Atomic Layer Deposition of Zirconium Oxide and Rare Earth Oxides from Heteroleptic Precursors

Sanni Seppälä

Department of Chemistry
Faculty of Science
University of Helsinki
Finland

DOCTORAL DISSERTATION

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Supervisor
Professor Mikko Ritala
Department of Chemistry
University of Helsinki
Helsinki, Finland

Reviewers
Professor Jaan Aarik
Institute of Physics
University of Tartu
Tartu, Estonia

Professor Mats Boman
Department of Chemistry
Uppsala University
Uppsala, Sweden

Opponent
Professor Sami Franssila
Department of Chemistry and Materials Science
Aalto University
Espoo, Finland

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Abstract

This thesis focuses on the development of new atomic layer deposition processes for zirconium oxide and rare earth oxides. Atomic layer deposition (ALD) is a chemical thin film deposition method that is capable of generating films with excellent properties including conformality, uniformity, high density and pinhole free structure. Because of these film properties, ALD has become the best and often the only method capable of fulfilling the demands of many applications, microelectronics being the best example. The unique properties of ALD films are enabled by the self-limiting growth mechanism of these films.

Traditionally, ALD metal precursors have been homoleptic, meaning that the compound contains only one type of ligands. In the search of precursors with higher thermal stability, growth rate and uniformity, heteroleptic precursors with more than one type of ligands have gained interest. However, properties of different ligand combinations are hard to predict which means that comprehensive studies on the precursors with different oxygen sources are needed.

In this work, heteroleptic precursors for rare earth oxides and zirconium oxide were studied. ZrO$_2$ and rare earth oxides are so called high-κ materials with a wide variety of applications ranging from microelectronics to fuel cells, optics and catalysis. For the ALD of ZrO$_2$, three metal precursors, Zr(Me$_5$Cp)(TEA), Zr(MeCp)(TMEA) and ZrCp(tBuDAD)(OiPr) were evaluated with water or ozone as the oxygen source. Self-limiting growth processes typical for ALD were found for two Zr precursors with ozone. The deposition temperature for the self-limiting Zr(Me$_5$Cp)(TEA)/O$_3$ process was as high as 375 °C making Zr(Me$_5$Cp)(TEA) one of the most thermally stable precursors for zirconium. ZrO$_2$ films with high purity were deposited with the three precursors especially when ozone was used as the oxygen source.

Heteroleptic cyclopentadiene-amidinate precursors RE(iPrCp)(iPramd) were studied for Y, La, Pr, Gd and Dy. Water and ozone were studied as oxygen sources. In addition to these common oxygen sources, also ethanol as well as water and ozone in the same deposition process separated by a purge period were tested for the La$_2$O$_3$ deposition. Self-limiting growth was confirmed for Y$_2$O$_3$, La$_2$O$_3$ and Gd$_2$O$_3$. 

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**Preface**

The research and experimental work for this thesis work were conducted at the University of Helsinki in the Laboratory of Inorganic Chemistry.

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This doctoral dissertation is based on the following publications, which in the text are referred to by their Roman numerals.


*The author made the deposition experiments and performed the thickness and crystallinity analyses for Gd2O3 and PrOx and partly for Y2O3 and Dy2O3 and took all the FESEM images. The author wrote the first draft and finalized the paper together with the co-authors.*


*The author made the deposition and annealing experiments and performed the thickness and crystallinity analyses. The author wrote the first draft and finalized the paper together with the co-authors.*


*The author made the deposition experiments and performed the thickness and crystallinity analyses. The author made the electrical measurements together with M.V. The author wrote the first draft and finalized the paper together with the co-authors.*


*The author made the deposition experiments and performed the thickness and crystallinity analyses for Gd2O3 and PrOx. The author participated in the finalizing of the paper that was mostly written by J.N.*
Abbreviations

AFM  Atomic force microscopy
ALD  Atomic layer deposition
amd  Amidinate, NR(CR´)NR
Cp   Cyclopentadienyl, C5H5
C7H14 Cycloheptatrienyl, C7H7
CMOS Complementary metal-oxide-semiconductor
CVD  Chemical vapor deposition
dmae Dimethylaminoethoxide, OC2H5N(CH3)2
dmb  2,3-dimethyl-2-butoxy, OC(CH3)2CH(CH3)
DPDMG N,N'-diisopropyl-2-dimethylamido-guanidinate, (iPrN)2CN(CH3)2
DRAM Dynamic random access memory
Me2pz 3,5-dimethylpyrazolate
MOSFET Metal-oxide-semiconductor field effect transistor
PEALD Plasma enhanced atomic layer deposition
RE Rare earth
ReRAM Resistive switching random access memory
SOFC Solid oxide fuel cell
Bu tert-butyl
thd Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)
XRD  X-ray diffraction
XRR  X-ray reflection
1 Introduction

Today, we live in a world full of technology. In order to make faster and more powerful electronic devices, the size of the components is shrinking, and new materials and designs are sought. The fast down-scaling of the microelectronic components has led to a situation where new materials are needed to maintain the pace of improvement. Atomic layer deposition (ALD) has become the number one method to produce high quality films for microelectronics. In fact, ALD is the only method that can enable the production at the nanoscale on demanding structures with precise thickness control as well as film conformity and uniformity.

Zirconium oxide and rare earth oxides are so called high-κ oxides. High-κ material refers to a compound with a high dielectric constant, also called relative permittivity, $\varepsilon_r$. Permittivity is related to the capability of a material to resist applied electric field. The relative permittivity of vacuum is 1.0. In microelectronics, a material is considered to have high dielectric constant if it is higher than the dielectric constant of SiO₂ which is 3.9. For example, Al₂O₃ is already a high-κ material with a dielectric constant of around 9.

Zirconia and rare earth oxides are amongst the promising materials for microelectronics, but they are very versatile materials with applications in many other areas as well, such as in fuel cells, catalysis and optics. In the recent years, the research focus has shifted from precursors and ALD process development more towards application development and only a few new metal precursors for Zr and RE elements have been reported lately. However, to answer the demanding expectations set for the future high-κ materials, multicomponent materials are increasingly studied. These materials include doped, ternary and quaternary compounds. With ALD, the complex compounds can be deposited by simply combining binary processes. Film composition can be tuned by varying the ALD cycle ratios of the binaries. The main requirement is that the binary processes have a common deposition temperature. This can be assured by developing ALD processes having wide deposition temperature range. For this, basic studies on precursors and processes are the key.

In this thesis work, atomic layer deposition processes were developed for zirconium and rare earth oxide materials from new heteroleptic precursors and the properties of the deposited films were studied. Heteroleptic compounds have at least two different types of ligands and they are used in an effort to combine the best properties of the parent homoleptic precursors to improve for example film purity and thermal stability of the precursors. The end result is often unpredictable, however, highlighting the importance of precursor development and process studies.

This thesis comprises four papers that study new precursors for the ALD of rare earth and zirconium oxides. The principles of ALD are introduced in Chapter 2, together with the requirements for ALD precursors and the different types of metal and oxygen precursors used in ALD. Chapters 3 and 4 focus on the properties and ALD processes of rare earth oxides and zirconium oxide. Some applications for these materials are introduced in Chapter 5. The experimental procedures related to papers I – IV are described in Chapter 6 and the results are summarized in Chapter 7. Conclusions of the work are collected in Chapter 8.
2 Atomic layer deposition

2.1 Principles of ALD

Atomic layer deposition (formerly called atomic layer epitaxy, ALE) was invented in Finland in the 1970s to manufacture thin film electroluminescent (TFEL) displays.\(^1\) ALD is a chemical deposition method based on alternating pulses of precursors separated from each other with purging periods. This ensures that the reactions occur only on the surface of a substrate with molecules adsorbed during the previous precursor pulse while all the precursors in the gas phase are purged away. There is only a certain number of active reaction sites on the surface meaning that when these have reacted, no more film can be formed. Because of this, the film growth in ALD is self-limiting and the film thickness is dependent only on the number of the deposition cycles.\(^2\) The by-products and unreacted precursor molecules are purged away before the next pulse. In this way conformal, uniform and pinhole free films can be deposited.\(^3\) Also the film composition can be easily tuned by varying cycle ratios of the different components.\(^4,5\)

One deposition cycle in ALD of binary metal oxides consists of four steps: pulse of the first precursor, purge, pulse of the second precursor, and purge (Figure 1). In the first step, the substrate is exposed to the gaseous precursor and the precursor is chemisorbed on the substrate surface. In the second step, the unreacted precursor molecules are purged away by an inert gas. In the third step, the second precursor is transported to the substrate and a reaction the surface species formed by the first precursor takes place. In the fourth step the excess of the second precursor molecules and the reaction byproducts are purged away.\(^6\) The self-limiting growth that is the key feature of ALD means that increasing the pulse length does not affect the growth rate, but it stays constant. If the precursor is decomposing, increasing pulse length leads to an increased growth rate. If the precursor is etching the already formed film, the growth rate is decreased from the self-limiting value (Figure 2).

In ALD the film grows on all surfaces exposed to the precursor. This means that ALD is an excellent method for coating high aspect ratio substrates. Substrate materials can vary from glass to polymers and from wafers to particles or nanotubes.\(^7\) The slowness of the film deposition is considered as the biggest drawback of ALD. However, in many applications the film thicknesses are in the range of nanometers and the slow growth time is not a problem for these applications. Also, the film quality achieved with ALD is superior to many other thin film methods making ALD the only practical way to deposit films for some demanding applications such as microelectronics.
Figure 1. Illustration of one ALD cycle. Reprinted from *J. Appl. Phys.* 113, 2013, 021301, V. Miikkulainen et al. with the permission of AIP Publishing.

Figure 2. Self-limiting film growth is achieved when the growth rate does not change with increasing precursor pulse length. Constantly increasing growth rate may be caused by precursor decomposition and decreasing growth rate by etching reactions.
For a given ALD process, there is a suitable temperature range that depends on the precursor properties. Figure 3 depicts the mechanisms that can affect the growth rate at different temperatures. If the temperature is too low, there might be precursor condensation that increases the growth rate above the self-limiting growth rate (b), or too low reactivity of the precursors causing decreased growth rate (c). On the other hand, if the temperature is too high, the precursor might decompose increasing the growth rate (d) or desorb from the surface decreasing the growth rate compared to the self-limiting conditions (e). In the correct deposition temperature range where the self-limiting growth occurs, the growth rate may be constant (a), or dependent on the process temperature (f). The temperature range where the growth rate is independent of the temperature is often called as an ALD window. However, it is not a prerequisite for an ALD process.\(^2\) More important is that the growth is self-limiting.

![Figure 3. Scheme of (a) an ALD processing window limited by (b) precursor condensation, (c) insufficient reactivity, (d) precursor decomposition and (e) precursor desorption. If the deposition rate is dependent on the temperature dependent number of available reactive sites as in (f), actual ALD window cannot be observed. Reprinted from Ref. 6, with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (2004).](image)

### 2.2 ALD precursors

#### 2.2.1 Precursor requirements

For successful ALD precursors, there are many requirements from which some are essential and the others good to have but not necessary (Table 1). In ALD, gaseous precursors are transported to the substrate meaning that the precursors need to be volatile. The reactions should be fast and complete to ensure fast growth, high film purity and efficient usage of the precursors. The precursor should not decompose by itself or dissolve into the substrate because these destroy the self-limiting growth which is the key feature of ALD. There should not be etching of the film or substrate and the precursors should be of sufficient purity, which depends on the process and application. The desirable properties include unreactive volatile byproducts to avoid corrosion and decrease of the growth rate by readdsorption or etching reactions, easiness of synthesis and handling, nontoxicity and environmental friendliness as well as affordable price.\(^3,4\)
### 2.2.2 Metal precursors

In ALD, the precursor can affect for example the purity and crystal phase of the films, making it of utmost importance to study different precursors to develop a process with the best properties for the chosen application. Options for the oxygen source are more limited than for the metal precursors, but in many cases the oxygen source has been shown to have a tremendous effect on the properties such as purity of the metal oxide films.

A variety of different kinds of metal compounds have been studied as ALD precursors. The diverse ligand types used in the metal precursors are shown in Figure 4. Some examples of the different ligand families are introduced in this chapter.

Metal halides are examples of inorganic metal precursors. They often have high thermal stability, but the byproducts are corrosive. These byproducts have been proposed to decrease film growth by poisoning the reactive sites or by etching the already grown film. In the etching, hydrogen halide byproduct reacts with the metal oxide film forming volatile metal halide or metal oxyhalide that is then purged away. Etching can also be caused by the precursor itself, like in the case of the NbCl₅/H₂O process: in a reaction between NbCl₅ and Nb₂O₅ film, a volatile NbOCl₃ is formed causing highly nonuniform and irreproducible film growth. Another drawback of the solid metal chloride precursors has been observed with the ZrCl₄/H₂O process where very fine precursor particles are transported by the carrier gas to the substrate and incorporated in the film.

Metal alkoxides and β-diketonates are examples of precursors with metal-oxygen bonds. Alkoxide ligands bond to the metal via one O atom and β-diketonates via two oxygen atoms. Alkoxide precursors tend to form oligomers because the ligands do not screen the metal atoms from other species nearby. For sufficient volatility, bulky alkoxide ligands with better screening property are often needed. The thd ligand, tris(2,2,6,6-tetramethyl-3,5-heptanedionato), that belongs to the β-diketonate group has been particularly important in the development of ALD processes for lanthanide oxides. Lanthanide ions are large and need high coordination numbers to satisfy their coordination spheres. The synthesis of the RE(thd)₅ chelates was first published by Eisentraut and Sievers in 1965.
Organometallic precursors have direct metal-carbon bonds. Cyclopentadienyl (Cp) and alkyl precursors belong to this group. Properties of the Cp precursors can easily be tuned by changing the substituents in the Cp ring which makes them very versatile ligands. Cyclopentadienyls are good electron donors and form stable bonds with metals which ensures reasonable thermal stability of the compounds. However, the bulky Cp can decrease the growth rate. The best known and very widely used metal alkyl precursor is trimethylaluminum which, when used with water, is the textbook example of an ALD process.

Examples of precursors with metal-nitrogen bonds are amides, amidinates and guanidinates. These precursors do not have a direct metal to carbon bond which might help decreasing carbon contamination in the films. In an analogy to the alkoxides and β-diketonates, alkylamide ligands bond to metal atoms via one nitrogen atom and amidinates and guanidinates via two nitrogen atoms. Alkylamide ligands effectively prevent interactions between neighboring molecules thus leading to high volatility. Amidinates have high thermal stability because of the chelating effect.

Traditionally, ALD metal precursors have been homoleptic, meaning that all the ligands in the molecule are similar to each other. An example of a homoleptic precursor is ZrCl_4. Heteroleptic precursors have at least two different kinds of ligands, for example CpZr(NMe_2)_3 is a heteroleptic Zr precursor. The aim of the heteroleptic approach is to combine the best properties of the parent homoleptic compounds. Desired properties include improved thermal stability, growth rate and volatility. However, it is hard to predict the outcome of the different ligand combinations and therefore they need to be studied experimentally. In the past ten years, more and more heteroleptic precursors have been reported in ALD. The reason is apparently the ever-increasing requirements for materials in the future microelectronic industry, which drives the development of many materials, and not least the high-κ dielectrics.
2.2.3 Oxygen precursors

Many oxygen sources have been studied for the deposition of metal oxides by ALD. The oxygen source can affect dramatically the film properties and by changing the oxygen source it is possible for example to tune the oxidation state of the metal or crystalline phase of the films. The most popular oxygen source is water which has many advantages such as user and environment friendliness. However, some materials, like RE oxides, are hygroscopic which means that they absorb water. Long purge times are needed to ensure self-limiting growth, but this approach is not always applicable in industrial processes.

Aqueous solution of H$_2$O$_2$ has also been studied as an oxygen source in ALD. H$_2$O$_2$ is more reactive than water and the idea is that it could improve film properties compared to water. Higher growth rate compared to water has been reported for example in In$_2$O$_3$ deposition. In the case of ZrO$_2$, growth mechanism and phase composition did not depend on the oxygen source, but lower permittivity and leakage current have been reported for the films deposited with the H$_2$O$_2$-H$_2$O solution as the oxygen source compared to water.
Some metal precursors have low reactivity towards water and need stronger oxidizer such as ozone or oxygen plasma. The RE(thd)$_x$ compounds are a good example of precursors having low reactivity towards water. They are usually used together with ozone. Although ozone can be very useful for ALD especially in those cases when water is not a good option, it has its own drawbacks. Because ozone is a strong oxidizer, it can oxidize also the substrate leading to undesirable interface layers. In microelectronic applications this can be detrimental as it decreases the total capacitance of the dielectric stack. Ozone is not very stable molecule and some substrate materials can catalyze its decomposition which might cause nonuniformity to the film especially in cross-flow reactors and in trenches and other high aspect ratio substrates.\textsuperscript{5} Also, carbonate formation has been observed when ozone has been used to deposit metal oxides prone to carbonate formation, such as lanthanum oxide and calcium oxide.\textsuperscript{19,20} On the other hand, efficient ligand removal by combustion with ozone can lead to increased film purity compared to water.\textsuperscript{21,111}

Several milder oxygen sources have been studied to avoid the interfacial layer formation between an oxide film and silicon substrate. These include carboxylic acids, alcohols, N$_2$O and O$_2$. Molecular oxygen is usually not reactive, but it has been used for example in the deposition of very thin ZrO$_2$ and La$_2$O$_3$ films (3 – 6 nm) with lanthanum tris(N,N’-diisopropylformamidinate) and zirconium tetrakis(diethylamine).\textsuperscript{22,23} Jeong et al.\textsuperscript{24} compared H$_2$O, O$_2$ and N$_2$O as oxygen sources in the deposition of ZrO$_2$. The zirconium source was tert-butoxide. With water, crystalline films were deposited at 170 °C whereas with O$_2$ and N$_2$O amorphous films were deposited. The interfacial layer between the film and Si substrate was slightly thinner when O$_2$ or N$_2$O were used compared to H$_2$O.\textsuperscript{24}

From alcohols, for example methanol, ethanol and isopropanol have been studied as oxygen sources in ALD. Aluminum oxide has been deposited from TMA and isopropanol successfully without interface layer formation at 350 °C on GaAs\textsuperscript{25} and at 250 °C on Si substrates.\textsuperscript{26} The growth rate at 350 °C on GaAs was 0.8 Å/cycle which is slightly lower than with water (1.0 Å/cycle).\textsuperscript{25} Marstell and Strandwitz have reported clearly higher carbon content in films deposited with isopropanol compared to water.\textsuperscript{27} In this thesis work, ethanol was studied as an oxygen source in the deposition of La$_2$O$_3$. It was noted that at a higher deposition temperature of 300 °C the growth rate increased significantly compared to lower temperatures. This was attributed to the water formation through dehydration of ethanol release during the deposition (see Chapter 7.2.1).\textsuperscript{11}

Another way to avoid the interlayer formation in ALD is to use reactions between carboxylic acid and metal alkoxide.\textsuperscript{28} Carboxylic acids have low oxidation power and the film is formed via surface esterification.\textsuperscript{29} Yet another approach that has been studied to deposit metal oxide films without interface layer is to use metal alkoxides as both metal and oxygen sources.\textsuperscript{30,31,32} The other precursor is a metal halide and the metal oxide is formed via an alkyl halide elimination. Metal alkyl precursors can also be used instead of halides.\textsuperscript{30} The metal can be the same in both precursors to form binary oxides or different so that mixed metal oxide films are obtained. For example, Al$_x$Zr$_y$O$_2$ has been deposited this way from Al(OEt)$_3$ and ZrCl$_4$ and Zr$_x$Ti$_y$O$_2$ from Ti(O$i$Pr)$_4$ and ZrCl$_4$.\textsuperscript{30,53}
This thesis work is focused on thermal ALD, but metal oxide films can also be deposited with plasma enhanced atomic layer deposition (PEALD). The advantage of PEALD is enhanced reactivity compared to the thermal ALD, especially at low deposition temperatures, which enables the use of temperature-sensitive substrates and metal precursors with low reactivity for example towards water. As a down side, the step coverage on high aspect ratio structures is often observed to be decreased with PEALD compared to the thermal ALD.\textsuperscript{34,35} Plasma enhanced ALD cannot be applied in batch processing of large number of substrates. Oxygen plasma is commonly used as an oxygen source in PEALD. The main reactive species in oxygen plasma are oxygen radicals. Due to the high reactivity of the oxygen plasma, interfacial oxide layer formation similar to the thermal ALD using ozone has been reported with PEALD.\textsuperscript{35}
3 Rare earth oxide thin films

3.1 Properties of rare earth oxides
Rare earth oxides refer to the oxides formed by scandium (atomic number 21), yttrium (39) and lanthanide metals (from lanthanum to lutetium, atomic numbers 57 - 71) (Figure 5). In the solid state, the stable oxidation state for rare earths is +3, and thus they are forming sesquioxides with a formula $\text{RE}_2\text{O}_3$. Ce, Pr and Tb are also stable at +4 oxidation state and Eu at +2 oxidation state.\(^{36}\)

The ionic radius of the lanthanide $\text{Ln}^{3+}$ ions decreases when moving from left to right along the series. This is caused by poor screening of the electrons on the 4f orbitals. Therefore, the effective nuclear charge experienced by the outer electrons increases with increasing atomic number, the electrons are pulled closer to the nucleus and the radius decreases.\(^{37}\) The decrease of the radius is called lanthanide contraction. The effective radius of the $\text{La}^{3+}$ ion is 103.2 pm and $\text{Lu}^{3+}$ 86.1 pm. In comparison, the effective radius of the $\text{Sc}^{3+}$ ion is 74.5 pm and $\text{Y}^{3+}$ 90 pm.\(^{38}\)

![Periodic table of the elements. The rare earth metals and zirconium are highlighted.](image)

Rare earth oxides are thermally stable compounds and rare earth metals readily form the oxides when in contact with oxygen. However, the oxides form hydroxides and carbonates with water vapor and carbon dioxide in the atmosphere. The tendency to form carbonates and hydroxides decreases when moving from left to right in the lanthanide series, lanthanum having the highest tendency.\(^{39}\) The hygroscopicity has been attributed to the lower electronegativity of the early lanthanides compared to the heavier ones.\(^{40}\) Changes in the surface morphology of an annealed $\text{La}_2\text{O}_3$ film after exposure to air are shown in Figure 6. Formation of $\text{La(OH)}_3$ increases the roughness and decreases the permittivity of the film making the $\text{La(OH)}_3$ formation very undesirable in microelectronic applications.\(^{41,42}\)
suppress the moisture absorption of La$_2$O$_3$, ternary oxides such as LaAlO$_3$,$^{43,44}$ LaLuO$_3$ $^{45,46}$ and La$_y$Zr$_{1-y}$O$_x$ $^{47}$ have been studied. Suppression of the hygroscopicity has also been achieved with PrAlO films as compared to the plain PrO$_x$ films.$^{48}$

![La$_2$O$_3$ film surface morphology after exposure to air for: a) 0 hours b) 6 hours and c) 12 hours. Reprinted from ref. 42 (MDPI publishing 2012).](image)

Figure 6. La$_2$O$_3$ film surface morphology after exposure to air for: a) 0 hours b) 6 hours and c) 12 hours. Reprinted from ref. 42 (MDPI publishing 2012).

### 3.2 Atomic layer deposition of rare earth oxides

Lanthanide 3+ ions are large and have high coordination numbers which favors the use of bidentate ligands to avoid oligomerization which leads to poorly volatile compounds. ALD of lanthanide oxides has been quite difficult because of the hygroscopicity of the films. This can lead to uncontrolled reactions: water is absorbed during the water pulse and if the purge period between the precursor pulses is not long enough, desorption continues during the next pulse allowing reaction between water and metal precursor destroying the self-limiting growth.$^{43}$ With ozone, carbonates have been observed to form along with oxides.$^{19}$ Also, Pr and Tb oxide films have been reported to have thickness gradients across the substrate when ozone is used as the oxygen source in cross-flow ALD reactors. The ability to adopt mixed oxidation state makes Pr and Tb oxides catalytically active, which may explain the nonuniformity of the films.$^{49}$
RE(thd)$_x$ precursors are the most studied for RE oxides and almost all RE metals have an ALD precursor with thd ligands.$^{49,50,51}$ These precursors typically have high thermal stability, but unfortunately the growth rates are very low, in the range of 0.2 – 0.4 Å/cycle. Praseodymium and terbium oxides have been shown to crystallize to RE$_6$O$_{11}$ and PrO$_2$ phases instead of the RE$_2$O$_3$ phase usually seen for the rare earth oxides.

There are not many examples of rare earth alkoxide precursors, Lu(O$i$Pr)$_3$ and Gd(dmb)$_3$ (dmb = 2,3-dimethyl-2-butokside) representing the few.$^{52,53}$ Many alkoxides of rare earths form oligomers that have low volatility and hence are not suitable as ALD precursors.$^{54}$ In the study on the Lu(O$i$Pr)$_3$/H$_2$O process, no other details of the process were given except the deposition temperature (330 °C).$^{52}$ The Gd(dmb)$_3$/H$_2$O process was studied at deposition temperatures of 250 – 400 °C and saturation of the growth rate was tested at 400 °C. The growth rates with different pulse lengths were scattered but no obvious trend of increasing growth rate with increasing Gd(dmb)$_3$ pulse length indicating thermal decomposition of the precursor was observed.$^{53}$

A donor functionalized alkoxide precursor, Ce(mmp)$_4$ (mmp = 1-methoxy-2-methyl-2-propanolate) has been used in the ALD of CeO$_2$ together with water using liquid injection delivery.$^{55}$ In this method, the metal precursor is dissolved in a solvent which is then injected into the evaporator. Liquid injection can enable the use of less thermally stable and less volatile precursors.$^{56}$ ALD-type growth of CeO$_2$ was confirmed at 300 °C with a growth rate of 1.2 Å/cycle.$^{55}$ Other rare earth mmp precursors, namely Pr(mmp)$_3$ and Gd(mmp)$_3$ have also been studied in liquid injection ALD of PrO$_x$ and Gd$_2$O$_3$ but saturation was not achieved.$^{56}$

Cyclopentadiene precursors have gained a lot of interest in the recent years.$^{57}$ In general, they show much higher growth rates than the RE(thd)$_x$ precursors and can be used with water or ozone. However, their thermal stability is often lower than that of the thd precursors. In some cases, even though self-limiting growth has not been achieved, films with good uniformity and low impurity levels have been reported. For example, Niinistö et al. reported low carbon impurity content of 0.5 at% and thickness nonuniformity less than 2 % along the gas-flow direction for the Gd(CpMe)$_3$/H$_2$O process even though self-limiting growth was not observed.$^{51}$

From the precursors with M-N bonds, simple rare earth alkylamides, RE(NR$_2$)$_3$, are unstable and involatile.$^{58}$ However, silylamine precursors, RE[N(SiMe$_3$)$_2$]$_3$, have been studied for La, Pr and Gd with water as the oxygen source. Unfortunately, self-limiting growth was not observed, and the films contained some residual Si.$^{58,59,60}$

Amidinates NR(CR´)NR and guanidinates NR(CNR´$_2$)NR have been studied successfully for the growth of various RE oxides. RE(DPDMG)$_3$ precursors (DPDMG=N,N’-diisopropyl-2-dimethylamido-guanidinate) have been studied for Y, Gd and Dy.$^{61,62,63}$ Self-limiting growth was reported at temperatures of 225 – 250 °C with growth rates of 1.0 – 1.1 Å/cycle depending on the metal. Acetamidinate compounds RE tris(N,N’-disopropylacet- amidinato) (RE(amd)$_3$) have been reported for many rare earth metals. Self-limiting growth has been observed around 300 °C for Sc$_2$O$_3$ and Y$_2$O$_3$ films with water as the oxygen source.
source. In contrast, praseodymium acetamidinate/H\textsubscript{2}O process was not self-limiting because of the absorption of water by the film. \textsuperscript{48} La(amd)\textsubscript{3} was used together with water to deposit La\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} nanolaminates\textsuperscript{43}. By depositing only thin layers of La\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} in between, the absorption of water was minimized and the water could be desorbed without excessively long purge times and self-limiting growth was achieved at 330 °C with a growth rate of 0.8 Å/cycle estimated for the La\textsubscript{2}O\textsubscript{3} part.\textsuperscript{43} ALD processes for RE oxides using homoleptic metal precursors are collected in Table 2.

### Table 2. Thermal ALD processes reported for RE oxides using homoleptic RE precursors.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Oxygen source</th>
<th>Studied T range (°C)</th>
<th>Self-limiting growth confirmed (°C)</th>
<th>Growth rate (Å/cycle)\textsuperscript{a}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc(thd)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>250 – 500</td>
<td>375</td>
<td>0.13</td>
<td>66</td>
</tr>
<tr>
<td>Sc(Cp)\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>175 – 500</td>
<td></td>
<td>0.75</td>
<td>66</td>
</tr>
<tr>
<td>Sc(PrCp)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>250 – 400</td>
<td>300</td>
<td>0.7</td>
<td>67</td>
</tr>
<tr>
<td>Sc(MeCp)\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>250 – 350</td>
<td>300</td>
<td>0.65</td>
<td>57, 68</td>
</tr>
<tr>
<td>Sc(Pramd)\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>290 – 360</td>
<td>290</td>
<td>0.3</td>
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</tr>
<tr>
<td>Sc(CpMe\textsubscript{4})\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>180 – 250</td>
<td>250</td>
<td>0.36</td>
<td>19</td>
</tr>
<tr>
<td>Sc(MeCp)\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>230 – 350</td>
<td>270</td>
<td>0.35</td>
<td>73</td>
</tr>
<tr>
<td>Sc(iPrCp)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>200 – 425</td>
<td>350</td>
<td>0.23</td>
<td>69</td>
</tr>
<tr>
<td>Sc(EtCp)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>250 – 350</td>
<td></td>
<td>0.23</td>
<td>69</td>
</tr>
<tr>
<td>Sc(iPramd)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>150 – 400</td>
<td></td>
<td>0.22</td>
<td>69</td>
</tr>
<tr>
<td>Sc(iPramd)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>150 – 400</td>
<td></td>
<td>0.22</td>
<td>69</td>
</tr>
<tr>
<td>Sc(DPDMG)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>150 – 280</td>
<td>225</td>
<td>1.1</td>
<td>61</td>
</tr>
<tr>
<td>Y</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y(thd)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>200 – 425</td>
<td>350</td>
<td>0.23</td>
<td>69</td>
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<tr>
<td>Y(thd)\textsubscript{4}(bipy)</td>
<td>O\textsubscript{3}</td>
<td>200 – 425</td>
<td>350</td>
<td>0.23</td>
<td>69</td>
</tr>
<tr>
<td>Y(thd)\textsubscript{4}(phen)</td>
<td>O\textsubscript{3}</td>
<td>200 – 425</td>
<td>350</td>
<td>0.22</td>
<td>69</td>
</tr>
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<td>YPc\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>175 – 500</td>
<td>250, 300</td>
<td>1.5 – 1.6</td>
<td>70</td>
</tr>
<tr>
<td>Y(MeCp)\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>175 – 450</td>
<td>250, 300</td>
<td>1.3</td>
<td>70</td>
</tr>
<tr>
<td>Y(EtCp)\textsubscript{3}</td>
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<td>150 – 400</td>
<td>250</td>
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<td>71</td>
</tr>
<tr>
<td>Y(PrCp)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>200 – 350</td>
<td>270</td>
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<td>72</td>
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<tr>
<td>Y(Pramd)\textsubscript{3}</td>
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<td>150 – 330</td>
<td>280</td>
<td>0.8</td>
<td>65</td>
</tr>
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<td>Y(DPDMG)\textsubscript{3}</td>
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<td>150 – 280</td>
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<td>61</td>
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<td>La</td>
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<td></td>
</tr>
<tr>
<td>La(thd)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>180 – 425</td>
<td>250</td>
<td>0.36</td>
<td>19</td>
</tr>
<tr>
<td>La(Cp)\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>230 – 350</td>
<td>270</td>
<td>0.35</td>
<td>73</td>
</tr>
<tr>
<td>La(CpMe\textsubscript{4})\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>260</td>
<td>not studied</td>
<td>-</td>
<td>74</td>
</tr>
<tr>
<td>La(PrCp)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>150 – 300</td>
<td>225</td>
<td>0.6</td>
<td>67</td>
</tr>
<tr>
<td>La[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>150 – 250</td>
<td>225</td>
<td>0.6</td>
<td>67</td>
</tr>
<tr>
<td>La(Prfamd)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>200 – 250</td>
<td>225</td>
<td>1.0</td>
<td>76</td>
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<tr>
<td>La(Prfamd)\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>200 – 250</td>
<td>225</td>
<td>0.2</td>
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<tr>
<td>La(Prfamd)\textsubscript{3}</td>
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<td>O\textsubscript{3}</td>
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<td>300</td>
<td>1.2</td>
<td>55</td>
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<td>Pr</td>
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<td>Pr(thd)\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>190 – 350</td>
<td>not self-limiting</td>
<td>0.52 (200)</td>
<td>78</td>
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<tr>
<td>Pr(EtCp)\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>130, 180, 250</td>
<td>130</td>
<td>0.7</td>
<td>79</td>
</tr>
<tr>
<td>Pr(PrCp)\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>175 – 225</td>
<td>not self-limiting</td>
<td>1.6 (175)</td>
<td>80</td>
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<tr>
<td>Pr(Pramd)\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
<td>200 – 315</td>
<td>not self-limiting</td>
<td>1.3 (?</td>
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<td>Pr[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{3}</td>
<td>H\textsubscript{2}O</td>
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<td>not self-limiting</td>
<td>0.3 (300)</td>
<td>60</td>
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<td>Pr(mmp)\textsubscript{4}</td>
<td>H\textsubscript{2}O</td>
<td>150 – 350</td>
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<td>Not reported</td>
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<tr>
<td>RE</td>
<td>Precursor/ makeshift</td>
<td>Oxidation State</td>
<td>Temp Range</td>
<td>Temp Studied</td>
<td>Growth Rate</td>
</tr>
<tr>
<td>-----</td>
<td>----------------------</td>
<td>-----------------</td>
<td>-------------</td>
<td>--------------</td>
<td>-------------</td>
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<tr>
<td>Nd</td>
<td>Nd(thd)$_3$</td>
<td>O$_3$</td>
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<td>Sm</td>
<td>Sm(thd)$_3$</td>
<td>O$_3$</td>
<td>200 – 400</td>
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</tr>
<tr>
<td>Eu</td>
<td>Eu(thd)$_3$</td>
<td>O$_3$</td>
<td>200 – 400</td>
<td>not studied</td>
<td>0.3 (300)</td>
</tr>
<tr>
<td>Gd</td>
<td>Gd(thd)$_3$</td>
<td>O$_3$</td>
<td>225 – 400</td>
<td>300, 0.3</td>
<td>51</td>
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<tr>
<td></td>
<td>Gd(CpMe)$_3$</td>
<td>H$_2$O</td>
<td>150 – 350</td>
<td>not self-limiting</td>
<td>2.5 (250)</td>
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<tr>
<td></td>
<td>Gd(PrCp)$_3$</td>
<td>H$_2$O</td>
<td>250</td>
<td>not self-limiting</td>
<td>2.5 (250)</td>
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<td></td>
<td>Gd(dimb)$_3$</td>
<td>H$_2$O</td>
<td>300 – 400</td>
<td>400, 0.4</td>
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<td></td>
<td>Gd(DPDMG)$_3$</td>
<td>H$_2$O</td>
<td>150 – 300</td>
<td>225, 250</td>
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</tr>
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<td></td>
<td>Gd[N(SiMe$_3$)$_2$]$_3$</td>
<td>H$_2$O</td>
<td>150 – 300</td>
<td>not self-limiting</td>
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<td>Gd(mmp)$_3$</td>
<td>H$_2$O</td>
<td>200 – 300</td>
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<td>Tb</td>
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<td>O$_3$</td>
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<td>0.85 (300)</td>
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<td>Dy</td>
<td>Dy(thd)$_3$</td>
<td>O$_3$</td>
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<td>Dy(DPDMG)$_3$</td>
<td>H$_2$O</td>
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<td>225, 250, 1.0</td>
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<td>Ho</td>
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<td>O$_3$</td>
<td>200 – 400</td>
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<tr>
<td>Er</td>
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<td>O$_3$</td>
<td>200 – 450</td>
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<td>Er(CpMe)$_3$</td>
<td>H$_2$O</td>
<td>175 – 450</td>
<td>250, 300, 1.5</td>
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<td>Er(Cp’Pr)$_3$</td>
<td>H$_2$O</td>
<td>200 – 300</td>
<td>250, 0.4</td>
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<td>Er(Cp’Bu)$_3$</td>
<td>H$_2$O</td>
<td>225 – 375</td>
<td>275, 0.8</td>
<td>92</td>
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<td>Er(TBuamd)$_3$</td>
<td>O$_3$</td>
<td>225 – 300</td>
<td>not self-limiting</td>
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<td>Er(DPDMG)$_3$</td>
<td>H$_2$O</td>
<td>150 – 350</td>
<td>200, 225, 1.1</td>
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<td>Tm</td>
<td>Tm(thd)$_3$</td>
<td>O$_3$</td>
<td>200 – 400</td>
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<td>0.2 (300)</td>
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<td>Tm(Cp)$_3$</td>
<td>H$_2$O</td>
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<tr>
<td>Yb</td>
<td>Yb(thd)$_3$</td>
<td>O$_3$</td>
<td>200 – 400</td>
<td>300, 350, 0.15</td>
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<tr>
<td></td>
<td>Yb(CpMe)$_3$</td>
<td>H$_2$O</td>
<td>200 – 400</td>
<td>250, 1.0</td>
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<td>Lu</td>
<td>Lu(thd)$_3$</td>
<td>O$_3$</td>
<td>300</td>
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</tr>
<tr>
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<td>Lu(PrCp)$_3$</td>
<td>H$_2$O</td>
<td>200 – 330</td>
<td>250, 0.75</td>
<td>89</td>
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</tbody>
</table>

*Growth rate at self-limiting growth conditions. If no self-limiting growth is detected or studied, marked is the growth rate at the temperature which is shown in parenthesis (°C). * Growth rate estimated from La$_x$Al$_{2-x}$O$_3$ deposition.

Table 3 summarizes the few heteroleptic precursors used in the ALD of RE oxides. Very recently, Rahman et al. studied heteroleptic scandium precursor Sc(MeCp)$_2$(Me$_2$pz) (Me$_2$pz = 3,5-dimethylpyrazolate).90,91 This precursor was designed to improve the reactivity of Sc(MeCp)$_3$. It was shown that saturative chemisorption is achieved on a SiO$_2$ surface after 1 s pulse above 150 °C and the resulting surface species are stable up to 400 °C.91 ALD growth was studied with ozone but only 20 cycles were made. Self-limiting growth mechanism was reported but because the scandium precursor was shown to react directly with the SiO$_2$ native oxide on the surface of the silicon substrate forming Sc$_2$O$_3$, and ozone oxidized the underlying Si substrate through the 20 cycle experiment, growth rate of the Sc$_2$O$_3$ film could not be derived.90
A heteroleptic erbium precursor, Er(MeCp)₂(iPr-amd) was studied by Blanquart et al. 92 Self-limiting growth was obtained at 250 °C with both water and ozone as the oxygen source. The growth rates were 0.4 Å/cycle with O₃ and 1.2 Å/cycle with H₂O. Oh et al. studied the same Er precursor with water as the oxygen source. 93 They reported constant growth rate of around 0.5 Å/cycle between 180 and 250 °C and a decrease in growth rate from 0.5 Å/cycle to 0.2 Å/cycle when the temperature was increased to 320 °C. Self-limiting growth was confirmed at 180 °C by Oh et al. Blanquart et al. reported a slight increase in the growth rate from 1.10 to 1.35 Å/cycle between 225 and 325 °C with water. 92 The growth rate is more than doubled compared to the work of Oh et al. No obvious reason for the different growth rates could be found from the articles. It could be partially related to the different ALD reactor types used in the two studies.

The homoleptic counterpart of the Er(MeCp)₂(iPr-amd) precursor, Er(MeCp)₃ has been studied previously with water or ozone as the oxygen source. 94, 95 With water, self-limiting growth was confirmed with a growth rate of 1.5 Å/cycle at 300 °C. 94 The growth rate is slightly higher than that reported for the Er(MeCp)₂(iPr-amd)/H₂O process by Blanquart et al. With ozone, the growth rate was reported to be three times higher than with the heteroleptic precursor over a wide temperature range from 170 to 330 °C but unfortunately the growth rate saturation was not studied. 95 Er(iPr-amd)₃ has not been reported in ALD of Er₂O₃ but another amidinate, Er(Bu-amd)₃ [tris(N,N′-di-tert-butylacetamidinato)erbium] has been studied with ozone. 94 The growth rate was 0.39 Å/cycle at 250 °C but self-limiting growth could not be confirmed. Interestingly, the growth rate was around 0.4 – 0.5 Å/cycle depending on the precursor pulse length, which is in the same range as with the heteroleptic Er(MeCp)₂(iPr-amd)/O₃ process at the same temperature. 92

Scarel et al. have studied heteroleptic Lu precursor, dimeric {Lu[Cp(SiMe₃)]₂Cl}₂. 96 Lu₂O₃ film deposition from {Lu[Cp(SiMe₃)]₂Cl}₂ with water as the oxygen source was reported only at a temperature of 360 °C and no evidence of self-limiting growth was shown. 96

The heteroleptic Y precursor Y(iPrCp)₂(iPr-amd) reported in Publication I in this thesis has been studied previously with water. 97, 98 Park et al. reported ALD of Y₂O₃ at a temperature range 250 – 450 °C. The growth rate decreased with increasing deposition temperature and self-limiting growth with a rate of 0.6 Å/cycle was obtained at 350 °C. 97 The saturation temperature was the same as in I but otherwise these results were somewhat different compared to the Publication I in this thesis. In I, the growth rate was observed to increase with increasing temperature from 200 to 350 °C. Decrease in growth rate with increasing temperature was not observed with any of the studied RE(PrCp)₂(Pr-amd) precursors. 11, 11, 11, 11 Also, the growth rate in Publication I was twice as high as the one obtained by Park et al. Lee et al. studied the Y(iPrCp)₂(Pr-amd)/H₂O process at 180 °C. They reported self-limiting growth with a rate of 0.4 Å/cycle. 98 In Publication I the lowest deposition temperature with water was 200 °C and the growth rate at this temperature was 0.7 Å/cycle.

Dy(PrCp)₂(Pr-amd), which in Publication I is shown to give growth rates between 0.8 and 1.4 Å/cycle when used with water at 200 – 350 °C, was previously reported to result in growth rates around 0.3 Å/cycle in plasma enhanced ALD at a deposition temperature range
of 150 – 230 °C, but no growth with water was achieved.\(^9\) Unfortunately, the deposition conditions and temperatures that were tried with the \(\text{Dy}(\text{PrCp})_2(\text{Pr-amd})/\text{H}_2\text{O}\) process were not mentioned in the article so a comparison between Ref. 93 and I is not possible. More detailed results of the Y, Dy and other heteroleptic RE precursors studied in this thesis (publications I, II, IV) are discussed in Chapter 7.

### Table 3. Heteroleptic RE precursors studied for thermal ALD of binary rare earth oxides.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Oxygen source</th>
<th>Studied T range (°C)</th>
<th>Self-limiting growth confirmed (°C)</th>
<th>Growth rate (Å/cycle)(^a)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>(\text{Sc(MeCp)}_2(\text{Me}_2\text{pz}))</td>
<td>(\text{O}_3) 225, 275  275</td>
<td>-</td>
<td>(90)</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>(\text{Y(PrCp)}_2(\text{Pr-amd}))</td>
<td>(\text{H}_2\text{O}) 250 – 450  350</td>
<td>0.6</td>
<td>(97)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{Y(PrCp)}_2(\text{Pr-amd}))</td>
<td>(\text{O}_3) 220 – 350  350</td>
<td>1.3</td>
<td>(97)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{Y(PrCp)}_2(\text{Pr-amd}))</td>
<td>(\text{H}_2\text{O}) 200 – 350  350</td>
<td>1.2</td>
<td>(97)</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>(\text{La(PrCp)}_2(\text{Pr-amd}))</td>
<td>(\text{O}_3) 200 – 325  225</td>
<td>1.0</td>
<td>(97)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{La(PrCp)}_2(\text{Pr-amd}))</td>
<td>(\text{H}_2\text{O}) 200 – 300  200</td>
<td>0.7</td>
<td>(97)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{La(PrCp)}_2(\text{Pr-amd}))</td>
<td>(\text{H}_2\text{O}/\text{O}_3) 200 – 325  200  200</td>
<td>1.3 (275)</td>
<td>(97)</td>
<td></td>
</tr>
<tr>
<td>Pr</td>
<td>(\text{Pr(PrCp)}_2(\text{Pr-amd}))</td>
<td>(\text{O}_3) 200 – 250  not self-limiting</td>
<td>-</td>
<td>(97)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{Pr(PrCp)}_2(\text{Pr-amd}))</td>
<td>(\text{H}_2\text{O}) 200 – 300  not self-limiting</td>
<td>-</td>
<td>(97)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{Pr(PrCp)}_2(\text{Pr-amd}))</td>
<td>(\text{H}_2\text{O}) 200 – 325  225</td>
<td>0.8</td>
<td>(97)</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>(\text{Gd(PrCp)}_2(\text{Pr-amd}))</td>
<td>(\text{O}_3) 200 – 350  225</td>
<td>0.8</td>
<td>(97)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{Gd(PrCp)}_2(\text{Pr-amd}))</td>
<td>(\text{H}_2\text{O}) 200 – 325  225</td>
<td>0.8</td>
<td>(97)</td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>(\text{Dy(PrCp)}_2(\text{Pr-amd}))</td>
<td>(\text{O}_3) Not reported 200 – 350  200</td>
<td>1.3 (300)</td>
<td>(93)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{Dy(PrCp)}_2(\text{Pr-amd}))</td>
<td>(\text{H}_2\text{O}) Not reported 200 – 350  200</td>
<td>1.3 (300)</td>
<td>(93)</td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>(\text{Er(MeCp)}_2(\text{Pr-amd}))</td>
<td>(\text{O}_3) 200 – 325  250</td>
<td>0.4</td>
<td>(92)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{Er(MeCp)}_2(\text{Pr-amd}))</td>
<td>(\text{H}_2\text{O}) 225 – 325  250</td>
<td>1.4</td>
<td>(92)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{Er(MeCp)}_2(\text{Pr-amd}))</td>
<td>(\text{H}_2\text{O}) 130 – 320  180</td>
<td>0.5</td>
<td>(93)</td>
<td></td>
</tr>
<tr>
<td>Lu</td>
<td>({\text{Lu[Cp(SiMe}_3}_2\text{Cl}})</td>
<td>(\text{H}_2\text{O}) 360  not studied</td>
<td>0.25 (360)</td>
<td>(96)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Growth rate at self-limiting growth conditions. If no self-limiting growth is detected or studied, marked is the growth rate at the temperature which is shown in parenthesis (°C). - film thickness could not be measured due to too thin samples (Sc) or nonuniformity (Pr).
4 Zirconium dioxide thin films

4.1 Properties of zirconium dioxide
Zirconium is the element number 40 and in the periodic table it is next to yttrium (Figure 5). Zirconium has one stable oxidation state, +4. Zirconium oxide has three different crystalline phases in normal pressure; monoclinic, tetragonal and cubic, and a fourth phase in high pressure, orthorhombic ZrO$_2$. In bulk ZrO$_2$, the monoclinic phase is stable at room temperature and the tetragonal and cubic phases at high temperatures. Phase changes in ZrO$_2$ generate high volume changes inducing cracks. For many applications the phase of zirconia needs to be stabilized. Often a small amounts of tri- or divalent cations are added to ZrO$_2$ as dopants to stabilize the phase and to prevent the phase changes. When Zr$^{4+}$ ions in the crystalline lattice are replaced by lower valence ions, oxygen vacancies are formed which leads to the phase stabilization.

In thin films, factors that may affect the phase stability include stress, grain size, impurities, deposition process in general, substrate and thickness. In very thin films and nanoparticles the surface area to bulk ratio becomes high which favors crystalline phases with lower surface energy. Figure 7 shows particle sizes and film thicknesses at which monoclinic, tetragonal and amorphous zirconia are the most stable phases. For the tetragonal ZrO$_2$ films the range is approximately between 3 and 15 nm, whereas in thicker films the monoclinic phase is the most stable. However, the other factors that affect the phase formation also need to be considered and for that reason, studies of deposition process conditions and precursor combinations are pivotal.

![Figure 7](image_url)

Figure 7. Enthalpy of nanophase zirconia plotted versus particle size (film thickness). Reproduced from Ref. 99 with permission from The Royal Society of Chemistry.
ZrO₂ has high relative permittivity, high thermal stability and a large band gap of 5.8 eV. These properties make it a good dielectric material for microelectronic applications. The permittivity is dependent on the crystalline phase. The high permittivity phases are desirable in microelectronics. The tetragonal zirconia has the highest permittivity of the three phases, above 40, the cubic phase above 30, and the monoclinic phase around 20 in bulk form. In thin films there are many factors affecting the permittivity and for example for the cubic and tetragonal phases values between 20 and 40 have been measured.

4.2 Atomic layer deposition of zirconium dioxide
Zirconium dioxide is very interesting material for microelectronics, which is probably the root cause why Zr precursors have been synthesized and studied so extensively. The first ALD Zr precursor was ZrCl₄. ZrCl₄ has been studied in a wide temperature range from 180 to 600 °C. Self-limiting growth has been confirmed as high as at 500 °C, demonstrating the excellent thermal stability of zirconium chloride. The produced ZrO₂ films have been reported to be of high purity with only small amounts of chlorine as an impurity. However, the HCl byproduct is corrosive and small precursor particles have been shown to transfer sometimes from the source to the substrate and incorporate in the film. From the halide family, also ZrI₄ has been studied as a zirconium source for ALD. The first studies were conducted with H₂O-H₂O₂ solution as the oxygen source. Growth rates around 0.8 Å/cycle were reported above 300 °C. Iodine impurities (0.8 – 1.3 at%) were detected at deposition temperatures of 250 – 350 °C but not at 375 – 500 °C. At a low deposition temperature of 275 °C the crystalline phase of the films was tetragonal ZrO₂ but at higher temperatures also monoclinic phase was seen.

Zr(thd)₄ has quite high thermal stability (375 °C) and the films produced with the Zr(thd)₄/O₃ process have low impurity contents of less than 0.5 at% of carbon and hydrogen. However, the growth rate is low, 0.24 Å/cycle, similar to the rare earth oxide films deposited with RE(thd)₃/O₃ processes. Zirconium amidinate precursor, namely tetrakis(N,N′-dimethylacetamidinate) zirconium, shows self-limiting growth with H₂O at 300 °C, but also with a low growth rate of 0.24 Å/cycle.

From the alkoxide family, zirconium tert-butoxide Zr(O'Bu)₄ has been studied as an ALD precursor for the ZrO₂ deposition. High dielectric constant of 32 was obtained with the Zr(O'Bu)₄/H₂O process but self-limiting growth was not achieved in the deposition range of 150 – 300 °C. The growth rate was highly dependent on the deposition temperature and above 300 °C the growth rate was zero due to Zr(O'Bu)₄ decomposition before reaching the substrate.

Hausmann et al. reported the synthesis of three alkylamide precursors, Zr(NMe₂)₄, Zr(NEtMe)₄ and Zr(NEt₂)₄, and their use in atomic layer deposition of ZrO₂ with water. Especially the Zr(NEtMe)₄ precursor (TEMAZ) has been widely used in the studies of ZrO₂ films for microelectronic applications. Films with good purity and a growth rate of
1 Å/cycle have been produced but the thermal stability of TEMAZ is limited to below 300°C.\textsuperscript{114,115} Table 4 lists some examples of the different types of homoleptic precursors used for the ALD of ZrO\textsubscript{2}.

**Table 4.** Examples of thermal ALD processes for ZrO\textsubscript{2} using homoleptic Zr precursors from different ligand families.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Oxygen source</th>
<th>Studied T range (°C)</th>
<th>Self-limiting growth confirmed (°C)</th>
<th>Growth rate (Å/cycle)\textsuperscript{a}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrCl\textsubscript{4}</td>
<td>H\textsubscript{2}O</td>
<td>500, 180 - 600</td>
<td>500</td>
<td>0.53</td>
<td>105, Virhe,</td>
</tr>
<tr>
<td>Zr(thd)\textsubscript{4}</td>
<td>O\textsubscript{3}</td>
<td>275 – 500</td>
<td>375</td>
<td>0.24</td>
<td>108</td>
</tr>
<tr>
<td>Zr(NEtMe\textsubscript{3})\textsubscript{4}</td>
<td>O\textsubscript{3}</td>
<td>300</td>
<td>Not self-limiting</td>
<td>1.1 (265)</td>
<td>115</td>
</tr>
<tr>
<td>Zr(Me\textsubscript{2}amd)\textsubscript{4}</td>
<td>H\textsubscript{2}O</td>
<td>150 – 350</td>
<td>Not studied</td>
<td>1 (250)</td>
<td>111</td>
</tr>
<tr>
<td>Zr(OtBu)\textsubscript{4}</td>
<td>H\textsubscript{2}O</td>
<td>150 – 325</td>
<td>300</td>
<td>0.24</td>
<td>110</td>
</tr>
</tbody>
</table>

Unlike in the case of the rare earths, heteroleptic zirconium precursors have been widely studied (Table 5). In general, low impurity levels are often reported for zirconia processes. ZrO\textsubscript{2} is not hygroscopic in the way as many lanthanide oxides are and it does not react with CO\textsubscript{2} in air either to form carbonates.

While the zirconium ion is too small for homoleptic zirconium precursors with four Cp ligands to exist, majority of the heteroleptic zirconium precursors have Cp rings as one of the ligands. The studied precursors include combinations of Cp-alkyl, Cp-halogen, Cp-alkylamide, Cp-cycloheptatrienyl (CHT) and three ligand combinations Cp-alkyl-alkoxide. Cp-alkylamide precursors with three NMe\textsubscript{2} ligands and one CpR ligand (R=H, methyl or ethyl) have been reported to deposit ZrO\textsubscript{2} films with low impurity levels, high-κ cubic crystalline phase and a growth rate of 0.9 Å/cycle at 300 °C.\textsuperscript{114} Higher saturation temperature but lower growth rate of around 0.5 Å/cycle has been demonstrated with Cp-alkyl precursors. ZrCp\textsubscript{2}Me\textsubscript{2} and Zr(CpMe)\textsubscript{2}Me\textsubscript{2} both showed self-limiting growth at 350 °C with water\textsuperscript{116,117} or ozone\textsuperscript{108,118} as the oxygen source. Self-limiting growth at 350 °C was also reported with the Zr(CpMe)CHT/O\textsubscript{3} process with a growth rate of 0.8 Å/cycle.\textsuperscript{119} It seems that 350 °C is the limit for the self-limiting growth for the current heteroleptic zirconium precursors.

Four precursors with three different ligands have been studied: Zr(CpMe)\textsubscript{3}(OMe)Me with water or ozone, ZrCp\textsubscript{2}(OMe)Me with ozone, Zr(CpMe)\textsubscript{3}(O\textsubscript{2}Bu)Me with water, and Zr(Cp\textsubscript{2}CMe)\textsubscript{2}(OMe)Me with ozone as the oxygen source. Only Zr(CpMe)\textsubscript{3}(OMe)Me showed self-limiting growth with rates of 0.50 and 0.65 Å/cycle with water and ozone at 350 °C.\textsuperscript{117,118} The saturation temperature is the same as for the two ligand analog
Zr(CpMe)_2Me_2 but Zr(CpMe)_2(OMe)Me has slightly higher growth rate with ozone. The ZrCp_2(OMe)Me/O_3 process was studied at 300 °C. The main focus of the article was on ternary La_2Zr_1-xO_x and no details on the ZrO_2 deposition were given. However, the ZrO_2 films were crystalline with a tetragonal phase and a dielectric constant of 30. Zr(Cp_2CMe)_2(OMe)Me is an ansa-metallocene precursor with bridged Cp ligands. It has been studied in the liquid injection ALD with ozone as the oxygen source. The deposited films were oxygen deficient with an O:Zr ratio of 1.62 while the stoichiometric value is 2.0. Zr(Cp_2CMe)_2Me_2 was examined in the same study and was also found to result in low O:Zr ratio of 1.57. Saturation of the growth rate was not studied. In contrast, liquid injection ALD using the Zr(CpMe)_2(O'Bu)Me/H_2O process produced films with excess oxygen, the O:Zr ratio being 2.55 at 300 °C and 3.54 at 350 °C.  

Of the few heteroleptic precursors without Cp ligands, the alkoxide-donor functionalized alkoxide precursors Zr('PrO)_2(dmae)_2 and Zr('BuO)_2(dmae)_2 did not show self-limiting growth when used with water as the oxygen source because of the low thermal stability of the alkoxide ligands. Similar problem was seen with the homoleptic alkoxide precursor Zr(’BuO)_4. Zirconium precursor with chloride and silylamine ligands Zr[N(SiMe_3)_2]ZrCl_2 did show saturation with H_2O at 250 °C with a high growth rate of 1.1 Å/cycle. However, 4 at-% of Si impurities were detected in the films at this temperature. 

Quite recently, two heteroleptic amido-guanidinate precursors have been studied, namely Zr(NEtMe)_2(guan-NEtMe)_2 and Zr(NEtMe)_3(guan-NEtMe). Both precursors showed self-limiting growth with water or ozone as the oxygen source and had higher growth rates with ozone than with water. The growth rates were 0.8 – 0.9 Å/cycle with water and 1.0 – 1.15 Å/cycle with ozone at the deposition temperature of the self-limiting growth. Zr(EtMeN)_2(guan-NEtMe)_2 was thermally slightly more stable as saturation was achieved at 300 °C compared to 275 °C with Zr(NEtMe)_3(guan-NEtMe). Film purity was better with ozone compared to water with both precursors. A similar trend in the impurity levels was also observed in publication II in this thesis work.
Table 5. Heteroleptic Zr precursors studied for thermal ALD of ZrO₂.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Oxygen source</th>
<th>Studied T range</th>
<th>Self-limiting growth confirmed (°C)</th>
<th>Growth rate (Å/cycle)a</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(iPrO)₂(dmae)₂</td>
<td>H₂O</td>
<td>190 – 340</td>
<td>not self-limiting</td>
<td>1.0 (240)</td>
<td>116,122,123</td>
</tr>
<tr>
<td>Zr(tBuO)₂(dmae)₂</td>
<td>H₂O</td>
<td>190 – 340</td>
<td>not self-limiting</td>
<td>0.9 (240)</td>
<td>116,122,123</td>
</tr>
<tr>
<td>ZrCp₂Me₂</td>
<td>H₂O</td>
<td>200 – 500</td>
<td>350</td>
<td>0.43</td>
<td>116,120</td>
</tr>
<tr>
<td>Zr(CpMe)₂Me₂</td>
<td>O₃</td>
<td>250 – 500</td>
<td>350</td>
<td>0.55</td>
<td>116,120</td>
</tr>
<tr>
<td>Zr(C₅H₄Me)₂Cl₂</td>
<td>O₃</td>
<td>200 – 375</td>
<td>250 – 375</td>
<td>not self-limiting</td>
<td>1.0 (300)</td>
</tr>
<tr>
<td>ZrCp₂Cl₂</td>
<td>O₃</td>
<td>200 – 375</td>
<td>200 – 375</td>
<td>not self-limiting</td>
<td>0.25 (300)</td>
</tr>
<tr>
<td>ZrCp₂(Me₅Cp)₂(TEA)</td>
<td>H₂O</td>
<td>400 – 425</td>
<td>300 – 375</td>
<td>not self-limiting</td>
<td>0.1 (400)</td>
</tr>
<tr>
<td>Zr(Cp₂Me)(NMe₂)</td>
<td>O₃</td>
<td>250 – 400</td>
<td>300</td>
<td>0.9</td>
<td>114</td>
</tr>
<tr>
<td>Zr(C₅H₄Me)(NMe₂)₃</td>
<td>O₃</td>
<td>250 – 400</td>
<td>300</td>
<td>0.9</td>
<td>114</td>
</tr>
<tr>
<td>Zr(C₅H₄Me)(C₅H₄NEtMe)</td>
<td>O₃</td>
<td>250 – 400</td>
<td>300</td>
<td>0.9</td>
<td>114</td>
</tr>
<tr>
<td>Zr[Me₃Si(N(SiMe₃)₂)]₂Cl₂</td>
<td>H₂O</td>
<td>150 – 350</td>
<td>250</td>
<td>1.1</td>
<td>114</td>
</tr>
<tr>
<td>Zr(C₅H₄Me)(OMe)₂</td>
<td>H₂O</td>
<td>300 – 500</td>
<td>350</td>
<td>0.5</td>
<td>117,118</td>
</tr>
<tr>
<td>Zr(C₅H₄Me)(OMe)₂</td>
<td>O₃</td>
<td>250 – 500</td>
<td>350</td>
<td>0.65</td>
<td>117,118</td>
</tr>
<tr>
<td>Zr(C₅H₄Me)(OBu)Me</td>
<td>H₂O</td>
<td>250 – 450</td>
<td>not studied</td>
<td>not reported</td>
<td>117,118</td>
</tr>
<tr>
<td>Zr(C₅H₄Me)(C₅H₄NEtMe)₂</td>
<td>O₃</td>
<td>200 – 350</td>
<td>not studied</td>
<td>not reported</td>
<td>117,118</td>
</tr>
<tr>
<td>Zr(C₅H₄Me)(BuDAD)(OPr)</td>
<td>H₂O</td>
<td>250 – 425</td>
<td>not self-limiting</td>
<td>0.43 (300)</td>
<td>117,118</td>
</tr>
</tbody>
</table>

*Growth rate at self-limiting growth conditions. If no self-limiting growth is detected or studied, shown is the growth rate at the temperature which is marked in parenthesis (°C).*
5 Applications of rare earth and zirconium oxide thin films

Rare earth oxides and ZrO₂ are very versatile materials with applications in various fields. Examples are luminescent materials, catalysts, protective layers and constituents in solid oxide fuel cells and oxide superconductors. More than a decade, they have been studied extensively as dielectric materials for microelectronics in both silicon and high mobility semiconductor-based devices. In this chapter, the use of rare earth and zirconium oxide films in microelectronics and solid oxide fuel cells is discussed in more detail.

5.1 Microelectronics

5.1.1 MOSFET

The fast evolution of smart phones and computers in general is due to the development of semiconductor industry which has been guided by Moore’s law. In 1965 Gordon Moore predicted that the number of metal-oxide-semiconductor field-effect transistors (MOSFET) in an integrated circuit doubles every year. Later he changed the prediction so that the doubling happens every two years. This has been the target of the industry ever since. To fulfill this expectation, sizes of the transistors have needed to shrink. Shrinking the devices increases the speed of the circuit and memory capacity and reduces the cost per bit. Silicon has been the choice of the semiconductor material for decades with silicon oxide SiO₂ as the dielectric gate oxide. However, the limits of this pair have been reached. The SiO₂ gate oxide has become so thin that direct tunneling of electrons and holes through the gate oxide cannot be avoided causing unbearable increase in leakage current.

By using a high-κ material, the dielectric layer can be thicker with similar capacitance as achieved with a thinner SiO₂ layer. This can be exemplified with a parallel plate capacitor. The capacitance C of the capacitor depends on the distance d between the plates i.e. the thickness of the dielectric, the relative permittivity ε₉ of the dielectric and the area A of the plates:

\[ C = \varepsilon_0 \varepsilon \varepsilon_0 \varepsilon_0 \varepsilon_0 \varepsilon_0 \varepsilon_0 \frac{A}{d}, \]  

where ε₀ is the permittivity of the vacuum. From equation (1) it is seen that a capacitor with a high-κ dielectric reaches the same capacitance as a capacitor with SiO₂ dielectric with a thicker high-κ film. In a transistor one of the metal plates is replaced by a semiconductor. Simply put, MOSFETs consist of a source, drain, channel, gate and gate dielectric (Figure 8). Source and drain are p- or n-type areas on a semiconductor substrate that has been doped with the opposite type of carriers. The SiO₂ or high-κ dielectric layer (gate oxide) lies between the substrate and the gate. With a certain gate voltage, electric field affecting through the gate oxide creates an inversion layer of the minority charge carriers on the interface of the gate oxide and substrate that serves as a channel for the carriers to move from the source to drain. Transistor acts as a digital switch that is turned on and off by changing the gate voltage. High-κ gate oxide was taken into high volume manufacturing for the first time in 2007.
The first high-κ oxides were hafnium based oxide materials. For the second generation, rare earth oxides and ternary or doped oxides have been considered. From the rare earth oxide family, La₂O₃ has been especially interesting since it is stable in the hexagonal crystal structure having considerably higher permittivity than the cubic phase where most of the rare earth oxides crystallize. Unfortunately, rare earth oxides have been observed to form silicates during post deposition annealing. The tendency to form silicates increases with increasing ion radius. Lanthanum has the largest radius of the rare earth oxides and hence the highest affinity towards Si atoms. Lamanga et al. reported high permittivity of 24 and 22 for ALD La₂O₃ thin films in metal-oxide-semiconductor capacitors on Si and Ge, but reactions with the substrate were observed in both cases: silicates and germanates were spontaneously formed during the film growth and annealing after the deposition. While silicates decrease the overall permittivity of the dielectric stack compared to La₂O₃ films without interfacial layer, they can improve the device performance by preventing electron mobility reduction in the channel.

To improve the stability as well as the dielectric properties, ternary rare earth containing oxides have been widely studied for microelectronics. LaAlO₃ has been successfully deposited to mitigate the hygroscopicity of La₂O₃. LaLuO₃ films deposited by ALD on Si and GaAs substrates have shown high dielectric constants of around 30. Rare earth scandates such as GdScO₃ and DyScO₃ have also been studied extensively. Higher dielectric constants than for the binary constituent oxides have been reported with values above 20 for RE scandate films deposited by ALD. The scandates doped with large rare earth ions have shown higher crystallization temperature but also slightly higher carbon content than the scandates doped with small rare earth cations. Amorphous films can reach lower leakage currents compared to crystalline films because of the lack of grain boundaries that act as leakage pathways. GdScO₃ and YScO₃ films deposited from the β-diketonate compounds RE(thd)₃ and ozone were reported to crystallize when annealed at 1000 °C. Interestingly, when cyclopentadienyl precursors were used with water instead of RE(thd)₃ and ozone, crystallization of YScO₃ films was observed already at 800 °C. Films with low
carbon (<0.2 at%) and hydrogen (<1 at%) contents were deposited with both processes but the films deposited with the thd-based process had around 1 at% of fluorine as an additional impurity.\textsuperscript{138}

RE oxides have also been utilized as dopants in HfO\textsubscript{2}. For example, cerium and erbium doping of HfO\textsubscript{2} have been reported to stabilize the higher permittivity phases of HfO\textsubscript{2}. Cerium doping stabilized the films in either the cubic or tetragonal phase depending on the cerium concentration with increased dielectric constant (39 at the highest) after annealing at 900 °C.\textsuperscript{55} Erbium doped hafnia films were cubic with a dielectric constant of 27 before annealing and 33 after the annealing at 900 °C. Undoped HfO\textsubscript{2} films were deposited for comparison. They were monoclinic with dielectric constants of 18 and 16 before and after the annealing.\textsuperscript{139}

While ZrO\textsubscript{2} is predominantly studied as a dielectric layer for memory applications, it has also been considered as a potential dielectric material for MOSFETs. ZrO\textsubscript{2} and HfO\textsubscript{2} are very similar to each other and form mixed oxides with any desirable metal ratio. Addition of zirconium to hafnium oxide has been reported to increase the film permittivity via stabilization of the tetragonal phase and to lower the threshold voltage shift as well as to increase the band gap.\textsuperscript{140,141}

\subsection{5.1.2 Memory devices}
Dynamic random access memory (DRAM) has been the main memory of computers for decades. DRAM memory cell consists of a capacitor that is connected to a bit line via an access transistor connected to a word line and acting as a switch. The capacitor stores each bit of data as positive or negative electrical charge that is written and read through the bit line.\textsuperscript{142} For a successful DRAM cell, two requirements need to be fulfilled: sufficient capacitance of 10 fF/cell and low leakage current of < 10\textsuperscript{-7} A/cm\textsuperscript{2} at the operating voltage.\textsuperscript{142} ZrO\textsubscript{2} based materials, such as rare earth doped ZrO\textsubscript{2} and different stacked dielectric layers have been studied as the capacitor oxides in DRAM.\textsuperscript{143} The three layer ZrO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3}–ZrO\textsubscript{2} (ZAZ) was shown to be an excellent dielectric for MIM capacitors and it replaced HfO\textsubscript{2} in the capacitors for the ≤45-nm technologynodes.\textsuperscript{142,144,145} However, ZAZ is reaching the limit of scaling down and materials with higher $\kappa$, such as perovskites ($\kappa$ values above 50) are needed in the future.\textsuperscript{146}

Of the emerging non-volatile memory devices, zirconium oxide is a potential material for resistive switching random access memories (ReRAM). ReRAM cell consists of two electrodes and a thin film insulator between them. By applying a voltage across the electrodes, the electrical conductivity of the thin film material can be reversibly changed, and the corresponding conductance values can be stored for a long time.\textsuperscript{147} In the metal-oxide-based ReRAM, a formation of a conductive filament is causing the conductivity in the originally insulating oxide layer.\textsuperscript{148}
5.2 Solid oxide fuel cells
Both rare earth oxides and zirconia have been studied and used in solid oxide fuel cells (SOFC). SOFCs are electrochemical devices that transform chemical energy of fuel and oxidizer into electricity and heat. They can operate with several different fuels, for example H₂, CH₄ and CO. Molecular oxygen from air is used as the oxidizer.¹⁴⁹ As the name implies, SOFCs are all solid state, which makes them more robust in use than fuel cells and batteries with liquid electrolytes. SOFCs can be used in small scale portable charging systems, residential size power generator as well as in large scale power plants. They can also be used in combined heat and power plants.¹⁵⁰

SOFCs consist of a cathode, an anode and an electrolyte between them (Figure 9). The electrodes are porous so that the gases can reach the electrolyte interface, but the electrolyte must be dense to avoid the mixing of the fuel and oxidizer. The electrolyte is an oxygen ion conductor that should not conduct electrons whereas the electrodes are electron conductors or mixed electron and oxygen ion conductors. The operation principle of SOFC is the following: O₂ is reduced at the cathode to O²⁻ ions which move through the electrolyte to the anode. At the anode the ions react with the fuel releasing electrons. Electrons are led through an external load to the cathode where they reduce oxygen.¹⁵¹

Figure 9. Operation principles of a solid oxide fuel cells using H₂ as the fuel.

Oxide compounds containing zirconium and rare earth elements have been studied especially as electrolyte materials for SOFCs. In high temperature SOFCs (700 – 1000 °C), yttria stabilized zirconia (YSZ) is the most used electrolyte material. It is chemically and thermally very stable and pure ion conductor in different oxygen partial pressures.¹⁵² If the operating temperature is decreased, the ion conductivity decreases. However, lowering of the temperature increases the fuel cell lifetime and enables the use of less expensive materials as interconnects between the cells. YSZ can be used at lower temperatures if the electrolyte thickness is decreased to minimize the ohmic polarization at the electrolyte and
this way retain the power density.\textsuperscript{153} Also other RE doped zirconia-based electrolytes have been studied for intermediate temperatures. Scandia stabilized zirconia has the highest oxide ion conductivity of all the stabilized zirconia materials. This is attributed to the low association enthalpy of defects because of the similar radii of \( \text{Zr}^{4+} \) and \( \text{Sc}^{3+} \) ions. The ionic conductivity of the \( \text{ZrO}_2\text{-RE}_2\text{O}_3 \) systems has been shown to decrease with increasing RE radius.\textsuperscript{154}

For intermediate temperature SOFCs, doped cerium oxide has been widely studied. The most common dopant materials are \( \text{Gd}_2\text{O}_3 \), \( \text{Sm}_2\text{O}_3 \) and \( \text{Y}_2\text{O}_3 \). They all have high conductivity and are compatible with high performance electrode materials. However, under reducing conditions these materials become electron conductors which decreases the output voltage of the cell.\textsuperscript{151} To overcome this problem, ceria electrolytes can be used together with thin YSZ electron blocking layers.\textsuperscript{155,156}

Other RE containing materials for SOFC electrolytes are La containing perovskites such as \((\text{La, Sr})(\text{Ga, Mg})\text{O}_{3-x}\) and \( \text{La}_2\text{Mo}_2\text{O}_9 \). Both have been shown to have good ion conductivity but there are some concerns on the long term stability of these materials.\textsuperscript{151}

In the traditional SOFCs, the electrolyte layer thickness varies from micrometers to a few hundreds of micrometers.\textsuperscript{157} Layers with these thicknesses are not possible to deposit with ALD. However, thin film SOFCs, so called \( \mu \)-SOFCs for portable use have been developed and can be fabricated using ALD.\textsuperscript{158} The electrolytes need to be dense and producing dense films is one of the advantages of ALD. In a study by Park et al., thin film electrolytes deposited by ALD showed peak power densities over two times higher than electrolytes deposited by sputtering.\textsuperscript{159} In addition to thin electrolytes, ALD deposited layers can also be used as diffusion and electron barriers between the electrodes and the electrolyte, protective layers for the interconnects and electrodes, and bonding layers and catalysts on the anode side enhancing the charge transfer in the oxidation of fuels.\textsuperscript{155} In addition, the long term stability of some electrode materials has been enhanced with a thin and conformal ALD \( \text{ZrO}_2 \) coating.\textsuperscript{160,161}
6 Experimental section

6.1 Precursors
All precursors as well as the thermogravimetric data and vapor pressures of the precursors were provided by Air Liquide. The data was collected with a Mettler Toledo TGA/DSC 1 STAlRe System. Measurements were done under nitrogen atmosphere with a nitrogen flow of 220 sccm/min in atmospheric pressure. TG analysis of Zr(Me₇Cp)(TEA) was also done under vacuum at a pressure of 27 mbar. A heating program of 10 °C/min was used in all the measurements. Vapor pressures were estimated by using evaporation rate at each temperature.

6.2 Film depositions
All the films were deposited in a hot-wall cross-flow F-120 ALD-reactor (ASM Microchemistry, Ltd). Studied metal precursors were rare earth bisisopropylecyclopentadienyl-diisopropylacetamidinate, RE(PrCp)₂(Pr-amd) (RE = Y, La, Pr, Gd or Dy), cyclopentadienyl N,N-bis(tertbutyl)ethene-1,2-diaminato isopropylalkoxo zirconium Zr(Cp)(BuDAD)(OPr), methylcyclopentadienyl tris[2-(methylamino)ethyl]aminate zirconium Zr(MeCp)(TMEA) and pentamethylecyclopentadienyl triethanolaminate zirconium Zr(Me₇Cp)(TEA). The precursors and deposition parameters are listed in Table 6. The precursors were stored in a glove box under N₂ atmosphere. Water and ozone were tested as the oxygen source for all the oxides. Due to the hygroscopicity and easy carbonate formation of La₂O₃ films, their deposition was studied also with alternative oxygen sources, i.e. ethanol as well as water and ozone in the same process separated from each other with a purge period (later marked as H₂O/O₃). The pressure in the chamber was on the order of 5 mbar. Nitrogen (AGA, 99.999%; H₂O, ≤3 ppm; O₂, ≤3 ppm) was used as the carrier and purging gas. Ozone with a concentration of 100 g/m³ was generated from O₂ (AGA, 99.999%) in an ozone generator (Wedeco Modular 4 HC). Soda lime glasses and Si(100) wafers cut to 5×5 cm² pieces were used as substrates. Native silicon oxide was not removed from the Si substrates before the depositions. For electrical measurements, ZrO₂ films were also deposited on Pt substrates.

Table 6. Rare earth oxide and Zr oxide processes studied in this thesis.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Oxygen sources</th>
<th>Subl./Evap. temperature (°C)</th>
<th>Deposition temperatures</th>
<th>Publication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(PrCp)₂(Pr-amd)</td>
<td>O₃, H₂O</td>
<td>135</td>
<td>200 – 350</td>
<td>I, IV</td>
</tr>
<tr>
<td>La(PrCp)₂(Pr-amd)</td>
<td>O₃, H₂O, EtOH, H₂O/O₃</td>
<td>126</td>
<td>200 – 325</td>
<td>II</td>
</tr>
<tr>
<td>Pr(PrCp)₂(Pr-amd)</td>
<td>O₃, H₂O</td>
<td>125</td>
<td>200 – 300</td>
<td>I, IV</td>
</tr>
<tr>
<td>Gd(PrCp)₂(Pr-amd)</td>
<td>O₃, H₂O</td>
<td>117</td>
<td>200 – 350</td>
<td>I, IV</td>
</tr>
<tr>
<td>Dy(PrCp)₂(Pr-amd)</td>
<td>O₃, H₂O</td>
<td>135</td>
<td>200 – 350</td>
<td>I</td>
</tr>
<tr>
<td>Zr(Cp)(BuDAD)(OPr)</td>
<td>O₃, H₂O</td>
<td>65</td>
<td>250 – 425</td>
<td>III</td>
</tr>
<tr>
<td>Zr(MeCp)(TMEA)</td>
<td>O₃, H₂O</td>
<td>120</td>
<td>200 – 400</td>
<td>III</td>
</tr>
<tr>
<td>Zr(Me₇Cp)(TEA)</td>
<td>O₃, H₂O</td>
<td>115</td>
<td>250 – 425</td>
<td>III</td>
</tr>
</tbody>
</table>
6.3 Characterization of the films
Films were characterized for thickness, crystallinity, morphology, and composition. The analysis methods used in this work are summarized in Table 7. RE oxide film thicknesses were determined by modeling the reflectance spectra measured within wavelengths of 370 – 1100 nm with a spectrophotometer (Hitachi, Model U-2000). Some thicknesses were confirmed with X-ray reflectivity (XRR) measurement (PANalytical X’Pert Pro MPD). ZrO$_2$ film thicknesses were measured with XRR (Rigaku SmartLab). The crystallinity and phase of the films were determined by grazing-incidence X-ray diffraction (GIXRD) with a PANalytical X’Pert Pro MPD X-ray diffractometer with Cu K$_\alpha$ ($\lambda = 1.5419$ Å) radiation and incident beam angle of 1°. PANalytical Highscore Plus was used for phase identification using ICDD and ICSD databases. In situ high temperature XRD (HTXRD) measurements were conducted on La$_2$O$_3$ films with an Anton-Paar HTK1200N oven.

Morphologies of the Y$_2$O$_3$, ZrO$_2$, PrO$_x$, Gd$_2$O$_3$ and Dy$_2$O$_3$ films were studied by field-emission scanning electron microscope (Hitachi S-4800). 2 nm thick metal coating (Cressington 208HR sputter coater with a Au/Pd target) was sputtered on some samples to avoid charging and thereby improving the image quality. La$_2$O$_3$ film morphologies were studied with a Multimode V atomic force microscope (AFM) equipped with a NanoScope V controller (Veeco Instruments) operated in the tapping mode. Images (500 × 500 nm$^2$ and 2 × 2 μm$^2$) were captured in air using silicon probes with a nominal tip radius of 8 nm and a nominal spring constant of 3 N/m (VLFM or FESP from Bruker). Roughness was calculated as a root-mean-square value (RMS) from 2 × 2 μm$^2$ images (512 × 512 pixels) obtained at 0.5–1.0 Hz scan rate. Roughness calculations and image processing were done with a Bruker Nanoscope Analysis 1.5 program.

Film compositions were measured with time-of-flight elastic recoil detection analysis (TOF-ERDA) at a detection angle of 40° by 40 MeV $^{79}$Br$^{7+}$ ions obtained from a 5 MV tandem accelerator (Model EGP-10-II).

Annealing experiments were done on La$_2$O$_3$ films at 700 °C in air or in N$_2$ atmosphere for 1 h. After the annealing the films were let to cool down slowly in the oven. XRD and TOF-ERDA were measured also from the annealed samples.

Metal-insulator-metal (MIM) parallel plate capacitors with Pt/ZrO$_2$/Al structures were made for electrical measurements. ZrO$_2$ films were deposited on Pt (40 nm) that was evaporated on Si wafer and aluminum dots (90 nm thick) with an area of 0.204 mm$^2$ were e-beam evaporated through a shadow mask on top of the ZrO$_2$ films. Samples were handled in normal room air between the film deposition steps. Current-voltage ($I – V$) characteristics were measured with a Keithley 2400 source meter with a step size of 0.2 V. Capacitance values were measured with an HP4284A LCR meter with a frequency of 10 kHz. Relative permittivities were calculated from the mean capacitances.
Table 7. Characterization methods used in this work.

<table>
<thead>
<tr>
<th>Method</th>
<th>Obtained information</th>
<th>Studied materials</th>
<th>Publication</th>
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<tr>
<td>AFM</td>
<td>Surface morphology</td>
<td>La$_2$O$_3$</td>
<td>II</td>
</tr>
<tr>
<td>Electrical measurements</td>
<td>Permittivity and leakage current</td>
<td>ZrO$_2$</td>
<td>III</td>
</tr>
<tr>
<td>HTXRD</td>
<td>Crystallinity</td>
<td>La$_2$O$_3$</td>
<td>II</td>
</tr>
<tr>
<td>SEM</td>
<td>Surface morphology</td>
<td>Y$_2$O$_3$, ZrO$_2$, Gd$_2$O$_3$, PrO$_x$, Dy$_2$O$_3$</td>
<td>I, III</td>
</tr>
<tr>
<td>Spectrophotometer</td>
<td>Film thickness</td>
<td>Y$_2$O$_3$, La$_2$O$_3$, Gd$_2$O$_3$, PrO$_x$, Dy$_2$O$_3$</td>
<td>I, II, IV</td>
</tr>
<tr>
<td>TGA</td>
<td>Precursor evaporation and decomposition</td>
<td>Y$_2$O$_3$, ZrO$_2$, La$_2$O$_3$, Gd$_2$O$_3$, PrO$_x$, Dy$_2$O$_3$</td>
<td>III</td>
</tr>
<tr>
<td>TOF-ERDA</td>
<td>Impurities, stoichiometry</td>
<td>Y$_2$O$_3$, ZrO$_2$, La$_2$O$_3$, Gd$_2$O$_3$, PrO$_x$, Dy$_2$O$_3$</td>
<td>I, II, III, IV</td>
</tr>
<tr>
<td>XRD</td>
<td>Crystallinity</td>
<td>Y$_2$O$_3$, ZrO$_2$, La$_2$O$_3$, Gd$_2$O$_3$, PrO$_x$, Dy$_2$O$_3$</td>
<td>I, II, III, IV</td>
</tr>
<tr>
<td>XRR</td>
<td>Film thickness and density</td>
<td>Y$_2$O$_3$, ZrO$_2$, La$_2$O$_3$, Gd$_2$O$_3$, PrO$_x$, Dy$_2$O$_3$</td>
<td>I, II, III</td>
</tr>
</tbody>
</table>
7 Results and discussion

7.1 Precursor properties

The molecular structures of the metal precursors studied in this work are depicted in Figure 10. RE(iPrCp)2(iPr-amd) precursors were liquid whereas the zirconium precursors were solid. Zr(Cp)(nBuDAD)(OiPr) and Zr(MeCp)(TMEA) melted in the reactor before deposition.

The thermogravimetric results of the RE(iPrCp)2(iPr-amd) precursors looked very similar to each other: evaporation in one step with low residues was observed for all the precursors. The highest residue (< 3 %) was observed for Gd(iPrCp)2(iPr-amd) (Figure 11). The TGA results indicate suitability of the precursors to ALD.

Figure 10. Molecular structures of the studied metal precursors. a) RE(iPrCp)2(iPr-amd) (RE = Y, La, Pr, Gd or Dy) b) Zr(Cp)(nBuDAD)(OiPr) c) Zr(MeCp)(TMEA) d) Zr(Me5Cp)(TEA).
Figure 11. Thermogravimetric analysis of the RE(PrCp)₂(Pr-amd) precursors. The TG curve for Pr compound is shown in the inset for clarity.

The idea behind the studied zirconium compounds was to generate precursors that have at the same time high thermal stability and relatively good volatility. The TG curve for Zr(Cp)(tBuDAD)(OiPr) showed evaporation with a residue of < 2 %. For the Zr(MeCp)(TMEA) precursor the residue was around 15 %. Zr(Me₅Cp)(TEA) showed two-step weight loss with 30 % residue when measured at atmospheric pressure. In vacuum the results were clearly better with a 15 % residue (Figure 12a). Although the TG measurements were not optimal for the Zr(Me₅Cp)(TEA) precursor, ALD experiments were successful and the first signs of decomposition were seen only at 400 °C, as there was coloration in the hot end of the precursor source tube that was not seen at lower temperatures. According to the vapor pressure data, Zr(Cp)(tBuDAD)(OiPr) was clearly more volatile than the other two Zr precursors (Figure 12b). This was also seen in the source temperatures, as the Zr(Cp)(tBuDAD)(OiPr) source temperature was 65 °C whereas the Zr(Me₅Cp)(TEA) and Zr(MeCp)(TMEA) source temperatures were 115 °C and 120 °C.
7.2 Rare earth oxide depositions

7.2.1 La$_2$O$_3$

Good quality lanthanum oxide films have been difficult to deposit by ALD because there are problems with the both most common oxygen sources, H$_2$O and O$_3$. As discussed in Chapter 4, the hygroscopicity of the La$_2$O$_3$ film destroys the important feature of ALD, the self-limiting growth, and causes very high growth rates with thickness nonuniformity when water is used as the oxygen source.\textsuperscript{43} With ozone, the problem is high carbon impurity levels caused by carbonate formation.\textsuperscript{19} Because of the issues related to O$_3$ and H$_2$O, also alternative oxygen sources were tested in this work. These were ethanol as well as water and ozone in the same deposition process. In the latter approach, the pulsing sequence was following: La(PrCp)$_2$(Pr-amd) pulse-purge-H$_2$O pulse-purge-O$_3$ pulse-purge.

High growth rates were observed with the La(PrCp)$_2$(Pr-amd)/H$_2$O process. Different purge lengths after the water pulses were studied and the growth rates decreased considerably with increasing purge length (Figure 13). However, saturation of the growth rate could not be achieved even with 20 s long purges.

Figure 12. a) TG curves and b) vapor pressures of the Zr precursors.
La$_2$O$_3$ growth rate as a function of H$_2$O purge length at 200 °C. The La(PrCp)$_2$(Pr-amd) precursor pulse and purge times were 1.0 s and 1.5 s and H$_2$O pulse 1.0 s.

With ozone, self-limiting growth was obtained at 200 and 225 °C (Figure 14). These films were amorphous and contained high levels of carbon impurities. However, in situ high temperature XRD studies in N$_2$ atmosphere showed that it is possible to crystallize the films to either the cubic or hexagonal La$_2$O$_3$ phase by tuning the annealing temperature (Figure 15a).

The approach of using both water and oxygen in the same deposition process proved to be successful. The carbon impurities caused by the ozone pulses suppressed the hygroscopicity of the film and shorter purge time after the water pulses could be used: the growth rate did not decrease when the purge time was doubled from 10 to 20 s. On the other hand, these films did not have as high carbon impurity levels as the films deposited with ozone as the only oxygen source. Saturation was achieved at 200 °C (Figure 14). Like with ozone, these films were amorphous, and the final phase could be tuned by annealing in N$_2$ atmosphere (Figure 15b).

The films deposited above 200 °C with the La(PrCp)$_2$(Pr-amd)/H$_2$O/O$_3$ process were cubic La$_2$O$_3$. Interestingly, annealing in air at 700 °C turned all the films deposited at 250 – 325 °C to the hexagonal La$_2$O$_3$, whereas with ozone as the only oxygen source, mixtures of the cubic and hexagonal phases were obtained after annealing the films deposited at 250 – 325 °C. With water, a mixture of the phases was observed in films deposited at 200 °C whereas only the hexagonal phase was detected in the films deposited above 200 °C.
Figure 14. La$_2$O$_3$ film growth rate as a function of La(PrCp)$_2$(Pr-amd) pulse length. Pulse time for H$_2$O was 0.8 s and for O$_3$ 1.0 s.

Figure 15. HTXRD patterns of the La$_2$O$_3$ films deposited at 200 °C with a) O$_3$ and b) H$_2$O/O$_3$ measured in N$_2$ atmosphere.

Ethanol was tested as an oxygen source for the deposition of La$_2$O$_3$ to see if it has a lower reactivity toward the La(OH)$_3$ formation than water. At 200 – 275 °C, the growth rates resembled the growth rates of the films deposited with O$_3$ or H$_2$O/O$_3$ as the oxygen source. However, at 300 °C the growth rate increased considerably, to the same level as with water at 300 °C (Figure 16). The clearly higher growth rate at 300 °C could be caused by ethanol dehydration that produces water and leads to CVD-type reactions. It has been reported before that metal oxide surfaces are catalytically active towards alcohol dehydration reactions.$^{162,163}$ Also, the TOF-ERDA depth profile showed high hydrogen concentration throughout the whole thickness of a film deposited at 300 °C whereas at lower deposition temperatures the hydrogen concentration was the highest on the surface and decreased deeper in the film (Figure 17). However, self-limiting growth was not observed at any deposition temperature with ethanol.
Figure 16. Growth rates of the La$_2$O$_3$ films at different temperatures deposited with La(PrCp)$_2$(Pr-amd)/H$_2$O (0.8 s precursor pulses, 20 s purge after H$_2$O), La(PrCp)$_2$(Pr-amd)/O$_3$ (1.0 s pulses), La(PrCp)$_2$(Pr-amd)/H$_2$O/O$_3$ (0.8 s La and H$_2$O pulses, 1.0 s O$_3$ pulse, 10 s purge after H$_2$O), and La(PrCp)$_2$(Pr-amd)/EtOH processes (0.7 s pulses).

Figure 17. TOF-ERDA depth profiles of the films deposited with the La(PrCp)$_2$(Pr-amd)/EtOH process at a) 300 °C and b) 200 °C.

In the films deposited with ethanol, XRD revealed mixtures of either cubic La$_2$O$_3$ and La(OH)$_3$ or hexagonal La$_2$O$_3$ and La(OH)$_3$ depending on the deposition temperature. Annealing in air at 700 °C did not remove all the hydroxyl species from the films deposited at 200 and 250 °C since LaO(OH) peaks were identified in addition to La$_2$O$_3$ peaks from the x-ray diffractograms measured after the annealing. In contrast, the film deposited at 300 °C was hexagonal La$_2$O$_3$ after the annealing.

There are not many successful La$_2$O$_3$ ALD processes reported in literature. The same problems as reported before with ozone and water could be seen in this study too. The combination of separate O$_3$ and H$_2$O pulses as the oxygen source suppressed the poor features of the processes using ozone or water alone.
7.2.2 PrO₃⁺₁⁻⁴
Praseodymium oxide suffers from the same problem with hygroscopicity as La₂O₃. Accordingly, praseodymium oxide films have so far been very difficult to deposit with ALD. Self-limiting growth has been reported only for the Pr(EtCp)₃/H₂O process at 130 °C.⁷⁹

Similar to the La(PrCp)₂(Pr-amd)/H₂O process, decreasing growth rate with increasing H₂O purge length was observed with the Pr(PrCp)₂(Pr-amd)/H₂O process. Uniform films were deposited at 200 °C but saturation was not quite achieved as the growth rate increased from 0.9 Å/cycle with 0.5 s pulses to 1.1 Å/cycle with 1.5 s pulses (Figure 18a). Different from the La₂O₃ deposition, Pr₂O₃ growth rate was nearly constant throughout the studied temperature range of 200 – 300 °C (Figure 18b). XRD results confirmed the films to be mainly cubic Pr₂O₃ with a couple of small peaks attributed to the hexagonal Pr₂O₃. Although self-limiting growth was not achieved, good quality, uniform films could be deposited making this process one of the best among the small group of ALD processes for praseodymium oxide films.

Pr(PrCp)₂(Pr-amd) together with ozone produced highly nonuniform films and it was impossible to measure the film thicknesses. For this reason, only a few films were deposited with this process. The nonuniformity of the films deposited with ozone has also been reported by Hansen et al. when using Pr(thd)₃ and O₃. They explained it by the catalytic activity of praseodymium oxide rising from the mixed oxidation states of praseodymium caused by the strong oxidant ozone.⁴⁹ From the rare earth elements studied in this thesis, Pr is the only one that has two possible oxidation states (+III and +IV) under the deposition conditions. Indeed, the other rare earth oxides did not exhibit thickness gradients similar to praseodymium oxide when deposited with ozone.
XRD measurements showed that the films deposited at 200 °C were crystalline. However, the peaks were so broad that the phase of the films could not be distinguished. Possible phases are Pr₆O₁₁ and PrO₂.

### 7.2.3 Gd₂O₃

Self-limiting growth was achieved with the Gd(iPrCp)₂(iPr-amd)/O₃ process at 200 and 225 °C with growth rates of 0.4 and 0.8 Å/cycle (Figure 19a). These films were amorphous with high carbon contents. Carbon contamination clearly decreased with increasing deposition temperature, from 15 at. % at 200 °C to 3 at. % at 300 °C. Cubic Gd₂O₃ films were deposited at 300 °C and mixtures of cubic and monoclinic phases at higher deposition temperatures. Annealing in air at 700 °C decreased the carbon contamination and for example the carbon content of a film deposited at 250 °C was 1.7 at. % after the annealing. High carbon content and excess oxygen due to carbonate type impurities have been reported also for the Gd(thd)₃/O₃ process. The main advantage of the Gd(iPrCp)₂(iPr-amd)/O₃ process over the Gd(thd)₃/O₃ process is the higher growth rate: at 225 °C the growth rate is 0.8 Å/cycle whereas the growth rate of the Gd(thd)₃/O₃ process is 0.3 Å/cycle at 300 °C.

With water, both short (1.5 s) and long (20 s) purges after the water pulses were tested at 200 °C. Saturation of the growth rate was not quite achieved even with the long purge time (Figure 19b). However, the film thickness followed linearly the cycle number and uniform films with the cubic Gd₂O₃ phase and a carbon content around 1 at. % were obtained. With a homoleptic Gd(MeCp)₃ precursor, results similar to ours were reported when it was used together with water: no saturation but uniform films with low carbon contents. In this regard, the heteroleptic Cp-amidinate precursor does not bring advantage over the homoleptic one when water is used as the oxygen source.

![Figure 19](image.png)

**Figure 19.** Gd₂O₃ growth rates as a function of Gd(iPrCp)₂(iPr-amd) precursor pulse length with a) ozone and b) water as the oxygen source. Pulse times for O₃ and H₂O were 1.0 s and O₃ purge 1.5 s.
7.2.4 Y$_2$O$_3$

Y(PrCp)$_2$(Pr-amd) resulted in self-limiting growth with both oxygen sources at as high temperature as 350 °C with a growth rate of 1.2 Å/cycle with O$_3$ and 1.1 Å/cycle with H$_2$O (Figure 20). Clearly, Y(PrCp)$_2$(Pr-amd) was thermally the most stable of the Cp-amd precursors examined. From the other Y$_2$O$_3$ ALD processes studied, only the Y(thd)$_3$/O$_3$ process saturates at this high temperature, but it has a growth rate of only 0.23 Å/cycle. The XRD results were similar to the La$_2$O$_3$ and Gd$_2$O$_3$ results in that crystalline films could be deposited with water at 200 °C whereas with ozone 300 °C was needed. The crystalline Y$_2$O$_3$ films deposited with ozone were cubic. The Y(PrCp)$_2$(Pr-amd)/H$_2$O process produced mainly cubic films with a few very small peaks designated to the monoclinic Y$_2$O$_3$ phase (Figure 21).

**Figure 20.** Y$_2$O$_3$ growth rate saturation at 350 °C.

**Figure 21.** X-ray diffractograms of Y$_2$O$_3$ films deposited at different temperatures with a) ozone and b) water as the oxygen source.
Compared to the homoleptic $\text{Y(}^{\text{iPr-amd)}_3$), the thermal stability of the heteroleptic $\text{Y(}^{\text{iPrCp)}_2(}^{\text{iPr-amd)}$ is considerably higher: saturation was achieved with the $\text{Y(}^{\text{iPr-amd)}_3/\text{H}_2\text{O}$ process at 280 °C with a growth rate of 0.8 Å/cycle.\(^6\) With homoleptic Cp precursors, $\text{YCp}_3$ and $\text{Y(MeCp)}_3$, self-limiting growth has been verified at 300 °C.\(^7\)

7.2.5 Dy\(_2\)O\(_3\)^1

Growth rates of the Dy\(_2\)O\(_3\) films were similar to the growth rates of the Y\(_2\)O\(_3\) films, especially at low deposition temperatures. Saturation was studied with water as the oxygen source at 300 °C and with ozone at 300 and 325 °C. With water, the growth rate was 1.3 Å/cycle with short Dy precursor pulse lengths but increased to 1.9 Å/cycle with longer pulse lengths. With ozone, the growth rate increased only moderately from 1.0 to 1.2 Å/cycle when the Dy\(^{\text{iPrCp)}_2(}^{\text{iPr-amd)}$ pulse length was increased from 0.7 and 1.3 s to 1.9 s (Figure 22). There are not many Dy precursors for the ALD of Dy\(_2\)O\(_3\). The Dy(DPDMG)\(_3$/\text{H}_2\text{O}$ process has been reported to exhibit saturative growth at 250 °C with a growth rate of 1.0 Å/cycle.\(^6\) Dy(thd)\(_3\) has been tested with ozone at 300 °C and the growth rate was quite low, 0.3 Å/cycle.\(^4\)

![Figure 22](image)

**Figure 22.** Dy\(_2\)O\(_3\) growth rate saturation studies with Dy\(^{\text{iPrCp)}_2(}^{\text{iPr-amd)}/\text{H}_2\text{O}$ and Dy\(^{\text{iPrCp)}_2(}^{\text{iPr-amd)}/\text{O}_3$ processes. H\(_2\)O and O\(_3\) pulses were 1.0 s and purge times 1.5 s.

7.2.6 Summary on the RE oxide studies

Self-limiting growth, the key feature of ALD, was achieved with the Y\(^{\text{iPrCp)}_2(}^{\text{iPr-amd)}/\text{H}_2\text{O}$, Y\(^{\text{iPrCp)}_2(}^{\text{iPr-amd)}/\text{O}_3$, La\(^{\text{iPrCp)}_2(}^{\text{iPr-amd)}/\text{O}_3$, La\(^{\text{iPrCp)}_2(}^{\text{iPr-amd)}/\text{H}_2\text{O}/\text{O}_3$, and Gd\(^{\text{iPrCp)}_2(}^{\text{iPr-amd)}/\text{O}_3$ processes (Figure 23a). Self-limiting growth could not be reached with the Pr and Dy precursors with neither water nor ozone. However, the Dy\(^{\text{iPrCp)}_2(}^{\text{iPr-amd)}/\text{O}_3$ process at 300 °C and the Pr\(^{\text{iPrCp)}_2(}^{\text{iPr-amd)}/\text{H}_2\text{O}$ process at 200 °C produced uniform films and the increase of the growth rate with increasing pulse lengths was moderate (Figure 23b). The key results are collected in Table 8. In all the studied rare earth oxide processes, the films deposited with water were crystalline at a deposition temperature of 200 °C whereas with ozone at least 300 °C was needed for proper diffraction peaks to
appear. PrO₃ made an exception since also the films deposited with ozone were crystalline at 200 °C. The reason for the high crystallization temperatures is most likely the high carbon contents of the films deposited at low temperatures with ozone that disturbs the crystallization. In this study, very high carbon contents at low deposition temperature were confirmed for La₂O₃ and Gd₂O₃ films when ozone was used as the oxygen source. The carbon content of Gd₂O₃ films decreased from 15 at% to 3 at% when deposition temperature was increased from 200 to 300 °C. In the case of La₂O₃, the carbon content was 19 at% at 200 °C and 4 at% at 325 °C.

![Figure 23](image)

**Figure 23.** a) Self-limiting growth processes for Y₂O₃, La₂O₃ and Gd₂O₃ and b) best processes for Pr₂O₃ and Dy₂O₃.
Table 8. Growth rates at optimal temperatures and summary of the crystallinities of the films deposited by the studied RE oxide processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Saturation temp. (°C)</th>
<th>GR at T_{sat} or T_{best} (Å/cycle)</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(PrCp)$_2$(Pr-amd)/H$_2$O</td>
<td>350</td>
<td>1.2</td>
<td>c Y$_2$O$_3$, at high T also small m peaks</td>
</tr>
<tr>
<td>Y(PrCp)$_2$(Pr-amd)/O$_3$</td>
<td>350</td>
<td>1.3</td>
<td>c Y$_2$O$_3$ above 300 °C, amorphous below</td>
</tr>
<tr>
<td>La(PrCp)$_2$(Pr-amd)/H$_2$O</td>
<td>-</td>
<td>1.2 (200 °C)*</td>
<td>Mixture of c and h La$_2$O$_3$</td>
</tr>
<tr>
<td>La(PrCp)$_2$(Pr-amd)/O$_3$</td>
<td>225</td>
<td>1.0</td>
<td>a, at low T, c La$_2$O$_3$ at 300 °C, above mixture of c and h La$_2$O$_3$</td>
</tr>
<tr>
<td>La(PrCp)$_2$(Pr-amd) /H$_2$O/O$_3$</td>
<td>200</td>
<td>0.7</td>
<td>c La$_2$O$_3$ at 300 °C and above, amorphous below</td>
</tr>
<tr>
<td>La(PrCp)$_2$(Pr-amd) /EtOH</td>
<td>-</td>
<td>-</td>
<td>Mainly La(OH)$_3$ at low T, at 300 °C La(OH)$_3$ and h La$_2$O$_3$</td>
</tr>
<tr>
<td>Pr(PrCp)$_2$(Pr-amd)/H$_2$O</td>
<td>-</td>
<td>0.9-1.2 (200 °C)</td>
<td>c or mixture of c and h Pr$_2$O$_3$ depending on temperature</td>
</tr>
<tr>
<td>Pr(PrCp)$_2$(Pr-amd)/O$_3$</td>
<td>-</td>
<td>-</td>
<td>Could not be measured</td>
</tr>
<tr>
<td>Gd(PrCp)$_2$(Pr-amd)/H$_2$O</td>
<td>-</td>
<td>0.65-0.78 (200 °C)</td>
<td>c Gd$_2$O$_3$ at 200 °C, mainly m Gd$_2$O$_3$ above</td>
</tr>
<tr>
<td>Gd(PrCp)$_2$(Pr-amd)/O$_3$</td>
<td>250</td>
<td>1.2</td>
<td>c Gd$_2$O$_3$ at 300 °C, c and m Gd$_2$O$_3$ above</td>
</tr>
<tr>
<td>Dy(PrCp)$_2$(Pr-amd)/H$_2$O</td>
<td>-</td>
<td>1.4 (300 °C)</td>
<td>c Dy$_2$O$_3$ above</td>
</tr>
<tr>
<td>Dy(PrCp)$_2$(Pr-amd)/O$_3$</td>
<td>-</td>
<td>0.9-1.2 (300 °C)</td>
<td>c Dy$_2$O$_3$ above 300 °C</td>
</tr>
</tbody>
</table>

* with 0.8 s precursor pulses and 20 s purge after water pulse

7.3 Zirconium oxide depositions **III**

7.3.1 Zr(MesCp)(TEA)

With the Zr(Me$_5$Cp)(TEA)/O$_3$ process, self-limiting growth was confirmed at 300, 350 and 375 °C (Figure 24). The growth rates were 0.30 Å/cycle at 300 °C and 0.40 Å/cycle at 350 and 375 °C. The resulting film purity was excellent at all these temperatures, as the carbon, hydrogen and nitrogen levels were even below the detection limit (0.1 at.%) of TOF-ERDA. 375 °C is the highest saturation temperature that has been achieved with the advanced heteroleptic Zr precursors and it is clearly higher than the saturation temperature reported for the widely used zirconium precursors heteroleptic CpZr(NMe$_2$)$_3$ (300 °C) and homoleptic Zr(NEtMe)$_4$ (below 300 °C). From the homoleptic precursors, ZrCl$_4$ has been reported to have higher saturation temperatures.
With water, 400 °C was needed to attain any growth at all. The growth rate was very low, only 0.1 Å/cycle with 1.0 s Zr precursor pulse and increased to 0.2 Å/cycle with 3.5 s pulse (Figure 24). At 425 °C, the growth rate was 0.2 Å/cycle but decomposition of the Zr precursor was already seen at that temperature. The film densities obtained from the XRR measurements showed that the densities of the films deposited with water were far from bulk densities, only 4.7 g/cm³ whereas the bulk density is around 6 g/cm³. Because of the low growth rates and film densities, only a few films were deposited with the Zr(Me₅Cp)(TEA)/H₂O process and they were not fully characterized. With ozone, the film densities were 5.8 – 5.9 g/cm³. The film thickness did not affect the density and also the thinnest films around 10 nm in thickness had density comparable to the thicker films.

![Figure 24. ZrO₂ growth rate saturation studies at different deposition temperatures. Pulse lengths for water and ozone were 1.0 s and purge lengths 1.5 s.](image)

The crystalline phase of the films deposited with the Zr(Me₅Cp)(TEA)/O₃ process varied with deposition temperature and film thickness. At low temperatures, only the tetragonal ZrO₂ phase was seen in XRD. The intensities of the monoclinic diffraction peaks increased with increasing temperature, but the tetragonal phase remained the dominant one assessed from the peak intensities. Very thin films were tetragonal also at higher deposition temperatures (Figure 25). All the films deposited with water as the oxygen source were tetragonal ZrO₂.
Figure 25. X-ray diffractograms of the films deposited with a) \(\text{Zr(Me}_5\text{Cp})(\text{TEA})/\text{O}_3\) process at 250 – 425 °C and b) \(\text{Zr(Me}_5\text{Cp})(\text{TEA})/\text{O}_3\) process at 300 °C with different film thicknesses. In a) the film thicknesses varied between 29 and 40 nm.

The dielectric constants of the films deposited at 300 – 375 °C with the \(\text{Zr(Me}_5\text{Cp})(\text{TEA})/\text{O}_3\) process decreased from 29 to 24 when the deposition temperature was increased from 300 to 375 °C. This decrease could be due to the higher amount of the lower dielectric constant monoclinic \(\text{ZrO}_2\) phase at higher deposition temperatures. Previously, dielectric constants between 20 and 40 have been reported for tetragonal/cubic \(\text{ZrO}_2\) films by ALD. Low leakage currents in the order of \(10^{-8}\) A/cm² at 1 MV/cm field were measured for all studied films (Figure 26).

Figure 26. Leakage current densities for films deposited at 300 – 375 °C with the \(\text{Zr(Me}_5\text{Cp})(\text{TEA})/\text{O}_3\) process.
7.3.2 Zr(Cp)(’BuDAD)(O’Pr)

With Zr(Cp)(’BuDAD)(O’Pr), deposition studies were carried out at 250 – 375 °C with ozone and at 250 – 425 °C with water as the oxygen source. Film densities varied considerably with the deposition temperature, especially with water (Figure 27). Self-limiting growth was verified at 250 °C with the Zr(Cp)(’BuDAD)(O’Pr)/O₃ process. The growth rate was 0.40 Å/cycle (Figure 28). However, the film densities at this low temperature were somewhat lower than the bulk value, 5.1 g/cm³. The main impurities at 250 °C were hydrogen and carbon, but their concentrations were quite low, around 1 at-%. Saturation of the growth rate was not achieved with water (Figure 28), but tetragonal ZrO₂ films could be deposited at as high temperature as 375 °C with a film thickness ranging from 9 to 70 nm (Figure 29). With ozone at 250 °C at least 50 nm thick films and below were tetragonal ZrO₂, whereas at 300 °C small monoclinic peaks were visible in XRD of already a 9 nm thick film.

Figure 27. Growth rates and densities of ZrO₂ films deposited at a) 250 – 375 °C with Zr(Cp)(’BuDAD)(O’Pr)/O₃ and b) at 250 – 425 °C with Zr(Cp)(’BuDAD)(O’Pr)/H₂O process. Pulses were 1.0 s and purges 1.5 s.

Figure 28. Growth rate saturation tests with water or ozone as the oxygen source. O₃ and H₂O pulses were 1.0 s.
Figure 29. a) X-ray diffractograms of ZrO$_2$ films with different thicknesses deposited with the Zr(Cp)(BuDAD)(OiPr)/H$_2$O process at 375 °C. b) Diffractograms of ZrO$_2$ films deposited with the Zr(Cp)(BuDAD)(OiPr)/O$_3$ process at different temperatures. Film thicknesses in b) are 47 nm (250 °C), 54 nm (300 °C) and 96 nm (375 °C).

Leakage current densities were in the range of $10^{-8} - 10^{-7}$ A/cm$^2$ at 1.0 MV/cm field for most samples deposited at 300 – 375 °C. The film deposited with water at 300 °C had clearly higher leakage current density of $1 \times 10^{-5}$ A/cm$^2$ (Figure 30). No obvious reason for this result could be found.

Figure 30. Leakage current densities of ZrO$_2$ films deposited at a) 250 and 300 °C and b) 375 °C.
7.3.3 Zr(MeCp)(TMEA)

Growth rates of the films deposited with the Zr(MeCp)(TMEA)/O$_3$ and Zr(MeCp)(TMEA)/H$_2$O processes were studied at 200 – 375 °C (Figure 31). With ozone the growth rate decreased from 0.65 Å/cycle at 200 °C to 0.51 Å/cycle at 375 °C. However, significant densification of the film occurred with increasing deposition temperature, from 3.6 g/cm$^3$ to 5.8 g/cm$^3$, meaning that the amount of material deposited at 350 and 375 °C is actually higher than at 250 and 300 °C even though the growth rate decreased (Figure 31a). With water, the growth rate slightly increased with increasing deposition temperature, from 0.23 to 0.33 Å/cycle. Film densification was also observed with water as the oxygen source (Figure 31b). Uniform films could be deposited with the Zr(MeCp)(TMEA)/O$_3$ and Zr(MeCp)(TMEA)/H$_2$O processes but full saturation was not achieved in either case (Figure 32).

![Figure 31](image1.png)

**Figure 31.** Growth rates and film densities for a) Zr(MeCp)(TMEA)/O$_3$ and b) Zr(MeCp)(TMEA)/H$_2$O processes.

![Figure 32](image2.png)

**Figure 32.** ZrO$_2$ film growth rates as a function of the Zr(MeCp)(TMEA) pulse length. Ozone and water pulses were 1.0 s and purges 1.5 s.
As with the other studied zirconium precursors, the deposition temperature as well as the film thickness affected the crystalline phase of the films. The tetragonal ZrO$_2$ phase was the dominating one but the intensity of the monoclinic peaks increased with increasing temperature (Figure 33). The leakage current densities of the films deposited with ozone were 1 – 2 orders of magnitude higher than with the other zirconium precursors depending on the deposition temperature and varying from $6 \times 10^{-6}$ to $2 \times 10^{-7}$ A/cm$^2$ at 1 MV/cm. With water, the leakage currents were in the same range as with ozone (Figure 34).

![Figure 33. Diffractograms of ZrO$_2$ films deposited with a) Zr(MeCp)(TMEA)/O$_3$ process (film thickness 40 – 52 nm) and b) Zr(MeCp)(TMEA)/H$_2$O process (43 – 51 nm).](image)

![Figure 34. Leakage current densities of ZrO$_2$ films deposited at a) 300 °C and b) 350 °C with the Zr(MeCp)(TMEA)/O$_3$ and Zr(MeCp)(TMEA)/H$_2$O processes.](image)
7.3.4 Summary of the ZrO₂ studies

Three new Zr precursors were evaluated for the ALD of ZrO₂. Zr(Me₅Cp)(TEA) was found to be the best one showing high thermal stability and depositing films with high density and very low impurity contents at the saturation temperature of 300 – 375 °C with ozone as the oxygen source. The exceptionally high thermal stability is apparently due to the chelating four-dentate TEA ligand with three oxygen atoms and one nitrogen atom as donors. For the same reason the reactivity of Zr(Me₅Cp)(TEA) with water was poor. The high degree of substitution on the Cp ring with electron donor groups can also increase thermal stability of the precursor by strengthening the bond between the metal and the Cp ring. Zr(Cp)(tBuDAD)(O'Pr)/O₃ process also showed self-limiting growth but at much lower temperature of 250 °C. At this temperature the impurity levels were low, but also the film density was low. With all three precursors both film thickness and deposition temperature affected the crystalline phase of the films. The effect of the film thickness on the phase was much stronger with ozone than with water. Very low leakage currents in the order of 10⁻⁸ A/cm² were obtained with the Zr(Me₅Cp)(TEA)/O₃ and Zr(Cp)(tBuDAD)(O'Pr)/O₃ processes. Table 9 summarizes the growth rates and crystalline phases of the films deposited with the studied processes.

Table 9. Growth rates and crystallinity of the studied ZrO₂ processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Saturation temp. (°C)</th>
<th>GR at T&lt;sub&gt;sat&lt;/sub&gt; or T&lt;sub&gt;best&lt;/sub&gt; (Å/cycle)</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(Me₅Cp)(TEA)/O₃</td>
<td>300-375</td>
<td>0.3-0.4</td>
<td>t ZrO₂ or mixtures of t and m depending on T and film thickness</td>
</tr>
<tr>
<td>Zr(Me₅Cp)(TEA)/H₂O</td>
<td>-</td>
<td>0.1 (400 °C)</td>
<td>t ZrO₂</td>
</tr>
<tr>
<td>Zr(Cp)(tBuDAD)(O'Pr)/O₃</td>
<td>250</td>
<td>0.5</td>
<td>t or mixture of t and m ZrO₂</td>
</tr>
<tr>
<td>Zr(Cp)(tBuDAD)(O'Pr)/H₂O</td>
<td>-</td>
<td>0.5 (375 °C)</td>
<td>t ZrO₂ or mixtures of t and m depending on T and film thickness</td>
</tr>
<tr>
<td>Zr(MeCp)(TMEA)/O₃</td>
<td>-</td>
<td>0.65 (250 °C)</td>
<td>mixture of t and m ZrO₂</td>
</tr>
<tr>
<td>Zr(MeCp)(TMEA)/H₂O</td>
<td>-</td>
<td>0.4 (300 °C)</td>
<td>t or mixture of t and m ZrO₂</td>
</tr>
</tbody>
</table>
8 Conclusions

In this thesis work, new heteroleptic metal precursors were studied and processes for atomic layer deposition of rare earth oxides and zirconium oxide were developed. Rare earth oxides and zirconium oxide have great potential in several fields of applications including microelectronics, catalysis and energy. Various heteroleptic precursors, where the ligands in the compound are of at least two different types, have been studied for the ALD of ZrO₂ whereas only a few heteroleptic precursors have been studied for the rare earth oxide deposition.

Rare earth precursors RE(PrCp)₂(Pr-amd) (RE = Y, La, Pr, Gd and Dy) were studied to deposit Y₂O₃, La₂O₃, PrOₓ, Gd₂O₃ and Dy₂O₃ thin films by ALD. Deposition processes with self-limiting growth were developed for Y₂O₃, La₂O₃, and Gd₂O₃. The Y(PrCp)₂(Pr-amd) precursor showed self-limiting growth with both water and ozone as the oxygen source at a high deposition temperature of 350 °C whereas La(PrCp)₂(Pr-amd)/O₃, La(PrCp)₂(Pr-amd)/H₂O/O₃ and Gd(PrCp)₂(Pr-amd)/O₃ processes saturated at 200 – 225 °C. Uniform Pr₂O₃ and Dy₂O₃ films could be deposited with Pr(PrCp)₂(Pr-amd)/H₂O and Dy(PrCp)₂(Pr-amd)/O₃ processes but the film growth was not self-limiting.

The same problems with hygroscopicity and carbonate formation as reported in literature were seen also here in the La₂O₃ depositions with water or ozone as the oxygen source. A double oxygen source consisting of H₂O and O₃ pulses separated by purges suppressed hydrogen and carbon levels in the films as measured by TOF-ERDA. It would be interesting to test this approach also for the other rare earth oxides, especially Gd₂O₃ which suffered from rather high carbon contents when deposited with ozone, and hydrogen contents when water was the oxygen source.

Three heteroleptic zirconium precursors were tested for ALD of ZrO₂: Zr(MeCp)(TMEA), Zr(Me₅Cp)(TEA) and Zr(Cp)(BuDAD)(OiPr). Zr(Me₅Cp)(TEA) was found to have high thermal stability as self-limiting growth was obtained with the Zr(Me₅Cp)(TEA)/O₃ process at 375 °C with a rate of 0.40 Å/cycle. However, the reactivity of Zr(Me₅Cp)(TEA) towards water was low. Zr(Cp)(BuDAD)(OiPr)/O₃ process showed saturation at 250 °C with a growth rate of 0.50 Å/cycle. Saturation was not quite achieved with the Zr(MeCp)(TMEA) precursor with either water or ozone as the oxygen source. Low impurity levels were detected especially with the processes using ozone as the oxygen source.

It has been reported in literature and was also seen in this thesis work that the cubic or tetragonal ZrO₂ phases are often the dominant ones at low deposition temperatures and/or low film thicknesses whereas the monoclinic peaks increase in intensity in XRD with increasing temperature and/or film thickness. Interestingly, with the Zr(Cp)(BuDAD)(OiPr)/H₂O process tetragonal films could be deposited at as high temperature as 375 °C with thicknesses of 9 – 70 nm.
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