, O₃</td>
<td>120 (solid)</td>
<td>250-400</td>
<td>Ruhr-University</td>
<td>II</td>
</tr>
<tr>
<td>NEtMe₂₂</td>
<td>V(NEtMe)₄</td>
<td>H₂O, O₃</td>
<td>65 (liquid)</td>
<td>Air Liquide</td>
<td>III</td>
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<tr>
<td>(BuO)₃Nb=NamyI</td>
<td>H₂O, O₃</td>
<td>60 (liquid)</td>
<td>200-325</td>
<td>ATMI</td>
<td>IV</td>
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<td>(EtMeN)₂Nb=NBu</td>
<td>H₂O, O₃</td>
<td>55 (liquid)</td>
<td>175-375</td>
<td>ATMI</td>
<td>IV</td>
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<td>65 (liquid)</td>
<td>150-375</td>
<td>ATMI</td>
<td>IV</td>
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<tr>
<td>(Et₂N)₃Ta=NBu</td>
<td>H₂O, O₃</td>
<td>65 (liquid)</td>
<td>100-475</td>
<td>ATMI</td>
<td>V</td>
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2.2 Film characterization

The oxide thin films were analysed by various technique for their composition, thickness, morphology, structure, and electrical properties. Table 12 lists the characterization methods used in this thesis and also summarizes the information obtained.

The thickness and crystalline properties of the thin films were evaluated by X-ray reflectivity (XRR) and X-ray diffraction (XRD) by using a Panalytical X’Pert Pro MPD X-ray diffractometer. High-temperature XRD (HTXRD) measurements were taken inside an Anton-Paar HTK1200N oven under either nitrogen, 99.999%, which had been further purified by an Entegris 35KF-I-4R inert gas purifier, or air.

Atomic force microscopy (AFM) studies were carried out by using a Multimode V equipped with Nanoscope V controller (Veeco Instruments). Image processing and data analyses were performed with NanoScope software version 7.30. Samples were measured in tapping mode in air using a phosphorus-doped silicon probe (RTESP) manufactured by Veeco Instruments. Several scans were performed on different parts of the samples to check the uniformity of the surfaces. Final images of a scanning area of 2 x 2 µm² were measured under a scanning frequency of 0.5 Hz and no image processing except flattening was made. The roughness of the films were quantified and derived as the root-mean-square values (rms).
The refractive indexes of the films were measured by a M-2000D (1.25–6.5 eV) spectroscopic ellipsometer made by J.A. Woollam. Measurements were taken on a goniometric stage at an incident angle of 75°.

The chemical compositions of the films were determined by means of X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed on a Thermo Scientific K-Alpha KA1066 spectrometer using monochromatic Al Kα X-ray sources (hv = 1486.6 eV). Photoelectrons were collected at a take-off angle of 60 degrees. A 200 µm diameter X-ray spot was used in the analysis. Samples were neutralized using a flood gun to correct for differential or non-uniform charging. XPS high-resolution scans of the appropriate chemical species were taken at a pass energy of 50 eV.

TOF-ERDA measurements were obtained using a 6.8 MeV $^{35}$Cl$^{3+}$ beam generated by 1.7 MV Pelletron accelerators. Some of these films were grown on trench substrates with high aspect ratio to evaluate their conformality. The cross-section of a film was then analyzed using a Zeiss NEON 40 EsB CrossBeam system which allows high resolution. Field emission scanning electron microscopy (FE-SEM) imaging was used to study the morphology and film thickness along the trench walls.

### Table 12. Films characterization methods used.

<table>
<thead>
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<th>Method</th>
<th>data obtained on</th>
<th>Material studied</th>
<th>Publication</th>
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<td>$I-V$</td>
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<tr>
<td>QCM</td>
<td>Reaction mechanism</td>
<td>ZrO$_2$</td>
<td>II</td>
</tr>
<tr>
<td>QMS</td>
<td>Reaction mechanism</td>
<td>ZrO$_2$</td>
<td>II</td>
</tr>
<tr>
<td>Spectrophotometer</td>
<td>Thickness</td>
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<td>IV</td>
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<td>XPS</td>
<td>Interfacial layer composition</td>
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<td>Crystalline properties, crystalline phases</td>
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<td>XRR</td>
<td>Thickness, density, interface</td>
<td>TiO$_2$, ZrO$_2$, VO$_x$, Nb$_2$O$_5$, Ta$_2$O$_5$</td>
<td>I,II,III,IV,VI</td>
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</tbody>
</table>
3. Results and discussion

This chapter summarises the main results of group 4 and group 5 oxides film growth and characterization. Details of the processes can be found in the corresponding publications.\textsuperscript{1,VI}

3.1 ALD of group 4 metal oxide thin films

3.1.1 ALD of titanium oxide from mixed alkylamide-alkoxide and amidinate-alkoxide precursors

Two novel heteroleptic titanium precursors, were introduced for the ALD of TiO\textsubscript{2}, titanium (N,N'-diisopropylacetamidinate)tris(isopropoxide), ((PrO)\textsubscript{3}Ti(NPr-Me-amd)) and titanium bis(dimethylamide)bis(isopropoxide), (PrO)\textsubscript{2}Ti(NMe\textsubscript{2})\textsubscript{2} with water being used as the oxygen source for both processes.\textsuperscript{1} These two precursors are liquid at room temperature and have high volatility, thermal stability and reactivity. The (PrO)\textsubscript{3}Ti(NPr-Me-amd)/water process had an ALD window at 300–350 °C in which the GR was 0.45 Å/cycle. In contrast, the (PrO)\textsubscript{2}Ti(NMe\textsubscript{2})\textsubscript{2}/water process did not present any region of constant GRs (Figure 4), had a high GR of 0.7 Å/cycle at 325 °C. The self-limiting ALD growth mode was confirmed at 325 °C for both precursors (Figure 5).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{growth_rates}
\caption{Growth rates of TiO\textsubscript{2} thin films as a function of temperature when deposited from either (PrO)\textsubscript{3}Ti(NPr-Me-amd) or (PrO)\textsubscript{2}Ti(NMe\textsubscript{2})\textsubscript{2} with water as the oxygen source.\textsuperscript{1}}
\end{figure}
All the TiO$_2$ films deposited were crystallized to the anatase phase regardless of the deposition temperature or the film thickness within the temperature range investigated. XPS analysis revealed that the films were pure and close to their respective and expected stoichiometric compositions. The ($^t$PrO)$_2$Ti(NMe$_2$)$_2$/H$_2$O process was applied onto trenches (aspect ratio 60:1) at 275 °C to study the conformal growth properties of the films. The cross-section image (Figure 6) shows that the film had undergone conformal growth onto the trenches.

**Figure 5.** Growth rate of TiO$_2$ thin films at 325 °C as a function of the precursor pulse length when deposited from either ($^t$PrO)$_3$Ti(N’Pr-Me-amd) or ($^t$PrO)$_2$Ti(NMe$_2$)$_2$ and water as the oxygen source.

In the past, TiO$_2$ thin films have been predominantly deposited from TiCl$_4$ and alkoxides such as Ti(O’Pr)$_4$. However, such a TiCl$_4$/water process forms HCl as a by-product and has only a relatively modest GR (0.5 Å/cycle). Furthermore, the alkoxide Ti(O’Pr)$_4$ has even lower GR (0.3 Å/cycle) and its thermal stability is limited to 250 °C. The alkylamide precursor Ti(NMET)$_4$ has the relatively rapid growth rate of about 0.65 Å/cycle but the process has very low thermal stability (<225 °C). Amongst the heteroleptic precursors available for the ALD of TiO$_2$, ($^t$PrO)$_2$Ti(thd)$_2$, ($^t$amylo)$_2$Ti(thd)$_2$, (CpMe$_5$)Ti(NMe$_2$)$_3$ and (CpMe$_5$)Ti(OMe)$_3$ are highly thermally stable and undergo self-limiting growth above 300 °C but their respective GRs were below 0.5 Å/cycle. Moreover, ($^t$PrO)$_2$Ti(thd)$_2$ and (Me$_5$Cp)Ti(OMe)$_3$ are unreactive with water. Precursors that exhibit high thermal stability in addition to high growth rates and high reactivity towards water are needed for the ALD of TiO$_2$ thin films. This need was successfully met in this study by introducing the two novel heteroleptic titanium precursors ($^t$PrO)$_3$Ti(N’Pr-Me-amd) and ($^t$PrO)$_2$Ti(NMe$_2$)$_2$. 

46
Figure 6. Representative scanning electron microscope cross-section image of TiO$_2$ thin film deposited at 275 °C from the (\textit{i}PrO)$_2$Ti(NMe$_2$)$_2$/water process on 60:1 high aspect ratio substrate.\textsuperscript{1}

### 3.1.2 ALD of zirconium oxide thin films from an alkylamide-guanidinate compound

The synthesis and thermal thin characterization of (EtMeN)$_2$Zr(guan-NEtMe$_2$)$_2$, bis-(ethylmethylamido)-bis-(N,N-disopropyl-2-ethylmethylamidoguanidinato)-zirconium), has recently been published.\textsuperscript{125} The compound possesses encouraging thermal properties as found by isothermal TG studies at ambient pressure, which revealed it to sublime at a constant and appreciable rate for long periods of time (>200 min in the temperature range of 80 to 120 °C). These results motivated the evaluation of (EtMeN)$_2$Zr(guan-NEtMe$_2$)$_2$ as a precursor for the ALD of ZrO$_2$.

It was demonstrated that (EtMeN)$_2$Zr(guan-NEtMe$_2$)$_2$ is a suitable precursor for the ALD of ZrO$_2$, as it allows the growth of high quality ZrO$_2$ thin films.\textsuperscript{8} When deposited with water as the oxygen source, the GR remained constant over a wide temperature range, whereas with ozone as the oxygen source the GR increased steadily with the deposition temperature (Figure 7). The characteristic self-limiting ALD-growth was confirmed by the study of the growth rate as a function of the precursor pulse length at 300 °C, with high GRs of 0.90 and 1.15 Å/cycle with water and ozone, respectively (Figure 8).
Figure 7. Growth rate of ZrO\(_2\) thin films as a function of temperature when deposited from \((\text{EtMeN})_2\text{Zr(guan-NEtMe}_2\text{)}_2\) with either water or ozone as the oxygen source.\(^\text{II}\)

Figure 8. Growth rate of ZrO\(_2\) thin films as a function of the precursor pulse length at 300 °C when deposited from \((\text{EtMeN})_2\text{Zr(guan-NEtMe}_2\text{)}_2\).\(^\text{II}\)

QCM and QMS results provided insight into the reaction mechanism and indicated that \((\text{EtMeN})_2\text{Zr(guan-NEtMe}_2\text{)}_2\) adsorbs onto the surface by releasing the two guan-NEtMe\(_2\) ligands. Compositional analysis by XPS revealed low contamination from carbon and nitrogen (<2 at.% when deposited with ozone as the oxygen source). The films had low rms-roughness, below 5% of the film thickness, in addition to excellent step coverage and conformality on 30:1 aspect ratio trench structures (Figure 9). The dielectric characterization was performed by ZrO\(_2\) MIM capacitors. The films had high permittivity and low leakage currents.
This novel precursor has several advantageous features for the ALD of ZrO\textsubscript{2} over those of conventional precursors. Importantly, the films present the high permittivity cubic phase in the as-deposited state even at the low film thickness of 6 nm and a deposition temperature as low as 250 °C (Figure 10). The HTXRD experiments found that the cubic phase was very stable as no change in the structure was observed when the films were submitted to heat treatments of up to 875 °C, in N\textsubscript{2}. It is extremely important that the high permittivity cubic and tetragonal phases are easily formed, preferably as early as in the as-deposited state because the main application of ZrO\textsubscript{2} thin films is as a dielectric layer in microelectronics. Amongst the precursors reported in the literature, only the homoleptic and heteroleptic alkylamide compounds have this interesting property.
Figure 10. XRD patterns of ZrO\textsubscript{2} thin films (thickness=42 nm) deposited at 300 °C from (EtMeN\textsubscript{2})\textsubscript{2}Zr(guan-NEtMe\textsubscript{2})\textsubscript{2} a precursor and ozone as the oxygen source. All the peaks could be attributed to the cubic phase of zirconium oxide.

3.2 ALD of group 5 metal oxide thin films

3.2.1 ALD of vanadium oxide thin films from a tetraethylmethylamide vanadium precursor

V(NEtMe\textsubscript{4}} with either ozone or water as the oxygen source was investigated for the ALD of vanadium oxide. When water was used as the oxygen source a range of constant GRs from 125 and 200 °C was observed. Self-limiting film growth was confirmed at 150 °C respectively for ozone and water (Figure 11). The water process had the rather high growth rate of 0.8 Å/cycle. Atomic force microscopy revealed that the films were smooth (rms <0.5 nm) and uniform. The compositions and oxidation states of the as-deposited films were examined by XPS. When deposited at 150 °C, about 3 at.% of carbon contamination could be detected in the films. Increasing the deposition temperature to 200 °C lowered the amounts of impurities detected in the films. It was found that the vanadium oxide thin films were deposited in a mixture of its +4 and +5 oxidation states (Figure 12).
Figure 11. Growth rate of VO\textsubscript{x} thin films, using ozone (left) or water (right) as the oxygen source, as a function of the deposition temperature. The inset displays the saturation curve at 150 °C.

The influence of the process conditions and post-deposition annealing treatment on the film composition and structure were investigated. It was found that the oxygen source did not influence the film composition and structure. However, by simply changing the annealing atmosphere from N\textsubscript{2} to air it was possible to form either monoclinic VO\textsubscript{2} or orthorhombic V\textsubscript{2}O\textsubscript{5} at moderate temperatures, of between 250 and 450 °C, respectively (Figure 13). The ability of the films to form preferably phase pure VO\textsubscript{2} or V\textsubscript{2}O\textsubscript{5} upon post-deposition annealing in different atmospheres might perhaps be explained by the mixed composition of vanadium +4 and +5 in the as-deposited films. However, different results have been reported in the literature. Detavernier and co-workers found that the V(NEtMe)\textsubscript{4}/ozone process deposited amorphous VO\textsubscript{2} thin films and that these crystallized into the monoclinic VO\textsubscript{2} when annealed at 450 °C under an inert atmosphere.\textsuperscript{72} In contrast, Premkumar et al. obtained amorphous V\textsubscript{2}O\textsubscript{5} with liquid injected V(NEtMe)\textsubscript{4} and ozone and the films remained amorphous even after annealing at 425 °C in N\textsubscript{2}.\textsuperscript{139} When annealed in the presence of oxygen, the films crystallized but the resulting phases were strongly dependent on the partial pressure of the oxygen.\textsuperscript{139}
A small number processes have been reported for the thermal ALD of vanadium oxide: VOCl\(_3\) and water,\(^{132}\) VO(PrO)\(_3\) with either water\(^{131}\) or ozone\(^{25}\) as the oxygen source, VO(acac)\(_2\) with O\(_2\),\(^{133}\) vanadium \(n\)-propoxide with CH\(_3\)COOH,\(^{140}\) and V(NEtMe)\(_4\) with ozone.\(^{72}\)

Among these processes, self-limiting growth was only found for VO(PrO)\(_3\) and V(NEtMe)\(_4\) with ozone. Moreover, only the VO(PrO)\(_3\)/ozone process was reported to achieve the conformal growth of vanadium oxide on high aspect ratio substrates. Unfortunately, the ALD-growth of vanadium oxide from VO(PrO)\(_3\) and either water or ozone has a very low growth rate (0.2 Å/cycle). The vanadium oxide ALD processes described in this present study suggest simple control over the phase formation in addition to low roughness, high growth rate and good conformality of the films. These features offer advantages for a wide range of applications such as resistance switching memory and smart-window.\(^{26-29}\)
3.2.2 ALD of niobium and tantalum oxide thin films from mixed imides-alkylamides precursors

Imido-amido complexes were discovered to be efficient precursors for the ALD of niobium and tantalum oxide films.\textsuperscript{IV, V, VI} High quality Nb$_2$O$_5$ thin films were grown from (Et$_2$N)$_3$Nb=NtBu and (EtMeN)$_3$Nb=NtBu with either water or ozone as the oxygen source.\textsuperscript{IV} A wide temperature range of constant GR, between 175 and 325 °C, was found for these precursors, regardless of the oxygen source (Figure 14). The typical self-limiting ALD growth was confirmed at 275 °C, the highest deposition temperature ever reported for the self-limiting growth of Nb$_2$O$_5$. All the examined films were amorphous in the as-deposited state and subsequently crystallized to the orthorhombic phase of Nb$_2$O$_5$ between 525–575 °C, regardless of the precursor or the oxygen source. TOF-ERDA analysis demonstrated the high purity of the films. Atomic force microscopy revealed that the films were smooth and uniform. This is the first report on the ALD of Nb$_2$O$_5$ thin films that used ozone as the oxygen source. This might be of importance for applications for which the slow desorption of water would lead to problems in the form of excessively long purge times. For example, when deposited in large batches on high aspect ratio structures at low temperatures.

![Figure 14](image.png)

**Figure 14.** Growth rate of Nb$_2$O$_5$ and Ta$_2$O$_5$ thin films as a function of the deposition temperature using alkylamides-imides as the metal precursors and ozone as the oxygen source.\textsuperscript{IV, VI}

These new processes are a clear improvement over the previously available precursors for the ALD of Nb$_2$O$_5$. The studies that reported the ALD-growth from halide precursors (NbCl$_5$\textsuperscript{30}, NbI$_5$\textsuperscript{141} and NbF$_5$\textsuperscript{44}) did not provide any evidence of self-limiting growth and Nb(OEt)$_5$ exhibited low thermal stability (≤230 °C).
The dielectric properties of the Nb$_2$O$_5$ thin films were also investigated. The films possessed very high permittivity values, especially when crystallized. However this was strongly influenced by the physical thickness (Figure 15). It was also found that the dielectric properties were highly sensitive to deposition parameters and post-deposition treatment. For instance, the leakage current was up to two orders of magnitude higher in the amorphous Nb$_2$O$_5$ films compared to the films crystallized in the orthorhombic phase. This could be explained by a higher band offset for the crystallized films as suggested by the higher band gap extracted from the ellipsometry measurements. Therefore, a careful tuning of the deposition parameters and post-deposition treatment is required to achieve high dielectric performance.

![Graph showing the effects of physical thickness on the k-values of Nb$_2$O$_5$ thin films in the as-deposited state and annealed at 600 °C.](image)

**Figure 15.** The effects of physical thickness on the k-values of Nb$_2$O$_5$ thin films in the as-deposited state and annealed at 600 °C.

The precursor (NEt$_2$)$_3$Ta=NtBu also performed well for the ALD of Ta$_2$O$_5$ and possessed high reactivity towards both ozone and water. A wide temperature range of constant GR was recorded between 150 and 350°C (Figure 13). The films deposited for both the ozone and the water processes were amorphous in the as-deposited state and crystallized at around 700 °C into orthorhombic Ta$_2$O$_5$. 
Figure 16. AFM images of 25 nm thick Ta$_2$O$_5$ films deposited by the ozone process, amorphous in the as-deposited state (left) and crystallized after annealing at 700 °C in N$_2$ (right).^V

The morphology of the Ta$_2$O$_5$ films was studied by AFM. Figure 16 displays representative images of Ta$_2$O$_5$ thin films that had been deposited with ozone as the oxygen source at 325 °C, in the as-deposited state and after annealing at 700 °C in N$_2$. The films were found to be very smooth (0.2–0.3 nm rms roughness for 30 nm thick films) when deposited at 325 °C, regardless of the oxygen source. The loss of homogeneity and the new features observable in the annealed films were attributed to the crystallization into the orthorhombic phase. Moreover, x-ray photoelectron spectroscopy demonstrated high purity of the films deposited at 325 and 400 °C (Figure 17), whereas significant amounts of carbon impurities (5–10 at.%) were detected in the films deposited at 225 and 125 °C.

Figure 17. XPS depth profile of the elemental composition of a Ta$_2$O$_5$ films deposited with the water process at 400 °C.\textsuperscript{V}
3.2.3 Growth of niobium oxide thin films from mixed imide-alkoxide precursors

The precursor (\(\text{tBuO})_3\text{Nb=N'amy1}\) process was found to have poor thermal stability and did not undergo self-limiting growth at any deposition temperature. The poor thermal stability caused the decomposition of the precursor to contribute significantly to the film growth, which resulted in high thickness non-uniformity, high surface roughness and high impurity levels. Consequently, \((\text{tBuO})_3\text{Nb=N'amy1}\) was not investigated further for the ALD of \(\text{Nb}_2\text{O}_5\). On the other hand, because of its high volatility and low decomposition temperature \((\text{tBuO})_3\text{Nb=N'amy1}\) might be a suitable as a CVD precursor.
4. Conclusions

This thesis is dedicated to the investigation of the ALD of thin films of groups 4 and 5 metal oxides, with a particular interest in novel heteroleptic precursors. Several new processes were studied in detail and their respective films have been thoroughly characterized. It was found that the new alkoxide-alkylamide and -amidinate precursors, \((\text{PrO})_2\text{Ti}(\text{NMe}_2)_2\) and \((\text{PrO})_3\text{Ti(N'Pr-Me-amd)}\) are suitable precursors for the ALD of \(\text{TiO}_2\). Compared to the recently described highly thermally stable \((\text{Me}_5\text{Cp})\text{Ti(OMe)}_3\), these precursors do not require ozone as an oxygen source as they are also reactive with water. Moreover, their GRs are higher by a factor of two to three compared to the \((\text{CpMe}_5)\text{Ti(OMe)}_3/O_3\) process. The \((\text{PrO})_2\text{Ti}(\text{NMe}_2)_2/H_2\text{O}\) process especially had a growth rate as high as 0.75 Å/cycle. The films were pure (C<0.6 at.%) and grew with high conformallity on high aspect ratio substrates.

It was also found that a novel zirconium alkylamide-guanidinate compound is a suitable precursor for the ALD of \(\text{ZrO}_2\). This precursor was found to be reactive with both ozone and water, had self-limiting growth at 300 °C and produced high growth rates (up to 1.2 Å/cycle with ozone as the oxygen source). Even more interestingly, \(\text{ZrO}_2\) was deposited in the high permittivity cubic phase, even at deposition temperatures as low as 275 °C. The homoleptic tetraethylmethylamide vanadium precursor was evaluated for the ALD of vanadium oxide. Self-limiting growth was confirmed at 175 °C using either ozone or water as the oxygen sources, and the highly conformal films grew on high aspect ratio substrates. This process was found to be very versatile. It was found that one could preferably form either crystalline hexagonal \(\text{VO}_2\) or orthorhombic \(\text{V}_2\text{O}_5\) by simply varying the post-deposition annealing atmosphere even though the films were deposited in an amorphous mixture of vanadium +IV and +V oxidation states.

Novel alkylamide-imide based processes were developed for the ALD of \(\text{Nb}_2\text{O}_5\) and \(\text{Ta}_2\text{O}_5\). These precursors were discovered to be reactive with ozone and with water and the processes occurred over wide temperature ranges of constant growth rate (150-325 °C) when using ozone as the oxygen source. The films were found to be very smooth (rms <0.5 nm), uniform and contained low amounts of impurities. The alkoxide-imide precursor \((\text{BuO})_3\text{Nb=Namyl}\) was also evaluated but found to be unsuitable for the ALD of \(\text{Nb}_2\text{O}_5\) because of its poor thermal stability, which led to the self-decomposition of this precursor.

Table 13 summarizes the properties of alkoxide, Cp and alkylamide heteroleptic precursors for the thermal ALD of groups 4 and 5 metal oxides. It was discovered that heteroleptic alkoxide compounds are systematically more thermally stable than the homoleptic alkoxides,
except when associated with donor-functionalized-alkoxides. Moreover, donor functionalized alkoxides were found to be unsuitable as ALD precursors, either in homoleptic or heteroleptic compounds, because of their low thermal stabilities and/or the high amounts of impurities in their respective deposited films. Heteroleptic Cp’s also generally perform well as ALD precursors, which allows the intriguing possibility of tuning the precursor properties by varying the degree of substitution and the nature of the substituents on the Cp ring(s). Heteroleptic alkylamide compounds provide high GRs and high films purity characteristic of the homoleptic alkylamides but are also generally more thermally stable. Moreover, when depositing zirconium oxide, heteroleptic alkylamide compounds retain the property of forming the high permittivity cubic phase in the as-deposited state.

As yet many potentially advantageous heteroleptic precursors have still not been evaluated. For instance, it was observed that those Cp precursors with a high degree of substitution possessed better thermal stability than unsubstituted Cp’s. In addition, biscyclopentadienyl heteroleptic precursors seemed to have higher thermal stability than the similar monocyclopentadienyls. Therefore, it would be interesting to evaluate those Cp-alkylamide compounds that have two Cp rings and/or higher degree of substitution. Ideally, the thermal stability must be improved, while maintaining high GRs. Moreover, β-diketonate precursors have very high thermal stability but also have low growth rates and are unreactive with water. It was observed that the heteroleptic β-diketonate-alkoxide titanium precursors have high thermal stabilities and low GRs. However, they also have the added benefit of reactivity towards water. Therefore, it would be interesting to examine whether β-diketonate-alkylamide compounds have high thermal stabilities combined with the high growth rates and reactivity towards water that are characteristic of the alkylamides.
Table 13. Summary of the recorded observations of the ALD precursor properties of group 4 and 5 heteroleptic compounds (heteroleptic precursors with three ligands are not listed).

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<th>Alkoxides</th>
<th>Cp’s</th>
<th>Alkylamides</th>
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<tbody>
<tr>
<td><strong>Cp’s</strong></td>
<td>• $T_{\text{max}}$ below 300 °C and low GR when one Cp ring</td>
<td>• $T_{\text{max}}$ above 300 °C and High GR when two Cp rings</td>
<td>• Highly substituted Cp’s seem to perform well</td>
</tr>
<tr>
<td></td>
<td>• $T_{\text{max}}$ above 300 °C and High GR when two Cp rings</td>
<td>• $T_{\text{max}}$ ≥ 300 °C</td>
<td>• Otherwise $T_{\text{max}}$ ≤ 300 °C</td>
</tr>
<tr>
<td></td>
<td>• Alkylamide</td>
<td>• Alkylamide</td>
<td>• High GR</td>
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<td>• Self-decomposition</td>
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<td>• Zr: high thermal stability and high GR</td>
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<td>• Ti: good thermal stability</td>
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<td>• Solid</td>
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<td>• Only reactive with ozone</td>
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NR: not reported
5. References


