Precursors for metal organic chemical vapor deposition (MOCVD) of ZrO$_2$ and HfO$_2$ thin films as gate dielectrics in complementary metal-oxide-semiconductor (CMOS) devices.
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Urmila Patil, M. Sc.
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Examiners: Prof. Dr. Roland A. Fischer
Prof. Dr. Martin Muhler

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Urmila Patil, M.Sc.
2005

Gutachter: Prof. Dr. Roland A. Fischer
             Prof. Dr. Martin Muhler

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<tr>
<td>acac</td>
<td>acetylacetone</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>ALE</td>
<td>Atomic layer epitaxy</td>
</tr>
<tr>
<td>bdmap</td>
<td>1,1-bis(dimethylamino)propan-2-ol</td>
</tr>
<tr>
<td>BJT</td>
<td>Bipolar junction transistor</td>
</tr>
<tr>
<td>BST</td>
<td>Barium-strontium titanate, (Ba,Sr)TiO$_3$</td>
</tr>
<tr>
<td>Butyllithium</td>
<td>BuLi</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary-metal-oxide-semiconductor</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>dbmal</td>
<td>Di-tert-butylmalonate</td>
</tr>
<tr>
<td>deacam</td>
<td>N,N-diethylacetacetamide</td>
</tr>
<tr>
<td>deae</td>
<td>N,N-diethylaminoethanol</td>
</tr>
<tr>
<td>dmae</td>
<td>2-dimethylaminoethanol</td>
</tr>
<tr>
<td>dmap</td>
<td>1-dimethylaminopropan-2-ol</td>
</tr>
<tr>
<td>DRAM</td>
<td>Dynamic random access memory</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential thermal analysis</td>
</tr>
<tr>
<td>EDAX</td>
<td>Energy dispersive analysis of X-rays</td>
</tr>
<tr>
<td>EGA</td>
<td>Evolved gas analysis</td>
</tr>
<tr>
<td>EI</td>
<td>Electron impact</td>
</tr>
<tr>
<td>EOT</td>
<td>Equivalent oxide thickness</td>
</tr>
<tr>
<td>FET</td>
<td>Field effect transistor</td>
</tr>
<tr>
<td>hfip</td>
<td>1,1,1,3,3,3-hexafluoroisopropanol</td>
</tr>
<tr>
<td>IC</td>
<td>Integrated circuit</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared spectroscopy</td>
</tr>
<tr>
<td>ITRS</td>
<td>International technology roadmap for semiconductors</td>
</tr>
<tr>
<td>LI-MOCVD</td>
<td>Liquid injection-metal organic chemical vapor deposition</td>
</tr>
<tr>
<td>MIM</td>
<td>Metal-insulator-metal</td>
</tr>
<tr>
<td>MIS</td>
<td>Metal-insulator-semiconductor</td>
</tr>
<tr>
<td>mmp</td>
<td>1-methoxy-2-methyl-2-propanolate</td>
</tr>
<tr>
<td>MO</td>
<td>Metalorganic</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal organic chemical vapor deposition</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>MOSFET</td>
<td>Metal-oxide-semiconductor field-effect transistor</td>
</tr>
<tr>
<td>Mp</td>
<td>Melting point</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>NVFRAM</td>
<td>non-volatile ferroelectric random access memory</td>
</tr>
<tr>
<td>OBu&lt;sup&gt;t&lt;/sup&gt;</td>
<td>tert-butoxide</td>
</tr>
<tr>
<td>OPr&lt;sup&gt;i&lt;/sup&gt;</td>
<td>isopropoxide</td>
</tr>
<tr>
<td>PZT</td>
<td>Lead zirconium titanate, Pb(Zr,Ti)O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>PLZT</td>
<td>(Pb,La) (Zr,Ti)O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford backscattering spectroscopy</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SIS</td>
<td>Silicon-insulator-silicon</td>
</tr>
<tr>
<td>SSP</td>
<td>Single source precursor</td>
</tr>
<tr>
<td>Subl.</td>
<td>Sublimation</td>
</tr>
<tr>
<td>tbaoac</td>
<td>tert-butylacetoacetate</td>
</tr>
<tr>
<td>TA</td>
<td>Thermal analysis</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimetry</td>
</tr>
<tr>
<td>thd or tmhd</td>
<td>2,2,6,6-Tetramethylhetan-3,5-dione</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>Tod</td>
<td>2,7,7-trimethyl-3,5-octanedione</td>
</tr>
<tr>
<td>TOPO</td>
<td>tri n-octylphosphine</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-Visible spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
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</table>
1 Introduction

Over the past few decades, semiconductor industry has witnessed dramatic exponential rise in the performance of integrated circuits and in the subsequent financial market growth. Performance improvement at lower cost in microelectronic integrated circuits (ICs) has been achieved by increasing transistor speed, reducing transistor size, and packing more transistors onto a single chip.\cite{1, 2} This trend was first foreseen by Intel co-founder Gordon Moore, who in his groundbreaking article in the year 1965 stated that the number of transistors the industry would be able to place on a computer chip would double every two years (Figure 1).\cite{3, 4} This prediction, now known as the Moore’s law is responsible for the evolution of today’s complementary metal-oxide-semiconductor (CMOS) technology. Recognition of this observation has triggered constant revolutions in the semiconductor industry and ever since the transistor has shrunk from the size of a pencil eraser to smaller than a bacterium (Figure 2).

The transistor has become the workhorse component of almost every electronic device after it was invented by John Bardeen, Walter Brattain and independently by William Schokley at the Bell Laboratories. They shared a Nobel Prize for their classic discovery of point-contact transistors\cite{5} and bipolar transistors\cite{6}. The salient feature of transistors which fuel the rapid growth of the information technology industry is the incredible increase in their speed and drop in cost per component as their size is reduced. In simple terms, a transistor can be described as a three terminal semiconductor device in which the input signal controls the output current and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1}
\caption{Increase in the transistor density: Moore’s Law}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{Shrinking of the transistor geometries.}
\end{figure}
which perform functions of switching and amplifying. Use of transistor is extended in areas like amplifying low frequency radio signals, high speed computers etc. Increase in the processor performance results not only from increase in the transistor density but also from the improvement in the transistor design. Based on design and operating behaviour, transistors are classified into two major types: Bipolar junction transistor (BJT) and Field-effect transistor (FET).\textsuperscript{[7]} In the 1960s the IC market was broadly based on bipolar transistors due to their high switching speed and low power consumption at smaller sizes. But since 1975, integration of FETs prevailed even though they were found to be slower switching devices than the bipolar transistors. This was because the bipolar transistors failed to demonstrate rapid decrease in the power per circuit than FETs and as linear dimensions reached the half-micron level in the early 1990s, the performance advantage of bipolar transistor was outweighed by FET (more specifically MOSFET, a modern and more practical variant of FET), then used in the CMOS circuit production till today (figure 3).

![Figure 3: Historical and future performance trends using bipolar and CMOS circuits. The straight lines represent the time averaged exponential improvement in the performance of the technology. (adapted from Ref. 8)](image)

1.1 **Metal-oxide-semiconductor field-effect transistor: fundamental device in the CMOS technology**

Metal-oxide-semiconductor field-effect transistor (MOSFET) is essentially a metal-insulator-semiconductor (MIS) junction provided with a source and drain as shown in figure 4. In a MOSFET structure, silicon dioxide (SiO\textsubscript{2}) is used as the insulation layer called as gate oxide
Chapter 1

which is placed between the gate electrode consisting of highly doped polycrystalline silicon and semiconductor called as channel which consists of silicon in the crystalline state. To understand the operating function of MOSFET, assume that the substrate is an n-type semiconductor, and the source and the drain are made up of doped p-type (denoted by p⁺) material. At zero gate bias, no drain current will flow in the circuit. By applying negative gate voltage, the material in the vicinity of the insulator will turn into p-type semiconductor and holes will then flow unimpeded from source to drain thus allowing the current to flow in the circuit. Field-effect transistors evolved from p-type MOSFETs (p-MOS) in the 1960s to n-type MOSFETs (n-MOS) in the 1970s and then to CMOS in the 1980s and 1990s. CMOS circuits combine both n-MOS and p-MOS in a way which greatly reduces consumption of power.

![Figure 4: Schematic illustration of a MOSFET.](image)

![Figure 5: Single transistor DRAM cell showing word line and bit line.](image)

MOSFETs also form the building units of the most significant ferroelectric device technologies namely the solid state computer memory systems, such as DRAM (dynamic random access memory) and NVFRAM (non-volatile ferroelectric random access memory). In a DRAM device, a transistor and a capacitor are paired to create a memory cell, which represents a single bit of data. The capacitor stores the charge and the transistor acts as a switch to charge or discharge the capacitor. Figure 5 shows schematic representation of a DRAM cell and array. Data are stored in an array of capacitors at the intersection of columns of bit lines and rows of word lines. Applying a voltage to one row of word lines turns “on” a row of transistors, allowing a row of capacitors to discharge onto their individual bit lines. During a read operation, a “sense amplifier” at the end of each bit line determines if the capacitor was
charged 1 or 0 and then rewrites that charge by applying the appropriate voltage prior to the word line turning “off”. Since the capacitors lose charge, the cells are recharged using a refresh operation; therefore, DRAM is a volatile memory. Non-volatile FRAM technology includes potential use in smart cards, RF tags, embedded memories, high speed telecommunications etc.\[11\]

For the past 20–25 years, development of DRAM products with a $4 \times$ increase in the storage capacity has been observed approximately every three years. DRAM industry has followed the Moore’s prediction very closely and this performance trend is expected to continue provided certain fundamental issues, discussed in the later sections, are addressed.

On one hand, CMOS technology which is based on MOS transistors, suffers from added process complexity, relatively lower performance and tendency for latch-up to occur, whereas on the other hand it displays excellent added logic capability and lower power dissipation. But since lower power dissipation facilitates fabrication of more components in an IC leading to increased performance, CMOS architecture has evolved as a dominant technology for modern integrated circuits.

### 1.2 Improved performance via scaling

‘Scaling’ is a practice term coined to describe reduction in the size of the device dimensions in order to cram more components on a single microchip. Calculated reduction of transistor geometries as well as the capacitor cell area in the IC has demonstrated spectacular expansion in the technology and communication markets such as high performance microprocessors, wireless systems etc.\[1, 2, 12, 13\] The prime element which enables the scaling of the Si-based metal-oxide-semiconductor field-effect transistor is the materials properties associated with the dielectric employed to isolate the transistor gate from the silicon channel. In the present day computer chip technology, CMOS devices consist essentially of thermally grown amorphous silicon dioxide as the gate dielectric which is the smallest feature of the device. SiO$_2$ layer has a major influence on the device electrical behaviour which acts as a perfect insulator between the gate and the channel thus preventing short circuit. As the transistor feature size is shrinking, the corresponding gate dielectric thickness is also decreasing rapidly. The problem associated with thinning of the oxide layer is its inability to store large amount of charge in it, that is, greater leakage current occurs through the dielectric layer. In an ideal situation, the gate
dielectric acts as a perfect insulator, but as it is made ever thin in order to improve the device performance, huge amounts of current leaks through it thereby resulting in undesirable effects. The transistor does not behave as it should and it consumes more power than it should, thus turning the device cost ineffective.

At normal device operating condition, the typical leakage current of SiO$_2$ at a gate bias of 1 Volt, changes from $10^{12}$ A cm$^{-2}$ at 35 Å to 1 A cm$^{-2}$ at gate oxide thickness of 15 Å. To avoid high leakage currents and still achieve the required gate capacitance, a material with higher permittivity is needed.

The following formula shows the device parameters that determine the resulting gate capacitance ($C$):

$$ C = \kappa \varepsilon_0 A / t $$ (1)

where $\kappa$ is the dielectric constant (also referred as the relative permittivity) of the material, $\varepsilon_0$ is the permittivity of free space ($8.85 \times 10^{-12}$ F m$^{-1}$), $A$ is the area of capacitor and $t$ is the thickness of the dielectric. Parameter $A$ which is the capacitor area will only be smaller in future semiconductor technologies. From equation 1 it is apparent that the dielectric layer thickness $t$ can be increased in order to avoid high leakage currents, only when a material with higher relative permittivity $\kappa$ is used. Dielectric layer of different materials can be compared with the use of the equivalent oxide thickness (EOT) parameter ($t_{eq}$). The term $t_{eq}$ epitomise the theoretical thickness of SiO$_2$ that would provide a particular capacitance density assuming standard dielectric constant of 3.9 (disregarding issues like leakage current and reliability).

Therefore equation 1 for capacitance can be rewritten in terms of $t_{eq}$ and $\kappa_{ox}$ (3.9, the dielectric constant of SiO$_2$) of the capacitor as follows:

$$ t_{eq} / \kappa_{ox} = t_{high-\kappa} / \kappa_{high-\kappa} $$ (2)

or simply

$$ t_{high-\kappa} = (\kappa_{high-\kappa} / \kappa_{ox}) t_{eq} = (\kappa_{high-\kappa} / 3.9) t_{eq} $$ (3)

For example,$^{[14]}$

<table>
<thead>
<tr>
<th>$\kappa_{ox}$ (SiO$_2$)</th>
<th>$C/A$ [fF μm$^{-2}$]</th>
<th>$\varepsilon_0$ [F m$^{-1}$]</th>
<th>$T_{eq} = 3.9\varepsilon_0(A/C)$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.9</td>
<td>34.5</td>
<td>$8.85 \times 10^{-12}$</td>
<td>10</td>
</tr>
</tbody>
</table>
Therefore from equation 3, a gate oxide material having dielectric constant of ~ 25 affords a physical thickness of ~ 64 Å to obtain $t_{eq}$ of 10 Å.

Although leakage current is a significant issue, it does not appear to be a real problem for microprocessors, where, critical design concern is speed. In contrast, leakage current presents a major serious problem for DRAM applications. Transistors display more relaxed leakage current requirements of less than $10^2$ A cm$^{-2}$ for high speed processors and ~ $10^3$ A cm$^{-2}$ for low power applications than memory capacitors which entail extremely low leakage currents generally of the order less than $10^{-9}$ A cm$^{-2}$ and very high capacitance density for charge storage. Since the invention of DRAM nearly 30 years ago, SiO$_2$ or [SiO$_2$ + Si$_3$N$_4$] has been used as the capacitor dielectric sandwiched between polysilicon used as both the bottom and the top electrode.$^{[10]}$ Structures containing these materials are called silicon-insulator-silicon capacitors (SIS or MIM). From expression 1, it is evident that high capacitance density which is the key requirement of a DRAM cell can be brought about by thinning the dielectric layer which then introduces undesirable high leakage currents in the device. Therefore alternative materials with high dielectric constant are urgently needed to allow further CMOS scaling.

### 1.3 Merits and limitations of benchmark SiO$_2$ dielectric

The accomplishments of complementary metal-oxide-semiconductor technology are due to the exceptionally remarkable qualities of SiO$_2$ such as high band gap (~ 9 eV), commendable thermal and chemical stability needed for high temperature device processing, superior insulating properties, electrically stable high quality Si–SiO$_2$ interface layer which allows greater carrier mobility through the MOSFET channel leading to high device performance. For three decades, SiO$_2$ formed the perfect gate dielectric material, successfully scaling from a thickness of 1000 Å (100 nm) 30 years ago to a mere 12 Å (1.2 nm) at today’s 90 nm process node. This represents a layer only five atoms thick. But continuous scaling of device dimensions in the CMOS technologies has impelled the Si–SiO$_2$ system to its very limits. According to the International Technology Roadmap for Semiconductors (ITRS)$^{[13]}$, the present structure of CMOS devices using SiO$_2$ gate oxides will change around 2005, when the SiO$_2$ thickness reaches 15–20 Å. Beyond this technology node, the physical thickness of the gate oxide can no longer shrink and SiO$_2$ will no longer be considered as insulator since the leakage currents due to direct quantum-mechanical tunnelling would be so high that will cause
the devices useless. In addition to the high leakage current as a result of decreasing feature size, issue of boron penetration through the SiO$_2$ gate oxide layer is also of significant concern. Large boron concentration gradient between the heavily doped poly-Si gate electrode, the undoped oxide and the lightly doped Si channel causes boron to diffuse rapidly through a sub-20 Å oxide upon thermal annealing during fabrication, which results in higher concentration of boron in the channel region. A change in channel doping alters the expected device properties in an unacceptable way.$^{[15]}$

Considering leakage current, boron penetration and therefore the reliability of ultra thin SiO$_2$ dielectric layer, it seems apparent that in order to sustain Moore’s prediction of rapid performance-doubling, alternative insulators with higher dielectric constant than SiO$_2$ are significantly essential.

### 1.4 Alternative candidates for high-$\kappa$ dielectric

Many materials have been proposed as future candidates to be used in deep sub-micron CMOS technologies as replacement for SiO$_2$ as gate oxide and are listed in table 1. Alternative gate dielectric which will emerge as a potential replacement for SiO$_2$ is expected to meet certain requirements over superior Si–SiO$_2$ system$^{[14]}$ such as–

1) Significantly high dielectric constant than amorphous silicon dioxide, ($\kappa > 3.9$).
2) Thermodynamically stable in contact with Si channel and capable of withstanding high processing temperatures (for example, annealing at 900–1000°C) in order to prevent poor quality interface which may degrade the carrier mobility.
3) Band gap sufficient enough to obtain low leakage current ($\sim$ 4–5 eV).
4) The alternative gate oxide must be reliable and compatible with the other materials used for processing CMOS structures as well as with the device manufacturing process.

Binary and pseudo-binary oxides of zirconium and hafnium$^{[16-20]}$ have attracted much recent attention as promising candidates as replacement for SiO$_2$ due to their relatively higher dielectric constant, high band gap and good thermal stability in contact with silicon.$^{[14, 21, 22]}$

Several research groups have reported interesting results on ZrO$_2$/Si, ZrSi$_x$O$_y$/Si and on HfO$_2$/Si, HfSi$_x$O$_y$/Si material properties from experimental methods as well as by theoretical approach.$^{[14, 22-27]}$ Copel et al. demonstrated deposition of 20 Å thin ZrO$_2$ film on intentionally
grown 15 Å SiO₂ layer by thermal oxidation. ZrO₂ dielectric was found to be highly uniform with very slight variation in the thickness and showed remarkable stability against silicate formation. The oxide was stable towards high temperature vacuum annealing up to temperatures as high as 900°C. However, studies carried out with ultra thin ZrO₂ films [29, 30] revealed that during high temperature annealing (> 900°C), oxygen is capable of traversing through the oxide layer leading to formation of low-κ interfacial layer (SiO₂ or silicate layer) which then may reduce the overall device performance.

The deficiencies associated with individual insulators can be overcome by combining and complementing the desirable properties from several other insulating materials. Mixing amorphous, stable low-κ material (SiO₂) into metal oxides such as ZrO₂ or HfO₂ produces pseudo-binary amorphous film of ZrSiₓOᵧ or HfSiₓOᵧ which have shown excellent thermodynamic stability. The overall permittivity exhibited by the pseudo-binary oxides is lower than displayed by individual dielectric oxide. But the relatively low dielectric property is compensated when compared with the improved stability for low leakage current and thereby the better performance obtained. Finally a robust gate oxide candidate will emerge by combining and further improving the device integration process, oxide layer deposition methods and the underlying precursor chemistry.

1.5 High-κ materials film growth

Thin layers of high-κ materials; metal oxides or metal silicates or metal nitrides can be deposited using several different techniques which are listed in table 2. Molecular beam epitaxy is a technique of epitaxial film growth by means of solid-source evaporation in an ultra-high vacuum environment. Although the process provides high degree of reproducibility as well as flexibility and allows fabrication of intricate alloy and superlattice structures, it exhibits problems with conformality/uniformity over large areas. In sputtering, atoms in a solid target material are ejected into the gas phase due to bombardment on the target material by energetic ions. Sputtering is largely driven by momentum exchange between the ions and atoms in the material due to collisions. The main disadvantage of employing sputtering techniques is the incorporation of impurities, non uniform composition control, or damage to the substrate. Solution deposition methods such as spin coating or spray pyrolysis are not that useful for growing thin films for device fabrication since very high
growth rate of the desired material is usually observed. These techniques are more relevant for obtaining thick films. Chemical vapor deposition (CVD) works very well for thin layer deposition, particularly metal organic chemical vapor deposition (MOCVD)\textsuperscript{[37, 38]} and atomic layer deposition (ALD)\textsuperscript{[39, 40]} CVD is a thin film synthesising technique in which vapours of chemical components called precursors react involving chemical reactions to form solid film or powder at some surface called as the substrate.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\kappa$</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>9</td>
<td>8.7</td>
</tr>
<tr>
<td>$\text{La}_2\text{O}_3$</td>
<td>30</td>
<td>4.3</td>
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<tr>
<td>$\text{Ta}_2\text{O}_5$</td>
<td>26</td>
<td>4.5</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>80</td>
<td>3.5</td>
</tr>
<tr>
<td>$\text{Y}_2\text{O}_3$</td>
<td>15</td>
<td>5.6</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>25</td>
<td>7.8</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>28</td>
<td>5.7</td>
</tr>
<tr>
<td>$\text{ZrSi}_2\text{O}_7$</td>
<td>13</td>
<td>$\sim 9$</td>
</tr>
<tr>
<td>$\text{HfSi}_2\text{O}_7$</td>
<td>13</td>
<td>$\sim 9$</td>
</tr>
<tr>
<td>$\text{Pb(Zr,Ti)}\text{O}_3$</td>
<td>$&gt; 1000$</td>
<td>$\sim 3.8$</td>
</tr>
<tr>
<td>(Ba,Sr)TiO$_3$</td>
<td>160-600</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1:** Candidate gate oxide (high-$\kappa$) materials.

On the basis of different deposition features used to obtain films, a number of forms of CVD are widely used. For example, Plasma enhanced CVD (PECVD) utilises plasma as the source material to enhance chemical reaction rates of the precursors and allows deposition at lower temperatures. Similarly Rapid thermal CVD (RTCVD) process uses heating lamps to heat the substrate. Low pressure CVD (LPCVD) allows depositions at sub-atmospheric pressures. Low pressures tend to reduce unwanted gas phase reactions and improve film uniformity across the substrate.

Among all different CVD processes known, MOCVD which employs metalorganic (MO) complexes as precursors for thin film deposition at reduced pressures and ALD (special
modification of CVD) have gained the most actual interest and are being commercialised to meet the industry demands. MOCVD has been established as a very useful fabrication process for the deposition of high quality films, particularly in microelectronic application, as it offers advantages of selective growth, conformal step coverage and large-scale capability. ALD relies on self limiting surface reactions and provides accurate film thickness control together with excellent conformality/uniformity over large areas. In this work, thin films of zirconium- and hafnium dioxide are obtained by metal organic CVD in which the precursors have been thermally activated and therefore theory and principles of MOCVD are discussed in detail. In addition, briefly the basic principle of ALD, which at present is the most rapidly developing film deposition technology, is also described.

Table 2: Various thin film deposition techniques.

<table>
<thead>
<tr>
<th>Physical vapor deposition (PVD)</th>
<th>Chemical vapor deposition (CVD)</th>
<th>Solution phase deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtering</td>
<td>Metal organic CVD (MOCVD)</td>
<td>Spray pyrolysis</td>
</tr>
<tr>
<td>Vacuum evaporation</td>
<td>Liquid injection CVD (LICVD)</td>
<td>Spin coating</td>
</tr>
<tr>
<td>Molecular beam epitaxy (MBE)</td>
<td>Plasma enhanced CVD (PECVD)</td>
<td>Electroplating</td>
</tr>
<tr>
<td></td>
<td>Rapid thermal CVD (RTCVD)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Atmospheric pressure CVD (APCVD)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low pressure CVD (LPCVD)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ultra-high vacuum CVD (UHVCVD)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Atomic layer CVD (ALCVD)</td>
<td></td>
</tr>
</tbody>
</table>

1.5.1 Principles of Metal organic chemical vapor deposition

MOCVD is a versatile and flexible chemical method for depositing thin films of wide variety of materials for ceramic coatings and to fabricate semiconductor devices for IC technology. MOCVD process involves a few number of sequential steps, starting from vapour
phase delivery to the reactor, progressing through a series of quasi steady-state sub-processes, and concluding with the formation of solid thin film or powder in its final microstructure. The MOCVD sequence is schematically illustrated in figure 6\(^{(45)}\) and the individual sub-processes are described below.

a) Supply of precursor

Single precursor component or mixture of components is delivered to the reactor in vapour phase. The precursor vapours are transported up to the reaction zone by inert gases such as nitrogen or argon and the rate of vapour supply depends on the velocity of the gases in the reactor as well as the precursor concentration in the carrier gas.

![Figure 6: Schematic representation of a MOCVD process. (adapted from Ref. 45)](image)

b) Reactions occurring in the gas-phase

The precursor molecules present in the reactor may interact with each other prior to deposition, thereby resulting in homogeneous nucleation and sometimes even in powder formation. Formation of particles in the gas phase endangers the homogeneity of the deposited films and hence gas phase reactions should be avoided.

c) Diffusion of the precursor molecules to the surface

Transport near to the solid surface is always dominated by diffusion mechanism. When uniformly distributed diluted precursor vapours are forced over a flat substrate, a velocity profile developed averages with no net motion, that is, the velocity is zero adjacent to the substrate or surface of the reactor tube. The gaseous layer between the
substrate and the position where the velocity is maximum of the average velocity is called the boundary layer. Through the boundary layer precursor vapours are not available by the carrier gas flow but via diffusion through the layer to the substrate surface. The rate of diffusion depends on the total reactor pressure, temperature and the concentration of precursor molecules in the gas phase present above the boundary layer.

d) Adsorption of the precursor molecules at the surface
The precursor molecules after diffusing through the boundary layer are adsorbed on the substrate surface. Usually the adsorbed reactants are assumed to be in equilibrium with the reactants in the gas phase.

e) Migration (surface diffusion) of the adsorbed species
The adsorbed species undergo surface diffusion phenomenon and migrate prior to reaction.

f) Precursor decomposition (surface reactions) at the surface and film growth on the surface
The adsorbed precursor molecules either react with their neighbouring molecules or with the molecules present in the gas phase to form a film.

g) Desorption and diffusion of the reaction by-products
The reaction by-products which are formed as a result of surface reactions, and which do not contribute in film formation, desorb from the surface and diffuse out through the boundary layer. Similarly the unreacted precursor molecules also desorb and diffuse through the stagnant boundary layer. In order to avoid contamination of the film, the by-products need to be in the gaseous state.

h) Removal of by-products
Volatile by-products and the unreacted precursor molecules are pushed out from the reactor by bulk gas flowing in the reactor. Since MOCVD process occurs through a sequence of sub-process, the slowest sub-process is the overall rate determining step.

Generally for a CVD process three different film growth regimes are apparent. In other words, growth rate is determined by:

1) Supply of the precursor to the reactor growth zone
When step a or h is the slowest step then the MOCVD process is said to be in the mass transport controlled region. Mass transport is responsible for precursor supply
to the reactor zone and removal of the reaction by-products as well as the unreacted reactants from the reactor.

2) Diffusion of the precursor molecules through the boundary layer
When step e or g is the slowest process when compared to the other processes, the CVD reaction is identified as being in the diffusion rate limiting region. Diffusion rate determining region is generally observed at relatively higher substrate temperatures. This is because at low substrate temperatures, precursor molecules with high rate of diffusion will not decompose quantitatively. Since growth controlled by diffusion begins at high temperatures where almost all the precursor molecules that touch the substrate surface react to form the film, further increase in the deposition temperature does not show significant effect on the growth rate. Thus diffusion controlled region can be said to be independent of substrate temperature where generally non-uniform and rough film surfaces due to gas flow dynamics are obtained.

3) Surface phenomenon occurring at the substrate
When either step d, e, f or g (desorption of the by-products) is the slowest process, the film growth is said to be limited by reaction-rate. Processes such as precursor adsorption, surface reactions and desorption of by-products are kinetic processes and hence this region is also called kinetically controlled region. Growth rate limited by chemical kinetics occurs at low temperatures and the growth increases exponentially with increase in temperature following the Arrhenius equation. Because the reactions are slow compared to the diffusion through the boundary layer, the diffusion length of the precursor molecule is long. This results in a smooth uniform film growth and enables conformal growth over large substrate area.

The growth rate is found to decrease with increasing substrate temperature because of an increased rate of desorption and depletion of precursor in the gas phase. This region is often referred to as the thermodynamically controlled region or depletion region. From the Arrhenius plot (figure 7), which is the plot of growth rate versus the inverse of temperature, influence of the three rate determining cases on the substrate temperature can be clearly understood.

Several studies on successful thin film growth of high-κ materials by MOCVD technique has been reported in the literature.\cite{46-50} The fundamental requirement for a MOCVD process is the availability of suitable precursors with appropriate thermal properties. Precursor chemistry and ligand concept, merits of CVD precursors and importance of thermal properties in determining
the properties of the deposited films is discussed in detail in § 1.8, and § 1.9 respectively. Another deposition technique which is worth mentioning is liquid injection MOCVD (LI-MOCVD) and the process is relatively new when compared with the classical MOCVD. In this variant of MOCVD, the precursor is injected in the solution phase at room temperature into the heated evaporator. The method thus offers significant advantage over conventional MOCVD by avoiding pre-reactions which has detrimental effects on the deposited films. Thin films from metalorganic precursors with relatively low vapour pressures can be easily deposited by LI-MOCVD which would otherwise be difficult to use in conventional MOCVD.

Inherent consequence of device scaling which requires alternative dielectric materials of few atom thickness and preferably low device process temperature (< 400°C) has raised significant interest towards ALD. Variety of metal oxide and metal nitride films has been successfully deposited employing the

**Figure 7:** Arrhenius plot displaying different film growth controlling region.

### 1.5.2 Principles of Atomic layer deposition

Atomic layer deposition (ALD), also known in some circles as atomic layer epitaxy (ALE) or atomic layer chemical vapor deposition (ALCVD), has been established as a potential method for the deposition of high-κ oxides. The method was introduced in late 1970s for fabrication of electroluminescent thin films which for a long time remained its only industrial application. Inherent consequence of device scaling which requires alternative dielectric materials of few atom thickness and preferably low device process temperature (< 400°C) has raised significant interest towards ALD. Variety of metal oxide and metal nitride films has been successfully deposited employing the
technique.[62-67] Atomic layer deposition relies on self-limiting surface reactions occurring on the substrate by alternate pulsing of the source materials into the reactor. Every ALD cycle consists of four steps and the basic principle involved is illustrated by ZrO$_2$ film deposition using ZrCl$_4$ and water as the precursor system.

a) Excess of ZrCl$_4$ is pushed into the reactor where ZrCl$_4$ reacts with the hydroxyl groups present on the substrate surface forming –O–ZrCl$_3$ and/or –(O)$_2$–ZrCl$_2$ species. All reactive surface groups (–OH), present are considered to be consumed under an ideal ALD conditions and thus this step is considered to be saturative.

b) The unreacted ZrCl$_4$ and HCl formed as the reaction by-product are carried out from the reactor either by purging an inert gas or evacuating the reaction chamber.

c) The second precursor H$_2$O, is then pulsed into the reactor. H$_2$O reacts with the surface adsorbed –ZrCl$_x$ moieties to form monolayer of ZrO$_2$ film covered with equal number of hydroxyl groups as were present at the beginning of the cycle.

d) Excess of H$_2$O and all chloride ions in the form of HCl are removed from the reactor via inert gas purging or evacuating the reaction chamber.

Since steps c and d are saturative, the film growth is said to be self-limiting. The film growth rate increases proportionally with the number of deposition cycles but the growth rate is independent of the deposition temperature. Thin film growth occurring through self-limiting surface reactions offer many potential advantages to the ALD process such as excellent uniform and conformal growth over large wafer area and precise control of the film thickness. One of the most distinct features of ALD process over CVD is the absence of gas phase reactions. This is because in ALD, both the precursors are pulse separately into the reactor chamber where the precursors have sufficient time to react quantitatively towards each other which results in high quality deposits even at lower substrate temperatures.

Thin films obtained due to low growth rates is seen as the main drawback of the ALD process. But IC technology especially requires dielectric layer of only a few atoms thick and therefore the inability of ALD process to produce thicker films increases its applicability even more in the microelectronic industry. Since ALD is a surface reaction related growth process, the underlying molecular chemistry plays an important key issue and the process needs tailored precursors for its successful utilisation.[68, 69] Generally speaking, precursors applicable to MOCVD and classical CVD processes are also used as ALD precursors provided they possess certain specific requirements in addition to the CVD precursors.[70] ALD precursors and their
properties are discussed in next sections with main emphasis on the precursors for MOCVD process.

![Diagram of ALD cycle for ZrO2 film deposition](image)

**Figure 8:** An example of an ALD cycle from ZrCl₄–H₂O process for ZrO₂ film deposition. (adapted from Ref. 56)

### 1.6 MOCVD of zirconium- and hafnium dioxide

Although there exist evidence for use of zirconium dioxide or zirconia in ancient times particularly as gemstones, it wasn’t until 1789 that a German chemist Martin Heinrich Klaproth discovered and coined zirconia. In 1824, a Swedish chemist Jons Jacob Berzelius, isolated the zirconium metal and it was further 120 years later that in 1950s zirconium was commercialised along with other metals as a range of ceramic oxide colours. Since then the potential of zirconium dioxide was well recognised and today zirconia has become a very important material in chemical, mechanical as well as in the semiconductor industry. Zirconium dioxide (ZrO₂) has been employed for use in thermal barriers[^71-73], oxygen sensors and fuel cells[^74-77], anti corrosion and optical coatings[^78, 79], due to its high thermal and chemical stability and its high refractive index. Inherent physical assets of ZrO₂ have attracted much recent attention in microelectronics. Zirconium dioxide has a dielectric constant of around 25 and is thermodynamically stable in contact with silicon which makes it a promising
candidate to replace SiO$_2$ ($\kappa = 3.9$) and Si$_3$N$_4$ ($\kappa = 9$) as gate dielectric for sub-0.1 $\mu$m complementary metal-oxide-semiconductor (CMOS) technology.$^{[14]}$ ZrO$_2$ is one of the components of the ferroelectric oxide such as [Pb (Zr,Ti)O$_3$] (PZT) and [(Pb,La) (Zr,Ti)O$_3$] (PLZT) for semiconductor memory application (DRAMs and NV-FRAMs).$^{[80-84]}$

The physical properties of zirconia are largely governed by the different crystal structures of ZrO$_2$. At normal pressure, bulk zirconium dioxide exists in three structural polymorphs namely monoclinic (baddeleyite), tetragonal and cubic.$^{[85]}$ In addition to these three phases, at high pressures orthorhombic phase of ZrO$_2$ prevails.$^{[86]}$ Monoclinic phase is the thermodynamically stable low temperature form whereas tetragonal and cubic structures are the high temperature forms of ZrO$_2$. At 1100°C monoclinic phase transforms into the tetragonal phase which is stable up to 2370°C after which the cubic phase exists up to the melting point of 2680°C.$^{[85, 87]}$

It is likely for thin films that the deposition parameters may sometimes shift these phase transformation boundaries. There have been reports in the literature which indicate that strain, lattice defects, film thickness and crystallite size affects the phase transformation in bulk ZrO$_2$. Garvie suggested that sometimes crystallite size stabilises the tetragonal phase at room temperature because the tetragonal form has low surface free energy than the monoclinic ZrO$_2$.$^{[88, 89]}$ It is well known that deliberate shift in the phase content of the thin films is brought about by adding other oxides as impurities. For example in thin films the cubic form of ZrO$_2$ is usually stabilised at low temperature by adding Y$_2$O$_3$ as dopant oxide and the zirconium dioxide then is called as Yttria stabilised zirconia (YSZ).$^{[90, 91]}$ YSZ has been studied and used typically as buffer layer for the deposition of high-Tc superconducting films$^{[92]}$, high temperature insulating shields and also for solid electrolyte application in oxygen pumps.$^{[93]}$

Like ZrO$_2$, hafnium dioxide, is also a potential candidate for gate dielectric in CMOS devices due to its high permittivity of $\sim$ 28–30 which is three to five units greater than ZrO$_2$.$^{[94, 95]}$

Apart from use as high-\(\kappa\) material, HfO$_2$ has been investigated for application in optics.$^{[96-98]}$ At normal pressures, three different phases of HfO$_2$ are identified. Under equilibrium conditions, monoclinic phase ($\alpha$-HfO$_2$) predominates which is the thermodynamically stable low temperature form of HfO$_2$. At temperature around 1700°C, $\alpha$-HfO$_2$ transforms into tetragonal HfO$_2$ ($\beta$-HfO$_2$), which in turn transforms into cubic phase ($\gamma$-HfO$_2$) at temperatures above 2200°C. Stable high pressure orthorhombic phase also exists in the Hf-O system. MOCVD has been used most frequently and efficiently for the deposition of ZrO$_2$ anf HfO$_2$ thin films particularly in ultra-large-scale-integrated (ULSI) technologies due to its well understood reactor design, high deposition rates with reliable compositional control and high
To exploit the maximum potential of the process in order to obtain reproducible high quality films, availability of precursors possessing appropriate thermal properties is the prime requirement. Since MOCVD involves transport of precursor in the vapour phase, the precursor essentially should have certain physical characteristics such as high vapour pressure, adequate process window between precursor evaporation temperature and decomposition temperature, suitable reactivity at the surface to yield films with desired stoichiometry through clean decomposition preferably at low deposition temperatures.

Number of precursors such as zirconium β-diketonates, alkoxides, donor functionalised alkoxides or alcohols, chlorides, nitrates, mixed ligand type etc has been employed for obtaining ZrO₂ and HfO₂ films by MOCVD process. Table 3 and table 4 summarise literature known zirconium and hafnium precursors used for MOCVD of ZrO₂ and HfO₂ respectively. [Zr(thd)₄]⁸¹,¹⁰⁰-¹⁰² and [Hf(thd)₄]¹⁶, are the most widely experienced CVD precursors among all zirconium- and hafnium β-diketonates like [M(acac)₄] and [M(tfac)₄] (M: Hf, Zr). Generally metal β-diketonates impart high atmospheric stability and require high bubbler and substrate temperatures during MOCVD. For example, [Zr(acac)₄] requires source temperature of 200°C for sufficient vaporisation and diffusion-controlled films are obtained at minimum substrate temperature of 350°C. In the case of [Zr(thd)₄], the bubbler temperature needs to be set between 200−300°C and minimum substrate temperature required for film growth is greater than 500°C.¹⁶, ⁷¹, ⁹⁷, ¹⁰³, ¹⁰⁴ Such high film growth temperature region is suitable for deposition of protective YSZ coatings, but however such high temperatures are incompatible with low processing temperatures needed in microelectronic applications. Even though metal-oxygen bond is present in the molecule, [Zr(thd)₄] cannot be used as an effective ‘single source precursor’ (SSP). The oxygen present in the metal precursor is unable to oxidise efficiently the organic matter and very often ZrO₂ films deposited especially at lower substrate temperatures are highly contaminated with carbon.⁷¹ Therefore, additional oxygen is fed into the deposition chamber which helps in minimising the carbon content and also lowers the onset temperature of ZrO₂ film growth.¹⁰⁵ Fluorinated β-diketonates decompose at relatively low temperatures of 300°C but the oxide growth suffers from highly undesirable fluorine contamination. In addition these precursors need only H₂O to reduce them to yield metal oxide during CVD.⁴⁷ More recently sterically hindered [Hf(tod)₄] and [Zr(tod)₄] has been used to deposit oxide films by pulsed liquid injection MOCVD.¹⁰⁶ Using these precursors high growth rate was observed and the onset of film growth was 500°C which is lower when compared to [Hf(thd)₄] and
Chapter 1

[\text{Zr(thd)}_4]. Metal alkoxides namely [\text{Zr(OC(CH_3)_3)}_4] and [\text{Hf(OC(CH_3)_3)}_4] which exhibit maximum volatility than other [\text{M(OR)}_4], (M: Zr, Hf and R: Et, Pr) show great potential as CVD precursors by yielding carbon free films at significantly lower deposition temperatures (350°C).\textsuperscript{107-111}

Chisholm and co-workers reported high-purity polycrystalline cubic-ZrO\textsubscript{2} thin films from [\text{Zr}_2(\text{OPr}^t)_8(\text{HOPr}^t)_2] and [\text{Zr(OBu}^t)_4] at 400°C without using any additional oxidant.\textsuperscript{112} But although being significantly more volatile and thermally less stable, extensive use of metal alkoxide in deposition of oxide films is restricted. This is because they contain positively charged M(IV) centre with an incomplete coordination sphere which makes them easily susceptible towards pre-reactions and oligomerisation. Gallegos et al. tried to inhibit oligomerisation by introducing bulky neo-pentoxide ligands but the resulting complex was identified as a dimer, [\text{Zr(µ-ONep)(ONep)}_3]_2.\textsuperscript{113}

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Physical property</th>
<th>Evaporator Temperature/°C</th>
<th>Minimum T\textsubscript{deposition}/°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{Zr(thd)}_4]*</td>
<td>180°C (subl.)/0.1 torr</td>
<td>200-230</td>
<td>&gt; 550</td>
<td>[101, 103, 116*]</td>
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<tr>
<td>[\text{Zr(acac)}_4]</td>
<td>171-173°C (mp)</td>
<td>150-220</td>
<td>350</td>
<td>[16]</td>
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<tr>
<td>[\text{Zr(tfac)}_4]</td>
<td>130°C (subl.)</td>
<td>130-180</td>
<td>300</td>
<td>[16]</td>
</tr>
<tr>
<td>[\text{Zr(COD)}_4]</td>
<td>180-190°C (subl.)/10\textsuperscript{-2} torr</td>
<td>280</td>
<td>500</td>
<td>[106]</td>
</tr>
<tr>
<td>[\text{Zr(OBu}^t)_4]*</td>
<td>1.00 torr @ 65°C</td>
<td>50-70</td>
<td>350</td>
<td>[112, 65*]</td>
</tr>
<tr>
<td>[\text{Zr(µ-ONep)(ONep)}_3]_2</td>
<td>–</td>
<td>160-180</td>
<td>300</td>
<td>[113]</td>
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<td>–</td>
<td>230</td>
<td>300</td>
<td>[120, 126*]</td>
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<td>[\text{Zr(OPr}^t)_4(dmae)_2]*</td>
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<td></td>
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<td>[119, 126*]</td>
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<tr>
<td>[\text{Zr(OBu}^t)_2(dmae)_2]*</td>
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<td>[119,117*,126*]</td>
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<td>[53]</td>
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<td>[\text{Zr(acac)}_2(hfip)_2]</td>
<td>dist. 80°C/10\textsuperscript{-3} mm</td>
<td>78</td>
<td>350</td>
<td>[181]</td>
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<tr>
<td>[\text{Cp}_2\text{Zr(CH}_3)_2]*</td>
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<td>85</td>
<td>400</td>
<td>[180, 116*]</td>
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<tr>
<td>[\text{ZrI}_4]*</td>
<td>–</td>
<td>200</td>
<td>400</td>
<td>[135, 134*]</td>
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<tr>
<td>[\text{ZrCl}_4]*</td>
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<td>158-200</td>
<td>&gt; 800</td>
<td>[133, 28*, 79*]</td>
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<tr>
<td>[\text{Zr(NO}_3)_4]</td>
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<td>75-85</td>
<td>285</td>
<td>[19, 129]</td>
</tr>
<tr>
<td>[\text{Zr(NEt}_2)_4]</td>
<td></td>
<td></td>
<td>500</td>
<td>[78]</td>
</tr>
</tbody>
</table>

\textbf{Table 3:} Tabular summarisation of literature reported precursors for ZrO\textsubscript{2} MOCVD. (* indicates the precursors are also used as ALD precursors)
MOCVD of the precursor resulted in ZrO$_2$ films containing less than 1 at. % carbon at 300°C. In order to inhibit oligomerisation, donar functionalised alkoxide ligands such as aminoalcohols or methoxy ethoxy (mmp) ligand has been combined with normal alkoxide ligands.$^{[50, 114, 115]}$ However insertion of dmae or dmap into [Zr(OR)$_4$] (R = Pr, Bu$^t$) produced assymetric binuclear complexes [Zr(OBu$_3$)$_2$(dmae)$_2$]$_2$$^{[117]}$ [Zr(OPr$_3$)(dmap)]$_2$$^{[118]}$ and [Zr(OPr$_3$)$_2$(bis-dmap)]$_2$$^{[118]}$ which exhibit low volatility and are susceptible towards disproportionation reactions in solution during LI-MOCVD.$^{[119]}$

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Physical property</th>
<th>Evaporator</th>
<th>Minimum</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Hf(thd)$_4$]</td>
<td>−</td>
<td>200-230</td>
<td>&gt; 500</td>
<td>[16, 17, 103]</td>
</tr>
<tr>
<td>[Hf(acac)$_4$]</td>
<td>−</td>
<td>~ 200</td>
<td>350</td>
<td>[16, 17, 103]</td>
</tr>
<tr>
<td>[Hf(tfac)$_4$]</td>
<td>−</td>
<td>190</td>
<td>300</td>
<td>[17, 18]</td>
</tr>
<tr>
<td>[Hf(tod)$_4$]</td>
<td>190-200°C (subl.)/10$^{-3}$ torr</td>
<td>280</td>
<td>500</td>
<td>[106]</td>
</tr>
<tr>
<td>[Hf(OBu)$_4$]</td>
<td>5.00 mm @ 90°C</td>
<td>−</td>
<td>−</td>
<td>[107, 111]</td>
</tr>
<tr>
<td>[Hf(OBu)$_3$(mmp)$_2$]*</td>
<td>100-104°C</td>
<td>130-150</td>
<td>350</td>
<td>[121, 182*]</td>
</tr>
<tr>
<td>[Hf(mmp)$_4$]</td>
<td>−</td>
<td>130-150</td>
<td>350</td>
<td>[122, 183*]</td>
</tr>
<tr>
<td>[HfI$_4$]*</td>
<td>−</td>
<td>300</td>
<td>300</td>
<td>[137, 137*]</td>
</tr>
<tr>
<td>[HfCl$_4$]*</td>
<td>320 (subl.)</td>
<td>150-200</td>
<td>&gt; 800</td>
<td>[107,132,138*,139*]</td>
</tr>
<tr>
<td>[Hf(NO$_3$)$_4$]*</td>
<td>95°C (subl.)/0.2 mm</td>
<td>75</td>
<td>250</td>
<td>[128, 129, 136*]</td>
</tr>
<tr>
<td>[Hf(NEt)$_4$]</td>
<td>−</td>
<td>350</td>
<td>300</td>
<td>[184, 185]</td>
</tr>
<tr>
<td>[Hf(NMe)$_2$]</td>
<td>−</td>
<td>130</td>
<td>300</td>
<td>[143]</td>
</tr>
</tbody>
</table>

Table 4: Tabular summarisation of literature reported precursors for HfO$_2$ MOCVD. (* indicates the precursors are also used as ALD precursors)

Related eight coordinated [Zr(dmae)$_4$] complex is suggested to be a monomer and ZrO$_2$ films were deposited by LI-MOCVD in the temperature range 300–480°C using n-butylacetate as precursor solvent.$^{[120]}$ The growth rate was found to be strongly dependent on the substrate temperature. The onset of deposition was 300°C in presence of oxygen and the growth rate decreased rapidly at temperatures above 360°C. This suggests [Zr(dmae)$_4$] has lower thermal stability. Electrical properties of the deposited ZrO$_2$ were measured by fabricating MIS capacitor with Al as the top electrode [Al/ZrO$_2$/p-type Si(100)] and the relative dielectric constant of the as-deposited ZrO$_2$ film was estimated to be in the range 15–20. Incorporation of
sterically hindered ligand like [OCMe₂CH₂OMe], (mmp) into [Zr(OBu)₄] and [Hf(OBu)₄] facilitated formation of mononuclear species [Zr(OBu)₄]₂, [Hf(OBu)₄]₂ and [Zr(mmp)₄], [Hf(mmp)₄] respectively. Thin films of ZrO₂ and HfO₂ were deposited over temperature range of 350–650°C by LI-MOCVD using precursor solution in toluene. In contrast to the temperature dependent growth rate of [Zr(dmae)₄], growth rate from [Zr(mmp)₄] shows little decrease at substrate temperature as high as 600°C. This may provide [Zr(mmp)₄] a rather broader range of low temperature MOCVD applications particularly in microelectronics. High frequency capacitance-voltage (C–V) measurements on [Al/MO₂/p-Si] capacitors containing ZrO₂ and HfO₂ layers grown from [M(OBu)₂(mmp)₂] and [M(mmp)₄] precursors displayed good dielectric properties.[123] In addition to solution MOCVD, [M(OBu)₂(mmp)₂] and [M(mmp)₄] complexes are potential precursors for conventional CVD as well. Mixed ligand (heteroleptic) complexes designed with the aim of combining high thermal stability of the metal β-diketonates with high volatility of metal alkoxides has resulted in potential MOCVD precursors. Heteroleptic [M(OPr)₂(thd)₂], where M = Hf and Zr, has been successfully tested for MO₂ films in the temperature range 350–600°C.[53, 119] NMR studies carried out on [M(OPr)₂(thd)₂] revealed that the monomer disproportionates into dimer, stable [M(thd)₄] and the parent alkoxide [M(OR)₄] which was also observed in MOCVD experiments. The dimer [Zr₂(OPr)₆(thd)₂] was investigated to be a reliable precursor for solution MOCVD.[125] ZrO₂ films were deposited over a wide temperature range of 250–600°C and onset of film growth was observed at ~ 450°C which is much less when compared to [Zr(thd)₄]. [Zr₂(OPr)₆(thd)₂] was also used to grow PZT films in combination with [Pb(thd)₂] and [Ti(OPr)₄(thd)₂].[127] During multicomponent film growth special care is needed in choosing a compatible set of precursors. By employing identical ligand system, the undesirable effects of ligand exchange can be efficiently suppressed. Also the formation of powders in the source delivery lines which tend to block the reactor lines can be significantly minimised. Using the above precursor ‘cocktail’ no clogging of reactor delivery lines was observed and stoichiometric films having good surface morphology were obtained.

Among the inorganic compounds, [M(NO₃)₄] are attractive precursors for MOCVD due to their high volatility and being carbon free. High-purity films were deposited at substrate temperatures as low as 300°C.[19, 128-131] But stringent precautions concerning their reactivity and forming corrosive nitric acid in presence of trace amount of moisture, limits their application. [ZrCl₄] and [HfCl₄] require high evaporator temperature between 150–200°C and deposition temperatures greater than 800°C during MOCVD and are less interesting for
microelectronic application because at such high temperatures the underlying Si-layer is not thermally stable.[132, 133] Recently, amides of group IVb have been used as potential precursors for depositing metal nitride films in combination with ammonia.[140, 141] In 1995, Bastianini et al. reported MOCVD of ZrO$_2$ films using [Zr(NEt$_4$)$_4$] and oxygen in the temperature range 500–580°C.[78] Due to its high volatility, recently [Hf(NEt$_4$)$_4$] has been used to deposit HfO$_2$ films by conventional MOCVD. It was found that by increasing the oxygen flow rate, the residual carbon and nitrogen content in the films reduced and at 450°C polycrystalline HfO$_2$ films were obtained. Another group at Motorola Incorporated, deposited amorphous HfO$_2$ films using the same tetrakis diethyl amido precursor at minimum substrate temperatures of 325°C by LI-MOCVD.[142] Annealing and deposition temperatures were found to influence the film microstructure, density and impurity content in the HfO$_2$ films. Significant interfacial layer growth of SiO$_2$ (6–9 Å) was observed for all annealed samples at 700°C. It was concluded that it is possible during the annealing process that excess oxygen in HfO$_2$ can out-diffuse to react and form SiO$_2$ at the Si interface. Electrical properties of the deposited HfO$_2$ layer were measured on [Pt/HfO$_2$/n-Si] capacitor at different conditions and deposition at 550°C showed dramatic improvement in the electrical leakage properties. Other nitrogen containing precursors used particularly for LI-MOCVD are [Hf(NMe$_2$)$_4$] and [Hf(ONEt$_2$)$_4$].[143]

1.7 MOCVD of zirconium- and hafnium silicates

For all gate dielectric applications, the interface with silicon plays a key role and in most cases is the dominant factor in determining overall electrical properties of the device. ZrO$_2$ and HfO$_2$ though robust, are not completely chemically and thermally stable on silicon and at high temperatures the silicon diffuse into ZrO$_2$ thus tending to form either interfacial layer of SiO$_2$ or metal silicates which eventually leads to high leakage current and reduces the performance of the device. Direct deposition of metal silicate layer onto the silicon substrate has been recognised as one of the reliable solution to minimise interface related concern. Metal silicates alloys such as Zr$_{1-x}$Si$_x$O$_y$ and Hf$_{1-x}$Si$_x$O$_y$ have gained much interest as potential high-κ materials.[14, 23] Although the dielectric constant of ZrSi$_x$O$_y$ and HfSi$_x$O$_y$ is less than ZrO$_2$ and HfO$_2$, the improved thermal stability obtained from them outperforms their low permittivity. But when compared to the dielectric constant of conventional SiO$_2$ (κ = 3.9), the permittivity of these alloys (κ = 12–13) is significantly high. Considerably, much less information on the
Hf-Si-O system is available than on the Zr-Si-O system. But since the two metals have similar chemical behavior (Zr and Hf are called as twin metals), comparison between the respective silicate system is possible. Blumenthal, and Bragg et al. described the Bravais lattice for the stoichiometric compound ZrSiO₄ (zircon) as a body-centred tetragon which belongs to point group D₄h. The crystal is composed of SiO₄ tetrahedra interspersed with Zr atoms, but can be considered as parallel chains of ZrO₂ and SiO₂ structural units as shown in figure 9.

Figure 9: Atomic model of the crystalline structure for the ZrO₂–SiO₂ (zircon) system described by Blumenthal (see Ref. 144). Black atoms= Zr (or Hf), white atoms= Si and gray atoms= O. Dashed lines represents bonds between Zr (or Hf) atoms of a given chain and O atoms of neighbouring chains, which gives three-dimensional stability to the structure. (adapted from Ref. 23)

Thin films of zirconium silicate and hafnium silicate have been deposited by sputtering, ALD, sol-gel and CVD. Two different approaches have been established for obtaining ZrSiₓOᵧ and HfSiₓOᵧ films, especially by MOCVD. The first approach deals with employing of Zr or Hf containing precursor and Si containing compound as two separate source. For example, ZrSiₓOᵧ and HfSiₓOᵧ films have been deposited by LI-MOCVD using [Zr(NEt)₂] or [Hf(NEt)₂] in combination with [Si(NMe₂)₄]. Hafnium silicate films were also deposited employing [Bu'Me₂SiOH] in combination with [Hf(NMe₂)₄]. In the second approach, the metal (Zr or Hf) source and the Si source is contained in one single precursor molecule. Precursors namely [Zr(OSiMe₃)₂(acac)₂] and [Zr(OSiMe₂Bu')₂(acac)₂] have been employed for obtaining ZrSiₓOᵧ films by single-source precursor approach. In these mixed ligand complexes the stoichiometry of the ZrSiₓOᵧ films was found to change by varying the
siloxide ligands attached to the metal centre. For instance higher amount of silicon content was
found in the ZrSi$_x$O$_y$ films grown from [Zr(OSiMe$_2$Bu$^t$P$^t$Bu)$_2$(acac)$_2$] as precursor. However, in
general, in the mixed ligand complexes, as the stoichiometric ratio of metal: silicon (1:2) is
fixed, the extent of Si incorporation into the resulting silicate films is limited and is considered
as a disadvantage. For example, HfSi$_x$O$_y$ films grown using [Hf(OSiBu$^t$Me$_2$P$^t$Me$_2$)$_4$(Et$_2$NH)] as a
single source precursor gave a fixed Si content of ca. 10–15 at. % whereas employing two
separate sources, [Hf(NMe$_2$)$_3$] and [Bu$^t$Me$_2$SiOH] allowed relatively good control of silicon
concentration in the films. XRD analysis showed more amorphous texture of the films
containing increased level of silicon content.

Although it is well accepted that metal silicate films with higher silicon content exhibit
composition closer to stoichiometric MSiO$_x$ (M: Zr or Hf) and are expected to show increased
dielectric constant while maintaining a low leakage current, obtaining the MSiO$_x$ stoichiometry
should not be necessary, however, especially since it is desirable to maintain an amorphous
structure. Therefore, precursors which allow deposition of low temperature amorphous films
with somewhat Si rich composition are suitable.

1.8 Precursor concept involved in the MOCVD of high-$\kappa$ materials

Industry has recognised the potential of MOCVD technique for deposition of various
electroceramic oxides like ZrO$_2$, HfO$_2$, HfO$_x$Si$_y$, [Pb(Zr,Ti)O$_3$] (PZT), [Ba(Sr,Ti)O$_3$] (BST) etc
in wide variety of applications ranging from dielectric layers in microelectronics to protective
coatings and catalysts in aerospace and petrochemical field. But commercialisation of the
process hinge critically upon the availability of suitable high-purity precursors with sufficient
volatility and stability.$^{[155, 156]}$ A number of books, articles and reviews have appeared which
address the role of molecular chemistry in influencing the physical properties of the precursor
leading to robust thin films by MOCVD process for successful ULSI strategy.$^{[50, 115, 155, 156]}$

Once a metal complex is synthesised for certain application, for example, as a MOCVD
precursor for gate oxide layer, it becomes necessary at first, to test the chemical composition
and purity of the complex to avoid later contamination of the films which may degrade the
quality of the film. Chemical composition as well as the purity is usually analysed by NMR
spectroscopy, single crystal X-ray structure, mass spectrometry and elemental analysis. In
addition to the desired chemical purity, appropriate physical properties like vapour pressure,
Evaporation and decomposition profile are the key criteria for a metal complex to be acknowledged as a suitable precursor for MOCVD process. Physical characteristics are extensively studied through thermoanalytical methods such as thermogravimetry (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) which are discussed in § 1.9.

Ideally a “good” MOCVD precursor must possess following properties—

a) Appreciable volatility and molecular stability of the vapours to avoid pre-gas phase reactions or decomposition of the vapours and to achieve film growth at moderate deposition temperatures.

b) Adequate temperature window between precursor evaporation and decomposition to get high quality deposits preferably at lower substrate temperatures which is generally required to prevent the underlying Silicon based circuitry for microelectronic applications.

c) Clean fragmentation of the organic matter at the surface substrate during film growth.

d) Commendable compatibility with the co-precursors in the case of multi-component ferroelectric oxide film growth like PZT or BST. Good co-precursor compatibility, in particular, becomes a more significant issue in LI-MOCVD where mixtures of precursor solution are introduced into a single headed point-of use evaporator maintained at a fixed temperature. The co-precursors therefore must evaporate at similar temperatures in order to obtain precise control of the mixed oxide film stoichiometry. Since the precursor solutions are prepared in inert solvents like toluene or n-octane etc, the precursors should be highly soluble and stable during their long period storage without undergoing any kind of solution dynamics in the solvent or reacting with other precursors present in the same solution.

e) Easily synthesised and purified in high yields at reduced cost, convenient during handling and transportation, possessing low degree of toxicity.

The probability of resulting all the above mentioned conditions and qualities in a single metal-organic precursor is very seldom and in order to avoid problem arising from the limitations of availability of ideal precursors, always a compromise is made between the precursor design and the MOCVD reactor design. Hence the goal of precursor engineering is to fine-tune the properties of the compounds in order to optimise volatility, long-term stability, thermal decomposition window, reactivity against moistures and oxidants. To obtain enhanced MOCVD performance, a much more detailed understanding of the underlying chemistry of the
precursors as a function of the chelating ligands and their substitution effect is needed. There has been considerable effort towards the development of MOCVD precursors for gate oxide application and four main precursor classes, based on the different ligand systems associated, are identified. They are metal $\beta$-diketonates, metal alkoxides, metal alkylamides and metal alkyls, although a number of heteroleptic precursors containing mixed ligand types (for example, metal alkoxy/ $\beta$-diketonates) have also used in the oxide MOCVD.

$\beta$-diketones are bidentate chelating ligands which exhibit keto-enol tautomerism as shown in figure 10. The tautomers exist in equilibrium with each other and structurally possess a cis configuration and a syn conformation. Under reactive conditions, the enolic hydrogen atom of the ligand can be replaced by a metal cation to produce a six-membered metallocycle which is stabilised by delocalisation of electron cloud in the chelate ring and thereby shifting the keto-enol equilibrium in favour of the enol form.

First series of metal $\beta$-diketonates, the acetylacetonates of sodium, beryllium, copper and nickel were reported during 1887−1894 by Combes$^{[157, 158]}$ but the first structurally reported metal $\beta$-diketonate was trimeric nickel bis(acetylacetonate) by Cotton and Holms in 1958. The physical and chemical properties of the $\beta$-diketonate ligands can be tailored due to the number of possible variations in the R group$^{[159, 160, 161]}$ and as a result, a number of metal $\beta$-diketonate complexes has been used as potential molecular precursors for MOCVD applications.$^{[50, 48]}$

Volatility of $\beta$-diketonate complexes can be increased by increasing the steric bulk of the R group, as seen for lead $\beta$-diketonates in which volatility increases in the order $[\text{Pb}(\text{acac})_2] < [\text{Pb}(\text{dhd})_2] < [\text{Pb}(\text{thd})_2]^{[162]}$ due to the increased shielding of the highly positively charged metal centre and reduction of intermolecular oxygen-metal interactions in solid state. Fluorine substitution on the R group also helps in increasing the volatility of metal $\beta$-diketonates. This is clearly observed from the increasing order of volatility of $[\text{Zr}(\text{acac})_4] < [\text{Zr}(\text{tfac})_4] < [\text{Zr}(\text{hfac})_4]$ due to reduction in the ligand electron density and because of larger size of fluorine compared to hydrogen, the metal ion is better protected in fluorinated $\beta$-diketonates.$^{[163]}$

MOCVD of fluorine containing precursors result in fluorine contamination in the film where it can form metal fluorides which produce unacceptable effects in microelectronics. Metal $\beta$-diketonates are relatively more stable in air and moisture than metal alkoxides, mainly because of the ligands property to saturate the coordination sphere of the central metal ion.
Metal alkoxide is another common class of MOCVD precursors for metal oxide deposition. Derivatives of boron and silicon appear to be the first homoleptic alkoxides described as early as 1846 but it was only since early 1980s, with the advances in single crystal X-ray determining techniques, definite solid state structure elucidation became feasible. Use of metal alkoxides for MOCVD has been well established due to the fact that their degree of volatility can be altered by “tailoring” the ligand structures. Metal alkoxides show strong inclination towards polymeric $[\text{M(OR)}_n]_\text{n}$ cluster formation due to an incomplete coordination sphere of central metal atom which results in reduced volatility of the metal complex. Two approaches have been often employed to inhibit oligomerisation in metal alkoxides. In the first approach, sterically more demanding alkoxide ligands such as tert-butoxide, which effectively shields the metal centre from metal-oxygen intermolecular interaction, are introduced. For example, Zr alkoxide volatility increases in the order $[\text{Zr(OEt)}_4] << [\text{Zr(OPr)}_3] < [\text{Zr(OBu)}_2]$. Second approach involves inclusion of donor functionalised alkoxo ligands where the donor groups are preferably ether or amino functions with oxygen or nitrogen being the donor site. Chelation occurs through this donating site, thereby leading to a more fully saturated metal centre, inhibiting oligomerisation and rendering the metal complex less susceptible to hydrolysis. The first volatile metal alkoxide stabilised by intramolecular donor functionalised concept was blue-green $[\text{Cu(OCH}_2\text{CH}_2\text{NEt}_2)_2]$, reported by Horowitz et al. in 1989. Atomic radius of the metal also plays a significant role in determining the volatility of the overall metal alkoxide complex. Zirconium and hafnium form monomeric tetra tert-butoxides whereas the larger thorium atom forms a less volatile oligomeric tert-butoxide, since larger the metal, the bulkier will be the alkoxide group necessary to prevent alkoxide bridging. Unlike Metal $\beta$-diketonates, metal alkoxides can be used as SSP because the alkoxide ligands are capable of incorporating the oxygen directly bonded to the metal atom during oxide film growth.

**Figure 10:** Keto-enol tautomerism in the bidentate $\beta$-diketone ligands.
Although high quality films have been deposited, oxidant is generally used to minimise the onset of film growth and carbon content in the films. Use of metal alkyls and metal alkylamides is not as widely explored as metal $\beta$-diketonates and metal alkoxides as precursors for oxide MOCVD. Alkylamides of a variety of metals including zirconium and hafnium are thermally stable and possess sufficient volatility to be used as MOCVD precursors.$^{[169, 170]}$ Using excess oxygen as reactive gas, metal oxide films are easily deposited from metal alkylamides. More significantly, these complexes pose as potential precursors for oxide film growth by ALD,$^{[78, 151]}$ due to the presence of weaker metal-nitrogen bond, which makes the amide complexes more reactive towards the hydroxylated surfaces.$^{[171]}$

### 1.8.1 Zirconium & hafnium based precursors developed for oxide MOCVD

A number of zirconium and hafnium precursors are known for obtaining ZrO$_2$ and HfO$_2$ thin films by MOCVD. [ZrCl$_4$]$^{[133]}$ and [HfCl$_4$]$^{[163]}$ are low volatile, white solid precursors which sublime at temperature around 300$^\circ$C and require high evaporation and growth temperatures. In contrast to MOCVD, Zr- and Hf metal chlorides are more suitable precursors for ALD of ZrO$_2$ and HfO$_2$ in which the films can be obtained at temperatures as low as 180$^\circ$C (Equation 4).$^{[28, 139 172, 79]}$

\[
\text{MCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{MO}_2 + 4\text{HCl}
\]

\[\text{M: Ti, Zr and Hf}\]

Gladfelter and co workers reported purely inorganic anhydrous [Zr(NO$_3$)$_4$] and [Hf(NO$_3$)$_4$] as precursors for ZrO$_2$ and HfO$_2$ film deposition which are completely carbon, hydrogen and chlorine free.$^{[19, 128-131]}$ By employing metal nitrates as CVD precursors, the possibility of carbon or chlorine contamination in the films is theoretically eliminated. The volatility of the anhydrous metal nitrate arises from the covalent nature of the interaction between the metal centre and the oxygen atoms of the chelating nitrato groups. [Zr(NO$_3$)$_4$] and [Hf(NO$_3$)$_4$] sublime at 95$^\circ$C under reduced pressure of 0.2 mm. Metal alkyl or organo zirconium$^{[173]}$ compounds including [ZrCp$_2$(OEt)$_2$]$^{[108]}$ and [Cp$_2$Zr(CH$_3$)$_2$]$^{[78]}$ have also used as precursors for
MOCVD but the films were analysed for heavy carbon contamination mostly from the expected cyclopentadienyl moieties. As mentioned before, metal alkylamides such as [Zr(NEt$_2$)$_4$]$_{[78]}$, [Hf(NEt$_2$)$_4$]$_{[67]}$ and amidites of the type [MN(RR’)$_4$]$_{[61, 151]}$ (R, R’ = alkyl) has been efficiently employed to get low temperature oxide deposition particularly by ALD. Due to high reactivity towards water, metal alkylamides are more suitable for ALD. 

Variety of β-diketonate complexes of Zr and Hf has been synthesised by altering the structure of β-diketone ligands. Eight coordinated zirconium and hafnium acetylacetonates, [Zr(acac)$_4$] and [Hf(acac)$_4$] are air and moisture stable, high temperature volatile precursors that result in high substrate temperature film growth (above 500°C) with considerable amount of carbon in the films.$^{[128, 163]}$ Relatively bulky metal β-diketonate precursors, complexes of 2,2,6,6-tetramethylheptan-3,5-dione (thd) or dipivaloylmethanone (dpm) namely [Zr(thd)$_4$] and [Hf(thd)$_4$] in which the methyl groups are modified with the tert-butyl groups are also eight coordinated and display good thermal stability than the metal acetylacetonates. Although they require sufficiently higher (200–230°C) evaporation temperature and also the films are obtained at high substrate temperatures greater than 500°C, but since [Zr(thd)$_4$]$^{[119, 174]}$ and [Hf(thd)$_4$]$^{[100, 101]}$ are used as benchmark precursors for ZrO$_2$ and HfO$_2$ MOCVD due to the high quality films (with some amount of carbon) they produce for increased microelectronic performance. Fluorinated [Zr(tfac)$_4$] and [Hf(tfac)$_4$] (where tfac = trifluoroacetylacetonate) are found to be more volatile because of the increased ligand steric bulk provided by the fluorine atoms than the hydrogen atoms of the methyl groups in the thd ligands.$^{[16]}$ Due to the fluorine contamination in the films, usefulness of fluorinated metal β-diketonates as CVD precursors is often seldom.

Metal alkoxides allow film growth at low deposition temperatures which makes them attractive precursors for MOCVD technique.$^{[113]}$ For example, from [Zr(thd)$_4$] the minimum deposition temperature required to obtain ZrO$_2$ films is 500°C whereas for [Zr(OBu$_4$)$_4$] is 300°C. Generally zirconium and hafnium alkoxides suffer from pronounced tendency to oligomerise due to the unsaturated metal (IV) centres. Although steric effect influences the volatility of metal alkoxides, relatively bulkier neo-pentoxide ligands give dimeric complex with zirconium.$^{[113]}$ However it is well known that steric hinderance on the α-carbon atom (the carbon which is close to the metal centre) favours volatility and thus prevents polymerisation effectively in metal alkoxides. Thus [Zr(OBu$_4$)$_4$]$^{[174, 109, 110]}$ and [Hf(OBu$_4$)$_4$]$^{[107, 111]}$ complexes which are examples of steric bulk at α-carbon are monomers exhibiting excellent volatility and they have been successfully used for MOCVD of carbon-free films of ZrO$_2$ and HfO$_2$.
respectively. The unsaturated metal centre acts as potential point for hydrolysis in Zr- and Hf-tert-butoxide precursors. In one of the reviews, Bradley report about tendency of [Zr(OBu')₄] to undergo “hydrolytic thermal decomposition” (Equations 5 and 6) in presence of trace water produced during decomposition process.

\[ [\text{Zr}(\text{OC}(	ext{CH}_3)_2)_4] + \text{H}_2\text{O} \rightarrow [\text{Zr}(\text{OC}(	ext{CH}_3)_2)_2] + 2 (\text{CH}_3)_2\text{COH} \]  

\[ 2 (\text{CH}_3)_2\text{COH} \rightarrow 2 \text{CH}_2=\text{C} (\text{CH}_3)_2 + 2 \text{H}_2\text{O} \]

Thus zirconium and hafnium alkoxides being highly susceptible to pre-reactions in presence of moisture, suitable ligand system or modification in the alkoxide system is needed to saturate the coordination sphere of the Zr(IV) and Hf(IV) metal centre and induced stability in the system.

The most well developed and successfully employed strategy is to combine the favourable properties, such as high volatility of metal alkoxides with fairly high stability of metal β-diketonate complexes. The modified [Zr(OPr')₃(thd)]₄, [Zr(OBu')₂(thd)]₂ precursors are six coordinated monomers whereas [Zr(OPr')₃(thd)] is a symmetric dimer deduced from single crystal X-ray analysis. However in the solution phase [Zr(OPr')₃(thd)] showed intermediate between the dimer [Zr₂(OPr')₆(thd)]₂, parent alkoxide [Zr(OPr')₄,Pr'OH] and the more stale species such as [Zr(thd)]₄. Thus NMR experiments proved useful to assess which compounds or mixtures are most likely to be reliable MOCVD precursors for solution delivery.

Another favoured approach is to incorporate functional alcohols like bidentate amino alcohol ligands into metal alkoxides. The resulting mixed metal species have been found to impart stability towards hydrolysis, reduced oligomerisation and give volatility to the complex (especially in the case of Ta- and Nb alkoxide system) and to some extent control the elemental stoichiometry. However, insertion of dmae or dmap ligands into [Zr(OPr')₄]₄ and [Zr(OBu')₄] resulted in asymmetric [Zr(OPr')(dmame)]₂ and [Zr(OBu')(dmae)]₂ complexes displaying relatively low volatilities and moderate air and moisture stability. Variable temperature NMR studies performed in benzene-d₆ indicated mixtures of monomer and dimer in the solution. Incorporation of sterically hindered mmp ligands into the metal alkoxides, however yielded promising MOCVD precursors of the type [M(OBu')₂(mmp)]₂ and [M(mmp)]₄ (M = Zr and Hf) which are six coordinated octahedral monomers in the solid state. Due to the saturated metal centre, the mmp complexes show significantly less reactivity.
towards air and moisture than the four coordinated \([M(\text{OBu}^t)_4]\). Unlike compounds containing amino alcohol ligands, no solution dynamics were observed in the NMR analysis for these complexes. The lack of ligand fluxionality in \([\text{Zr(mmp)}_4]\) and \([\text{Hf(mmp)}_4]\) is in marked contrast to analogous complexes such as \([\text{Zr(dmae)}_4]\), \([\text{Zr(\text{OPr}^i)_3(\text{dmap})}_2]\) and \([\text{Zr(\text{OBu}^t)_2(\text{dmae})}_2]\).

A variety of precursors have been synthesised and investigated for MOCVD of Zr- and Hf silicate such as mixed ligand complex of the type \([\text{M(acac)}_2(\text{OR})_2]\), where M is Zr or Hf and R is \(\text{SiMe}_3\) or \(\text{Bu}^t\text{Me}_3\).[150, 175] In these complexes the metal is expected to be six coordinated resulting in a improved stability with respect to oxygen and moisture while maintaining good volatility. Single crystal X-ray structure of \([\text{Hf(\text{OSiBu}^t\text{Me}_2}_2(\text{Et}_2\text{NH})}\) revealed the hafnium center to be 5-coordinated.[154] The combination of metal alkylamide \([\text{M(NR}_2)_4]\) (M = Zr, Hf) and alkoxy silanols, \((\text{RO})_3\text{SiOH}\), has been proposed as a general method for the CVD of \(\text{ZrSi}_x\text{O}_y\) and \(\text{HfSi}_x\text{O}_y\) by Hausmann et al.[151] ALD has also been employed to grow \(\text{HfSi}_x\text{O}_y\) films using \([\text{Hf(\text{NM}_2}_2)_4]\) and \([\text{Bu}^t\text{O})_3\text{SiOH}]\).[148]

### 1.9 Thermal analysis: an essential evaluation tool for MOCVD precursors

Thermal analysis (TA) plays a central role in the evaluation of metal organic complexes as precursors for CVD applications compared to other chemical characterisation methods such as NMR, IR or mass spectroscopy. Earlier applications of thermoanalytical techniques include extensive study on inorganic materials especially to determine the temperature and weight changes which helps to elucidate the compound decomposition pathways.[176, 177] With the introduction of thin film deposition technology and in particular, chemical vapor deposition technique, the magnitude of TA is widened in the field of microelectronics and optoelectronics.[178, 179] CVD is a vapour phase deposition method which requires availability of suitable precursors which are expected to demonstrate a number of physical and chemical properties including sufficient volatility, reactivity, high standards of purity etc.

Thermal analysis is a general term used for physical and thermodynamic properties of materials obtained involving heat changes. From the CVD precursor point of view, thermal analysis mainly includes thermogravimetric analysis (TGA) and differential thermal analysis (DTA). TGA measures the amount of weight change of a material, either as a function of
increasing temperature, or isothermally as a function of time, in an inert atmosphere of nitrogen or helium; air or reactive gases like oxygen, hydrogen etc, or under vacuum. Thermogravimetric curve affords information regarding volatility, evaporation rates, and thermal stability of the precursor. The thermal energy changes, either exothermic or endothermic, which occur in the course of heating, are revealed by DTA. The plot provides hints on the physical properties like melting point, sublimation temperature, evaporation temperature, and decomposition temperature of the precursors. Generally, combining TG with DTA yields the maximum quality information which helps further in precisely deciding the suitability of the precursor under investigation for CVD purpose. In addition, simultaneous TG/DTA is often employed to determine ‘shelf life’ of the precursor for verifying that the precursor does not deteriorate over long storage periods. Studies performed under isothermal conditions reveal if the precursor vaporise at a constant and appreciable rate for long periods of time which is an ideal requirement for a CVD precursor so as to ensure reproducibility by having a constant precursor vapour transport. Evaporation rates measured as a function of time at different temperatures for individual precursor under investigation often helps in optimising the temperature at which the precursor vapouriser (bubbler temperature) should be maintained during CVD. Liquid precursors are more desirable because solid precursors are susceptible to particle sintering during long time runs in isothermal measurement and later also during the actual film growth. This leads to a varying surface area available for sublimation / evaporation, resulting in unstable vapour pressure characteristics, which may lead to ambiguity in deciding the “first-hand” CVD parameters. Thus it becomes necessary to fine-grind the solid precursor during sample preparation for an isothermal or for an actual CVD run to minimise errors by providing uniform surface area.

1.10 Scope of the present work

As discussed in § 1.2–1.4, alternative candidates with suitable materials properties are significantly needed as replacement for SiO₂ as gate oxide in the sub 0.1 μm CMOS technology. ZrO₂, HfO₂ and the Zr and Hf silicates are considered as a potential replacement and MOCVD technique has been employed in obtaining thin metal oxide films. MOCVD relies on the availability of precursors with appropriate thermal properties but some problems are
associated with the existing precursors and designing an ideal MOCVD precursor which will satisfy every required characteristic precursor property is a big challenge. Nevertheless, improved precursors of zirconium and hafnium for metal oxide MOCVD has been obtained by combining the advantages of β-diketones with metal alkoxide precursors. Following the same basic approach, Chapter 2 deals with the rational development of metalorganic precursors of Zr and Hf by systematic variations in the ligand sphere of mixed β-diketonate/alkoxide type precursors for deposition of metal oxides films. The main aim of these variations in the ligand sphere is to tune the precursor thermal characteristics to ensure stable and easy handling together with decomposition at lower temperatures compared to the standard ZrO$_2$ and HfO$_2$ precursors. In this work, modified β-diketonate ligands namely β-ketoester and β-ketoamide as derivatives of the acac or thd ligands has been employed. Use of functional alcohols and amide ligands is also demonstrated. Formation of interface layer between the gate oxide and the underlying silicon substrate as a result of high temperature post-annealing is an issue of great concern in the field of microelectronics. As a solution, efforts are focused on direct deposition of the metal silicate layer on silicon substrate. The last section in Chapter 2, therefore demonstrates the synthesis and characterisation of single source precursors for deposition of Zr- and Hf silicate films. Among variety of deposition techniques, MOCVD offers potential for high-quality film deposition with conformal growth coverage over large area. Chapter 3 deals with the MOCVD experiments performed using precursors from Chapter 2. ZrO$_2$/HfO$_2$ films have been grown in a home-built horizontal cold-wall CVD reactor. Films grown are characterised for surface morphology, crystallinity and for stoichiometric elemental composition. Preliminary CVD experiments using the test MOCVD reactor showed the potential of [Zr(OPr$_i$)$_2$(tboa)ac]$_2$ (1) for CVD applications. Therefore it was interesting to test compound 1 in an actual industrial tool and a small part in chapter 3 describes Li-MOCVD of ZrO$_2$ films using 1. Electrical properties of the films are also described in brief. Thermal analysis (TG/DTA) has been used as a very effective tool by material chemists for testing the suitability of the compound as a CVD precursor. In Chapter 4, extensive thermal analysis (TG/DTA and isothermal) has been performed on the novel precursors and their relative volatilities, thermal stability and evaporation rates are determined. Thermal characteristics of these precursors are compared with the thermal properties of standard, benchmark precursors employed for obtaining ZrO$_2$ and HfO$_2$ films. In Chapter 5, synthesis and characterisation of ZrO$_2$ nanocrystals from a metalorganic precursor and employing non-hydrolytic pyrolysis route has been shown.
1.11 References


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2 Rational development of Zr and Hf based compounds as precursors for chemical vapor deposition (CVD)

Abstract

Synthesis and characterisation of mixed alkoxide/β-ketoester and β-ketoamide as well as mixed silinolate/β-ketoester complexes of zirconium and hafnium have been reported. The reaction of \([\text{Zr}_2(\text{OPr}^\dagger)_8.\text{(HOPr}^\dagger)_2]\) with β-ketoester and β-ketoamide resulted in complexes namely, zirconium bis(isopropoxide)bis(tert-butylacetoacetate) \(1\), zirconium tris(isopropoxide)(tert-butylacetoacetate) \(2\), zirconium tetrakis(tert-butylacetoacetate) \(3\) and zirconium bis(isopropoxide)bis(N,N-diethylacetoacetamide) \(4\) and they were characterised by elemental analysis, NMR, IR and Mass spectrometry. The molecular structure of the compounds as determined by single crystal X-ray diffraction revealed that compounds \(1\) and \(4\) exist as monomers while compound \(2\) exhibits a nearly symmetric dimeric structure. TG/DTA analysis on compounds \(1\), \(2\) and \(4\) indicated they melt at low temperatures and possess thermal properties that are promising for MOCVD of ZrO\(_2\) and related oxide thin films. Synthesis of mixed tert-butoxide/β-ketoester and β-ketoamide complexes of zirconium and hafnium via alcoholysis route yielded mononuclear zirconium bis(tert-butoxide)bis(tert-butylacetoacetate) \(5\), zirconium bis(tert-butoxide)bis(N,N-diethylacetoacetate) \(6\) and the analogous hafnium compounds namely hafnium bis(tert-butoxide)bis(tert-butylacetoacetate) \(7\) and hafnium bis(tert-butoxide)bis(N,N-diethylacetoacetate) \(8\). The new complexes were characterised by elemental analysis, NMR, IR, MS and TG/DTA performed on them revealed the modified compounds had further improved thermal characteristics compared to their isopropoxide analogues. In addition, zirconium bis(diethylamide)bis(di-tert-butylmalonate) \(9\) and zirconium bis(isopropoxide)bis(N,N-diethylaminoethanol) \(10\) were also synthesised and characterised. Low melting, volatile compounds namely, zirconium bis(trimethylsilinolate)bis(tert-butylacetoacetate) \(11\) and hafnium bis(trimethylsilinolate)bis(tert-butylacetoacetate) \(12\) were synthesised via transesterification reaction occurring between \([\text{Zr(OPr}^\dagger)_2(tbacoac)]_2\) and trimethylsilylacate. The complexes were thoroughly characterised by NMR, IR, MS and elemental analysis. X-ray single crystal studies revealed zirconium bis(trimethylsilinolate)bis(tert-butylacetoacetate) to exist as a monomer in
the solid state. The compounds 9 and 11 also showed thermal properties suitable for MOCVD applications in terms of volatility and decomposition profile.

2.1 Introduction

Thin films of zirconium- and hafnium dioxide and the silicates namely ZrSi$_x$O$_y$ and HfSi$_x$O$_y$ reflect variety of technological applications ranging from protective coatings to dielectric layers in the CMOS devices.$^{[1-4]}$ Various deposition techniques are known for obtaining the above mentioned materials; of which, metal organic chemical vapor deposition (MOCVD) is the most appealing one. As discussed in § 1.8, the volatile metalorganic (MO) compounds used as precursors for this process play a crucial role in the resulting film properties. In order to obtain high-quality films, the goal of precursor engineering is to fine-tune the properties of the compounds in order to optimise volatility, long-term stability, thermal decomposition window, reactivity against moisture and oxidants which are some of the required characteristics of MOCVD precursors. The combination of the advantages of β-diketonates with alkoxide precursors including the concept of intramolecular adduct stabilisation has been employed for obtaining improved zirconia and hafnia precursors. These compounds fall into the mixed alkoxide/β-diketonate type of precursor class. The first ever synthesis of mixed alkoxide/β-diketonate and β-ketoesterate was reported independently by Mehrotra et al.$^{[5]}$ and Puri et al.$^{[6]}$ in the year 1970. The characteristic feature of metal alkoxides to react readily with β-diketones and β-ketoesters to yield homo- and heteroleptic derivatives involving metals in the novel coordination states and geometries is the underlying chemical phenomenon for the formation of mixed alkoxide/β-diketonate and β-ketoester complexes. The synthesis of mixed alkoxide ligand derivatives is carried out quantitatively, particularly in the case of metal isopropoxides by azeotropic fractional distillation of the liberated alcohol with a suitable solvent like benzene. General reactions are illustrated by equations (1) and (2).

Formation of mixed metal alkoxide/β-diketonate complex:

\[
M(\text{OR})_x + y R'\text{COCH}_2\text{COR}^\text{−} \rightarrow M(\text{OR})_{x-y}(R'\text{COCHCOR})_y + y \text{ROH}
\]  

(1)
Formation of mixed metal alkoxide/β-ketoester complex:

\[
M(OR)_{x+y} + y R'\text{COCH}_2\text{COOR}' \rightarrow M(OR)_{x+y}(R'\text{COCH}_2\text{COOR}')_y + y \text{ROH}
\]  \hspace{1cm} (2)

The alkoxide groups in these mixed complexes are found to be much more reactive than the β-diketonate ligands. Hence this synthesis route was further extended for obtaining other suitable complexes by alcoholysis or transesterification reactions as shown in equations (3)–(6). Reactions of aluminium alkoxide are taken as representative examples.

\[
\text{Al}(OR)_3 + x R'\text{COCH}_2\text{COR}' \rightarrow (\text{RO})_{3-x}\text{Al}(\text{OC}(R')\text{CHCOR}')_x + x \text{ROH}
\]  \hspace{1cm} (3)

where R = Et, Pri and R', R'' = Me; or R' = Me, R'' = C₆H₅ or R' = Me, R'' = OEt; x = 1-3

\[
\text{Al(OPr)}^i_{3-x}(\beta-\text{dik})_x + (3-x) \text{BuOH} \rightarrow \text{Al(OBu)}^i_{3-x}(\beta-\text{dik})_x + (3-x) \text{Pr}^i\text{OH}
\]  \hspace{1cm} (4)

\[
\text{Al(OPr)}^i_{3-x}(\beta-\text{dik})_x + (3-x) \text{R}_3\text{SiOH}
\]  \hspace{1cm} \text{or} \hspace{1cm} \text{Al(OSiR)}^i_{3-x}(\beta-\text{dik})_x + (3-x) \text{Pr}^i\text{OH}

where R = Me, Et and β-dik = acetylacetonate; x = 1, 2

\[
\text{Al(OPr)}^i_{3-x}(\beta-\text{dik})_x + (3-x) \text{LH} \rightarrow \text{Al}(\beta-\text{dik})_x(\text{L})_{3-x} + (3-x) \text{Pr}^i\text{OH}
\]  \hspace{1cm} (6)

Variety of homo-and heteroleptic derivatives of metals including titanium, zirconium and hafnium have been successfully prepared and the general synthesis route is shown in equation 7.

\[
(\text{RO})_{4-x}\text{M}(\text{L})_x + (4-x) \text{R'OH} \rightarrow (\text{RO})_{4-x}\text{M}(\text{L})_x + (4-x) \text{ROH}
\]  \hspace{1cm} (7)

where, M: Ti, Zr, Hf

In 1999 Morstein described the synthesis of volatile heteroleptic compounds of general formula [Zr(acac)$_2$(OR)$_2$] [R=SiMe$_3$ and CH(CF$_3$)$_2$] via salt elimination reaction between [Zr(acac)$_2$Cl$_2$] and lithium trimethylsilanolate and 1,1,1,3,3,3-hexafluoropropanol & diethylamine, starting from ZrCl$_4$ as the metal source. These reactions being very selective,
stringent reaction conditions and careful monitoring of the reaction is needed for obtaining high yields of the products.

\[
\text{ZrCl}_4 + \text{Hacac (excess)} \xrightarrow{\text{ether reflux}} \text{Zr(acac)_2Cl}_2 + \text{HCl}
\]

\[
\text{Zr(acac)_2Cl}_2 + 2 \text{LiOSiMe}_3 \xrightarrow{\text{pentane}} \text{Zr(acac)_2(OSiMe)_2} + 2 \text{LiCl}
\]

Taking into consideration the necessary precautions involved during reaction and the formation of probable side products by reaction with the evolved HCl when modified \(\beta\)-diketones such as \(\beta\)-ketoester, \(\beta\)-ketoamide, malonates etc are used, and also the tedious reaction work up, it is worthwhile to mention that as compared to anhydrous \(\text{ZrCl}_4\), crystalline \([\text{Zr(OPr}^\dagger\text{PiPr}^\dagger\text{HOPr}^\dagger]\) is a more suitable and convenient choice of starting material. Preparation of zirconium isopropoxide is relatively simple (equation 8) and the final product obtained after the reaction work up is pure with moderately high yields.

\[
\text{ZrCl}_4 + 5 \text{Pr}^\dagger\text{OH} + 4 \text{NH}_3 \xrightarrow{\text{benzene}} \text{Zr(OPr}^\dagger\text{)}_4 \cdot \text{Pr}^\dagger\text{OH} + 4 \text{NH}_4\text{Cl}
\]  (8)

The reaction of \([\text{Zr(OPr}^\dagger\text{)}_4 \cdot (\text{Pr}^\dagger\text{OH})]\) with \(\beta\)-diketones, for example acetylacetone, readily yields \([\text{Zr(acac)}_2(\text{OPr}^\dagger\text{)}_2]\)\(^5\) and further taking advantage of the possible alcoholysis reactions\(^8\) or transesterification reactions,\(^9\) other suitable precursors can be prepared.

The reactions of alkoxides such as \([\text{Zr(OPr}^\dagger\text{)}_4 \cdot (\text{Pr}^\dagger\text{OH})]\) with varying molar equivalents (1, 2 or 3) of the chelating ligands has been previously reported. Puri described monoisopropoxide tris-\(\beta\)-diketonate derivatives with acetylacetone, benzoylacatone, methylacetooacetate, and phenylsalicylate, all of which were monomeric in boiling benzene.\(^6\) Bharara et al. reacted zirconium isopropoxide with some fluoro-\(\beta\)-diketones such as hexafluoroacetylacetone, benzoyl trifluoroacetone and 2-thionyl trifluoroacetone, and found the products to be white to yellow crystalline solids which were all monomeric in boiling benzene.\(^10\) Saxena et al.\(^5\) studied the reactions of zirconium isopropoxide with varying molar ratios of acetylacetone, benzoylacetone, di-benzoylmethane and ethyl benzoylacetate and obtained a number of monomeric zirconium \(\beta\)-diketonate derivatives. On the basis of molecular weight estimated ebulloscopically in benzene; the tris-isopropoxide-mono-\(\beta\)-diketonate (molar ratio 1:1)
derivatives showed tendency to dimerise. The dimeric nature of \([\text{ZrL(OPr}^\text{i})_3]\) suggested a six coordinate zirconium with isopropoxy bridges (I), the structure which was later confirmed by crystallographic studies carried out in the Jones group.\[^{[11]}\]

![Image of structure (I)](image)

However, the corresponding tert-butoxide derivatives \([\text{ZrL(OBu}^\text{i})_3]\), were found to be monomeric with an apparently five coordinated zirconium atom.

While investigating the reactions of zirconium isopropoxide with N-methyl- and N,N-dimethyl aminoalcohols and aminopropanols in refluxing benzene, Bharara in 1974 obtained either white creamy solids or yellow viscous liquids which were unstable and the analysis of them was not informative.\[^{[12]}\] 25 years later, Jones and co workers described the formation of mixed alkoxide/ aminoalkoxide and \(\beta\)-diketonate complexes of zirconium which were asymmetric binuclear species with the empirical formula \([\text{Zr}_2(\text{OPr}^\text{i})_6(L)_2]\) with unusual 6 and 7 coordinated Zr centre. Only the dmae analogues, \([\text{Zr(OR)}_2(\text{dmae})_2]\) \([R = \text{Pr}^\text{i} \text{ or Bu}^\text{i}]\) are monomeric, probably due to the less bulky nature of the chelating aminoalkoxide ligands in comparison to the dmap, thd and bdmap ligands. The NMR spectra obtained from these compounds, specifically, \([\text{Zr}_2(\text{OPr}^\text{i})_6(\text{dmap})_2]\), \([\text{Zr}_2(\text{OPr}^\text{i})_6(\text{bdmap})_2]\) and \([\text{Zr}_2(\text{OBu}^\text{i})_6(\text{bdmap})_2(\text{OH})]\) are far from being simple and showed evidence for \(\text{cis-trans}\) isomerisation.\[^{[13]}\] Similar results were observed in case of the titanium analogue.\[^{[14]}\]

Following the above approach of precursor designing by insertion of \(\beta\)-diketonate or aminoalkoxide groups into the alkoxides of Ti, Zr and Hf, we have selected \(\beta\)-ketoester and \(\beta\)-ketoamide as derivatives of the acac or thd ligands. The main aim of these variations in the ligand sphere was to tune the precursor thermal characteristics to ensure stable and easy handling together with decomposition at lower temperatures compared to the standard precursors. Substitution of one or two alkyl moieties in the acac or the thd ligands against the alkoxy groups, for example, OBu\text{i} or NEt\text{2} is expected to serve as targeted cleavage points during MOCVD process. In addition, the presence of an ester may probably act as an intrinsic oxidant enabling MOCVD of oxide films without the use of an additional oxidant. Comparison
of the pKa figures of β-ketoester with a series of substituted β-diketonates suggested the Lewis acidity at the metal centre decreases, moving from β-diketonates to β-ketoesters. However, it is also possible that the β-ketoester can undergo facile transesterification reaction in the presence of catalytically active Lewis acidic centres as the zirconium metal is expected to be and we were curious to see the effect in case of combination of tert-butylacetoacetate with isopropoxide as the ligand set at the zirconium centre. Among the alkoxides of titanium, zirconium and hafnium, the metal tert-butoxides are more volatile than their corresponding metal isopropoxides and these sterically demanding ligands have been employed to limit oligomerisation in the past. Thus we were keen to see if there will be further improvement in the thermal properties when similar ligands are inserted into the bulky tert-butoxides of zirconium and hafnium.

Polymerisation in metal alkoxides have also been suppressed by saturating the Zr or Hf metal centre by inserting donor functionalised bidentate aminoalkoxide ligands in the 4 coordinated metal alkoxide system. Accordingly, we introduced \( \text{HOCH}_2\text{CH}_2\text{NC}_2\text{H}_5 \) ligand to modify the zirconium alkoxide to derive more stable zirconium mixed alkoxide/aminoalkoxide complex.

Fundamental research on the chemistry of metal alkylamide complexes of group IVb was established many years ago by Bradley and co-workers and more recently they have been considered as potential precursors for the deposition of metal oxide thin films. But like metal alkoxide precursors, four coordinated metal alkylamides such as \([\text{Ti(NMe}_2]_4\), \([\text{Zr(NEt}_2]_4\) and \([\text{Hf(NEt}_2]_4\) exhibit high reactivity towards air and moisture which further makes their handling difficult. So one of the aims was to establish Zr compounds based on alkylamides to form saturated six coordinated Zr compounds. Thus the concept of metal mixed ligand complex was applied and accordingly zirconium mixed diethylamido malonate complex have been synthesised which is expected to be less reactive and easier to handle during MOCVD than the coordinatively unsaturated \([\text{Zr(NEt}_2]_4\) complex. Trimethylsiloxide or trimethylsilinolate are known to enhance volatility and usually are employed to produce organic silylether derivatives. In a systematic attempt of designing MOCVD precursors for obtaining zirconium- and hafnium silicate films, mixed trimethylsilinolate/β-ketoester complexes of zirconium and hafnium have been synthesised and fully characterised.
2.2 General experimental aspects

2.2.1 Laboratory techniques

All manipulations, involving air and moisture sensitive compounds were carried out by carefully heating the glassware under dynamic vacuum and using standard Schlenk techniques or glove box (O₂:1 ppm, H₂O< 1 ppm). Argon (99.998 %) was employed as the inert gas and was dried by passing over CuO catalyst and 4 Å molecular sieves. Processes such as distillation, sublimation, drying of organometallic compounds etc were carried out under dynamic high vacuum with Edwards vacuum pump, (P< 10⁻² torr) or Edwards turbomolecular pump (P< 10⁻⁵ torr).

Organic solvents

The required solvents for the reactions were dried using standard procedures.[20] Hexane, pentane, toluene, tetrahydrofuran, diethyl ether were dried over sodium-paraffin, distilled and stored over pre-vacuum dried 4 Å molecular sieves under saturated argon atmosphere. Methanol was dried by refluxing with magnesium turnings and distilling under static vacuum. Isopropanol was purified by refluxing with CaO, and distilling under reduced pressure. Benzene-d₆ for NMR spectroscopy was dried by allowing the solvent to stand over vacuum dried (110°C) 4 Å molecular sieves for about 36 hours, distilling and storing under argon atmosphere in the glove box.

2.2.2 Characterisation methods

Nuclear magnetic resonance spectroscopy (NMR)

¹H and ¹³C NMR spectra of the synthesised compounds were measured on Bruker Avance DPX200 and DPX250 NMR spectrometer in dry benzene-d₆. The chemical shifts referenced to TMS are reported in ppm.
Chapter 2

**Infrared spectroscopy (IR)**

IR spectra were recorded in degassed nujol between carefully dried NaCl plates on a Perkin Elmer 1720X FTIR spectrophotometer. IR spectra of the compounds are collected as the difference spectra w.r.t. nujol.

**Mass spectrometry (MS)**

Samples for mass spectrometry, were filled in a thin, elongated crucibles supplied with lids in the glove box. The mass spectra in the Electron Impact (EI) mode were recorded on a CH 5 Varian MAT (1970) spectrometer supplied with an ionising energy of 70 eV or 15–20 eV by Mrs. J. Schäfer.

**Elemental analysis**

Analyses for elemental C, H and N were carried out with a CHNSO Vario EL (1998) elemental analyser on samples sealed in tin capsules by Mrs. K. Bartholomäus. The analysis was provided by the central facility of the Ruhr-University Bochum. Few samples for C, H, N-analyses were measured at the microanalytical laboratory in the Department of Chemistry, University of Essen by Mrs. K. Brauner.

**X-ray single crystal structure determination**

Data collections for compounds 1 (CCDC no. 197510), 2 (CCDC no. 1975111), 4 (CCDC no. 207421) and 7 (CCDC no. 273578) were performed on a Bruker AXS CCD1000 diffractometer, equipped with a cryogenic nitrogen cold stream to prevent loss of solvent and using graphite monochromated MoK$_\alpha$ radiation (0.7103 Å). The temperature for data collection for 1, 2, 4 and 7 was 213 K, 213 K, 213 K and 213 K respectively. The structures were solved by direct method using SHELXL-97\textsuperscript{[21, 22]} software package and refined by full matrix-least-squares methods based on $F^2$ with all observed reflections. Empirical absorption corrections were applied to the data by SADABS (version 2.03)\textsuperscript{[23]}. All non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were placed in the calculated positions.
The crystal structure of compounds 5, (CCDC no. 273579) 8, 9 and 11 (CCDC no. 264730) were measured on a Xcalibur 2 diffractometer from Oxford and using graphite monochromated MoK$_\alpha$ radiation (0.71073 Å). The temperature for data collection for 5, 8, 9 and 11 was 203 K, 100 K, 111 K and 203 K respectively. The structures were solved using SHELXL-97 software package$^{[21, 22]}$ and refined against $R^2$ on all data by full matrix-least-squares methods. The single crystal data analyses were done by Mrs. M. Winter and all structure projections were done using DIAMOND software package.

**Melting point determination**

The melting points (uncorrected) were determined with a Gallenkamp melting point apparatus for samples filled in glass capillaries under argon atmosphere and then flame sealed.

**Thermal analysis**

Thermal analyses (TA) were acquired using a TG/DTA EXSTAR 6200 SII thermogravimetric analyser from Seiko under 99.9999 % purity nitrogen (300 ml min$^{-1}$) gas stream and employing a heating rate of 10°C min$^{-1}$ from ambient to 600°C. About 10 mg of sample was prepared and finely ground before placing in the aluminium crucible for measurement. Isothermal measurements were performed on carefully measured 10 mg samples heated at the set temperature for 240 min and employing a heating rate of 10°C min$^{-1}$.


2.2.3 Chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Source</th>
<th>Safety, storage and purification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Butyllithium (15 % solution in hexane)</td>
<td>Merck</td>
<td>Highly moisture sensitive</td>
</tr>
<tr>
<td>2. Diethylamine, GC&gt; 99 %</td>
<td>Merck</td>
<td>Used without purification</td>
</tr>
<tr>
<td>3. Diisopropylmalonate, 99 %</td>
<td>Aldrich</td>
<td>Used without purification</td>
</tr>
<tr>
<td>4. Di-tert-butylmalonate, 98 %</td>
<td>Aldrich</td>
<td>Used as received</td>
</tr>
<tr>
<td>5. N,N-diethylacetoacetamide, 97 %</td>
<td>Aldrich</td>
<td>b.p: 0.3mm/ 90-91°C, distilled before use,</td>
</tr>
<tr>
<td>6. N,N-diethyleneamine</td>
<td>Acros Organics</td>
<td>Used as received</td>
</tr>
<tr>
<td>8. tert-butanol, GC&gt; 99.5 %</td>
<td>Riedel-de Haën</td>
<td>Stored at room temp. and used without purification</td>
</tr>
<tr>
<td>9. tert-butyloactoacetate, 97 %</td>
<td>Aldrich</td>
<td>Used without purification</td>
</tr>
<tr>
<td>10. 2,2,6,6-Tetramethyl-3,5 heptanedione, 98 %</td>
<td>Acros Organics</td>
<td>Used without purification</td>
</tr>
<tr>
<td>11. Tri-methylsilylacete, 97 %</td>
<td>Aldrich</td>
<td>Used as received</td>
</tr>
<tr>
<td>12. Zirconium (IV) chloride, 99.5 ± %</td>
<td>Aldrich</td>
<td>Moisture sensitive, stored in glove box</td>
</tr>
<tr>
<td>13. Zirconium (IV) isopropoxide isopropanol complex, 99.9 %</td>
<td>Aldrich</td>
<td>Moisture sensitive, stored in glove box</td>
</tr>
</tbody>
</table>

2.2.4 Synthesis of literature reported compounds

Tetrakis(2,2,6,6-tetramethylheptane-3,5-dionate)zirconium, [Zr(thd)₄] (Ref. 11)

Zr(OPr₃)₄(HOPr₃) (3.88 g, 10 mmol) was dissolved in hexane and thd (8.38 ml, 40 mmol) was added to the resulting solution. The solution was stirred at reflux for 1 hour, after which time all volatiles were removed in vacuo to yield a white solid. This was redissolved in minimum
amount of hot hexane and left to stand overnight at 0°C. Colourless crystals of \([\text{Zr}(\text{thd})_4]\) were filtered off. Yield: 6.67 g (81 \% based on \([\text{Zr}(\text{OPr}_i^t)_4, (\text{HOPr}_i^t)])].

\(^1\text{H NMR}\) (room temp, 250 MHz, \(\text{C}_6\text{D}_6\)): \(\delta\) (ppm) 1.23 (72H, s, \(\text{C}_3\text{H}_3\)), 5.89 (4H, s, \(\text{CH}\)).

\(^{13}\text{C}\) \(^{1\text{H}}\text{NMR}\) (room temp, 250 MHz, \(\text{C}_6\text{D}_6\)): \(\delta\) (ppm) 28.71 (\(\text{C}_3\text{H}_3\)), 40.50 (\(\text{C(CH}_3)_3\)), 91.70 (\(\text{CH}\)), 196.88 (\(\text{CO}\)).

**Elemental analysis** calcd. for \(\text{C}_{44}\text{H}_{76}\text{O}_8\text{Zr}\): C, 64.11; H, 9.29 Found: C, 63.08; H, 8.83.

**Tetrakis diethylamide zirconium, \([\text{Zr}(\text{NEt}_2)_4]\) (procedure modified from Ref. 24)**

41.25 ml BuLi (66 mmol) was added to 30 ml toluene and the schlenk was allowed to cool under ice bath. A dense pale yellow precipitate was formed with dropwise addition of diethylamine (6.18 ml, 60 mmol) which was stirred from 0°C to room temperature for 2 hours. Then to the precipitate of lithiated diethylamine, a suspension of \(\text{ZrCl}_4\) (3.50 g, 15 mmol) in 10 ml toluene was added over a period of 30 min via cannulation under low temperature of ice bath. A dark brown solution was obtained after complete addition of \(\text{ZrCl}_4\) and the solution was refluxed further for 2 hours. The reaction mixture was cooled to room temperature and then clear orange-brown solution was cannulated which was reduced under vacuum to get a viscous product. The viscous liquid was distilled at 110°C under reduced pressure of turbomolecular pump (~ 10\(^{-5}\) torr) to get pale yellow-orange liquid. Yield: 3.07 g (54 \% based on \([\text{ZrCl}_4]\)).

\(^1\text{H NMR}\) (room temp, 200 MHz, \(\text{C}_6\text{D}_6\)): \(\delta\) (ppm) 1.13 (24H, t, \(\text{NCH}_2\text{CH}_3\), \(\text{J} = 7.01\) Hz), 3.31 (16H, q, \(\text{NCH}_2\text{CH}_3\), \(\text{J} = 6.98\) Hz).

\(^{13}\text{C}\) \(^{1\text{H}}\text{NMR}\) (room temp, 200 MHz, \(\text{C}_6\text{D}_6\)): \(\delta\) (ppm) 16.27 (\(\text{NCH}_2\text{CH}_3\)), 43.63 (\(\text{NCH}_2\text{CH}_3\)).

**Elemental analysis** calcd. for \(\text{C}_{16}\text{H}_{40}\text{O}_4\text{Zr}\): C, 50.63; H, 10.55; N, 14.77 Found: C, 49.11; H, 9.68; N, 14,30.

**Hafnium (IV) isopropoxide, \([\text{Hf}(\text{OPr}_i^t)_4]\) (procedure modified from Ref. 17)**

Large excess (57.1 ml) of isopropanol was added to a suspension of 24.5 g (76.5 mmol) of \(\text{HfCl}_4\) in 200 ml of toluene which gave a clear solution. Bubbling ammonia gas through the solution resulted in immediate precipitation of \(\text{NH}_4\text{Cl}\) involving an exothermic reaction. In
total, ammonia was bubbled for 30 min and the reaction mixture was stirred for additional 1 hour. Ammonium chloride was filtered through a G-4 frit and the filtrate was evaporated under reduced pressure to get a white solid product. Recrystallisation from excess of boiling isopropanol gave \([\text{Hf}(\text{OPr}_i)_{4.5} \text{ (HOPr}_i)]\) which was further heated for about 2 hours at 100°C under vacuum (10⁻² torr) to remove the coordinated isopropanol. Yield: 24.5 g (77.29 % based on \([\text{HfCl}_4\text{B}_4\text{B}_4]\)).

\(^1\text{H} \text{NMR}\) (room temp, 250 MHz, \(\text{C}_6\text{D}_6\)): \(\delta\) (ppm) 1.43 (24H, d, \(\text{CH}_3 \text{OPr}^i\), \(^1\text{J} = 6.18 \text{ Hz}\)), 4.71 (4H, m, \(\text{CH} \text{OPr}^i\), \(^1\text{J} = 6.13 \text{ Hz}\)).

\(^{13}\text{C}\ \{^1\text{H}\} \text{NMR}\) (room temp, 250 MHz, \(\text{C}_6\text{D}_6\)): \(\delta\) (ppm) 1.43 (24H, d, \(\text{CH}_3 \text{OPr}^i\)), 4.71 (4H, m, \(\text{CH} \text{OPr}^i\)), 1.40 (18H, s, \(\text{CH}(\text{CH}_3)_3 \text{tbaoac}\)), 1.39 (12H, d, \(\text{CH}_3 \text{OPr}^i\), \(^1\text{J} = 5.96 \text{ Hz}\)), 5.09 (2H, m, \(\text{CH} \text{OPr}^i\)).

Elemental analysis calcd. for \(\text{C}_{12}\text{H}_{28}\text{O}_4\text{Hf}\) (%): C, 34.74; H, 6.75 Found: C, 34.59; H, 6.68.

2.3 Synthesis of zirconium and hafnium containing complexes

2.3.1 Mixed isopropoxide/β-ketoester and β-ketoamide complexes of zirconium

Zirconium bis(isopropoxide)bis(tert-butylacetoacetate), \([\text{Zr}(\text{OPr}^i)_2\text{tbaoac}]\) (1)

To a clear solution of \(\text{Zr}(\text{OPr}^i)_{4.5} \text{ (HOPr}_i)\) (1.94 g, 5 mmol) in hexane (30 ml), tert-butylacetoacetate (1.66 ml, 10 mmol) was added. The reaction mixture was refluxed for 90 min with vigorous stirring and the solvent was removed under reduced pressure to get a sticky white product which was distilled at 90°C (10⁻² torr) to yield a white crystalline solid. The product was recrystallised from saturated hexane at −30°C to yield X-ray quality transparent single crystals. Yield: 2.6 g (84 % based on \([\text{Zr}(\text{OPr}^i)_{4.5} \text{ (HOPr}_i)\])).

\(^1\text{H} \text{NMR}\) (room temp, 250 MHz, \(\text{C}_6\text{D}_6\)): \(\delta\) (ppm) 1.76 (6H, s, \(\text{CH}_3 \text{tbaoac}\)), 1.40 (18H, s, \(\text{C}(\text{CH}_3)_3 \text{tbaoac}\)), 1.39 (12H, d, \(\text{CH}_3 \text{OPr}^i\), \(^1\text{J} = 5.96 \text{ Hz}\)), 5.09 (2H, s, \(\text{CH} \text{tbaoac}\)), 4.59 (2H, m, \(\text{CH} \text{OPr}^i\)).

\(^{13}\text{C}\ \{^1\text{H}\} \text{NMR}\) (room temp, 250 MHz, \(\text{C}_6\text{D}_6\)): \(\delta\) (ppm) 28.52 (\(\text{C}(\text{CH}_3)_3 \text{tbaoac}\)), 25.53 (\(\text{CH}_3 \text{tbaoac}\)), 27.06 (\(\text{CH} \text{OPr}^i\)), 90.23 (\(\text{CH} \text{tbaoac}\)), 71.76 (\(\text{CH} \text{OPr}^i\)), 185.66 (\(\text{OCCH}_3 \text{tbaoac}\)), 173.87 (\(\text{CO} \text{tbaoac}\)), 80.95 (\(\text{OC}(\text{CH}_3)_3 \text{tbaoac}\)).
**Mass spectrum** (positive-ion EI): m/z 405 [Zr(tbaoac)_2]^+; 209 [Zr(OPr^i)_2]^+; 268 [Zr(OPr^i)_3]^+; 307 [Zr(OPr^i)(tbaoac)]^+; 366 [Zr(OPr^i)_2(tbaoc)]^+.

**FT-IR** (ν/cm\(^{-1}\), nujol, NaCl): 1630, 1608, 1577, 1524, 1475 ν(C=O) + ν(C=C); 1155, 1062, 1377 ν(C-O); 574 ν(Zr-O).

**Elemental analysis** calcd. for C\(_{22}\)H\(_{30}\)O\(_8\)Zr (%): C, 50.46; H, 7.64 Found: C, 50.42; H, 7.84.

**Melting point (Mp)**: 43–45°C (uncorrected).

**Zirconium tris(isopropoxide)(tert-butylacetoacetate), [Zr(OPr^i)_6(tbaoac)_2]** (2)

The chelating ligand, tert-butylacetoacetate (2.49 ml, 15 mmol) was added to 5.82 g (15 mmol) of Zr(OPr^i)_4(HOPr^i) in hexane (40 ml) and the reaction mixture was refluxed for 90 min with vigorous stirring. White crystalline product was precipitated out slowly from a cold mixture of acetone/dry ice (−10°C to −50°C). The compound was recrystallised from saturated hexane at −30°C to obtain X-ray quality single crystals. Yield: 6.51 g (86.11 % based on [Zr(OPr^i)_4(HOPr^i)])).

\(^1\)H **NMR** (room temp, 250 MHz, C\(_6\)D\(_6\)): δ (ppm) 1.80 (6H, s, CH\(_3\) tbaoac), 1.52 (18H, s, C(CH\(_3\))\(_3\) tbaoac), 1.41(36H, bs, CH\(_3\) OPPr^i), 5.18 (2H, s, CH tbaoac), 4.61 (6H, m, CH OPPr^i).

\(^13\)C \{\(^1\)H\} **NMR** (room temp, 250 MHz, C\(_6\)D\(_6\)): δ (ppm) 28.93 (C(CH\(_3\))\(_3\) tbaoac), 25.95 (CH\(_3\) tbaoac), 27.09 (CH\(_3\) OPPr^i), 89.56 (CH tbaoac), 71.19 (CH OPPr^i), 186.55 (OCCH\(_3\) tbaoac), 174.22 (CO tbaoac), 80.52 (OC(CH\(_3\))\(_3\) tbaoac).

**Mass spectrum** (positive-ion EI): m/z 405 [Zr(tbaoac)_2]^+; 209 [Zr(OPr^i)_2]^+; 268 [Zr(OPr^i)_3]^+; 307 [Zr(OPr^i)(tbaoac)]^+; 366 [Zr(OPr^i)_2(tbaoc)]^+; 576 [Zr(OPr^i)_4(tbaoc)]^+; 694 [Zr_2(OPr^i)_6(tbaoc)]^+; 792 [Zr_2(OPr^i)_3(tbaoc)]^+; 268 [Zr(OPr^i)_3]^+.

**FT-IR** (ν/cm\(^{-1}\), nujol, NaCl): 1630, 1514, 1460 ν(C=O) + ν(C=C); 1155, 1063, 1377 ν(C-O); 538 ν(Zr-O).

**Elemental analysis** calcd for C\(_{34}\)H\(_{60}\)O\(_{12}\)Zr\(_2\) (%): C, 47.93; H, 7.99 Found: C, 48.04; H, 8.04.

**Melting point (Mp)**: 110–112°C (uncorrected).
Zirconium tetrakis(tert-butylacetoacetate), [Zr(tbaoac)$_4$] (3)

To a solution of Zr(OPr$_i$)$_4$(HOPr$_i$) (1.94 g, 5 mmol) in hexane (35 ml), tert-butylacetoacetate (3.32 ml, 20 mmol) was added dropwise. A dense white precipitate was obtained immediately after ligand addition, which was allowed to stir further under reflux for 90 min. The product remained insoluble at the end of the reaction and the solvent was removed under reduced pressure, which resulted in a white dry powder. The product decomposed without melting above 260°C. Yield: 3.36 g (93.33 % based on [Zr(OPr$_i$)$_4$(HOPr$_i$)]).

$^1$H NMR (room temp, 250 MHz, C$_6$D$_6$): δ (ppm) 1.81 (12H, s, CH$_3$ tbaoac), 1.53 (36H, s, C(CH$_3$)$_3$ tbaoac) 5.15 (4H, s, CH$_2$ tbaoac).

$^{13}$C($^1$H) NMR (room temp, 250 MHz, C$_6$D$_6$): δ (ppm) 28.57 (C(C(CH$_3$)$_3$) tbaoac), 25.58 (C(CH$_3$)$_3$ tbaoac), 90.42 (CH tbaoac), 185.69 (OCCH$_3$ tbaoac), 173.95 (CO tbaoac), 81.02 (OC(CH$_3$)$_3$ tbaoac).

Mass spectrum (positive-ion EI): m/z 562 [Zr(tbaoac)$_3$]$^+$, 405 [Zr(tbaoac)$_2$]$^+$, 248 [Zr(tbaoac)]$^+$. FT-IR (ν/cm$^{-1}$, nujol, NaCl): 1620, 1535, 1465 ν(C=O) + ν(C=C); 543 ν(Zr-O).

Elemental analysis calcd for C$_{32}$H$_{52}$O$_{12}$Zr (%): C, 53.38; H, 7.28 Found: C, 52.45; H, 7.13.

Zirconium bis(isopropoxide)bis(N,N-diethylacetoacetamide), [Zr(OPr$_i$)$_2$(deacam)$_2$] (4)

A total of 1.82 g (4.7mmol) of Zr(OPr$_i$)$_4$(HOPr$_i$) was dissolved in 25 ml of hexane, and 1.49 ml (9.4 mmol) of N,N-diethylacetoacetamide was added. The reaction mixture was stirred for two hours under reflux and solvent was removed under vacuum, which resulted in pale brown viscous oil. The viscous product was dissolved in minimum amount of hot hexane and stored at 4°C for 24 hours to get pale yellow crystals, which were characterised by single crystal X-ray diffraction. Yield: 2.47 g (87.17 % based on [Zr(OPr$_i$)$_4$(HOPr$_i$)]).

$^1$H NMR (room temp, 250 MHz, C$_6$D$_6$): δ (ppm) 1.90 (6H, s, CH$_3$ deacam), 1.47 (6H, d, CH$_3$ OP$_i$, $^1$J = 5.97 Hz), 0.7 (6H, t, NCH$_2$CH$_3$a, $^1$J = 6.75 Hz), 0.96 (6H, t, NCH$_2$CH$_3$b, $^1$J = 6.59 Hz), 2.66 (4H, q, NCH$_2$a CH$_3$, $^1$J = 7.23 Hz), 3.09 (4H, q, NCH$_2$b CH$_3$, $^1$J = 6.59 Hz), 4.69 (2H, s, CH OP$_i$), 4.76 (2H, s, CH deacam).
\(^{13}\text{C}\{^1\text{H}\}\text{NMR}\) (room temp, 250 MHz, C\(_6\)D\(_6\)): \(\delta\) (ppm) 41.28 (NCH\(_2\)CH\(_3\)), 42.38 (NCH\(_2\)CH\(_3\)), 27.03 (CH\(_3\) OP\(^{t}\)), 26.59 (CH\(_3\) deacam), 13.03 (NCH\(_2\)CH\(_3\)\(_a\)), 13.06 (NCH\(_2\)CH\(_3\)\(_b\)), 86.18 (CH deacam), 70.62 (COCH\(_3\) deacam), 168.84 (C\(_{15}\)OCH\(_3\) deacam).

Mass spectrum (positive-ion EI): m/z 365 [Zr(OPr\(^t\)\(_2\)(deacam)]\(^+\), 306 [Zr(OPr\(^t\))(deacam)]\(^+\), 462 [Zr(OPr\(^t\))(deacam)]\(^+\), 449 [Zr(OPr\(^t\)\(_2\)\((\text{deacam})_2\)-N(Et)\(_2\))]\(^+\), 377 [Zr(OPr\(^t\)\(_2\)\((\text{deacam})_2\)-2N(Et)\(_2\))]\(^+\).

FT-IR (\(\nu\)/cm\(^{-1}\), nujol, NaCl): 1609, 1632, 1526 \(\nu\)(C=O) + \(\nu\)(C=C); 1155, 1016 \(\nu\)(C-O); 501 \(\nu\)(Zr-O).

Elemental Analysis calcd. for C\(_{22}\)H\(_{42}\)O\(_6\)N\(_2\)Zr (%): C, 61.34; H, 9.76; N, 5.37 Found: C, 60.92; H, 9.10; N, 4.97.

Melting point (Mp): 60–62°C (uncorrected).

### 2.3.2 Mixed tert-butoxide/\(\beta\)-ketoester and \(\beta\)-ketoamide complexes of zirconium & hafnium

**Zirconium bis(tert-butoxide)bis(tert-butylacetoacetate), [Zr(OBu\(^t\)\(_2\)(tbaoac)\(_2\)]** (5)

Tert-butylacetoacetate (3.32 ml, 20 mmol) was added to a solution of Zr(OPr\(^t\)\(_4\)(HOPr\(^t\)) (3.88 g, 10 mmol) in dry hexane (20 ml) at room temperature. The resulting clear solution was refluxed for 90 min after which time the solvent was vacuum evaporated to get a sticky white solid of composition [Zr(OPr\(^t\)\(_2\)(tbaoac)\(_2\)]. To the white solid, 10 ml of toluene and large excess of tert-butanol (30 ml) was added and the solution was refluxed for next two hours. Removal of solvent and excess of alcohol under reduced pressure gave a white product which was distilled quantitatively at 100°C (10\(^{−2}\) torr) to get a dry powder. In total, addition of 30 ml of tert-butanol was done four times to push the reaction towards completion. The white product was recrystallised from saturated hexane by cooling to −30°C for about a week. Yield: 5.19 g (94 % based on [Zr(OPr\(^t\)\(_4\)(HOPr\(^t\))]).

\(^{1}\text{H}\text{NMR}\) (room temp., 250 MHz, C\(_6\)D\(_6\)): \(\delta\) (ppm) 1.75 (6H, s, CH\(_3\) tbaoac), 1.48 (18H, s, C(CH\(_3\))\(_3\) tbaoac), 1.39 (18H, s, OC(CH\(_3\))\(_3\)), 5.07 (2H, s, CH tbaoac).
\( ^{13} \text{C} \{^1 \text{H}\} \text{ NMR} \) (room temp., 250 MHz, \( \text{C}_6 \text{D}_6 \)): \( \delta \) (ppm) 28.57 (C(CH\(_3\))\(_3\) tbaoac), 25.53 (CH\(_3\) tbaoac), 32.68 (OC(CH\(_3\))\(_3\)), 90.08 (CH tbaoac), 75.74 (OC(CH\(_3\))\(_3\)), 185.50 (OCCH\(_3\) tbaoac), 173.73 (CO tbaoac), 80.76 (OC(CH\(_3\))\(_3\) tbaoac).

\textbf{Mass spectrum} (positive-ion El): m/z 248 [Zr(tbaoac)]\(^+\), 321 [Zr(OBu')\((\text{tbaoac})\)]\(^+\), 364 ([Zr(OBu')(tbaoac)]\(_2\)\)-2(C(CH\(_3\))\(_3\))]\(^+\), 421 ([Zr(OBu')(tbaoac)]\(_2\)-(C(CH\(_3\))\(_3\))]\(^+\), 478 [Zr(OBu')(tbaoac)]\(_2\)\(^+\), 551 [Zr(OBu')\(_2\)\((\text{tbaoac})\)]\(^+\).

\textbf{FT-IR} (v/cm\(^{-1}\), nujol, NaCl): 1634, 1610, 1580, 1526, 1413 v(C=O) + v(C=C); 1191, 1158, 1062, 1211 v(C-O); 573, 537 v(Zr-O).

\textbf{Elemental analysis} calcd. for C\(_{24}\)H\(_{44}\)O\(_6\)Zr (%): C, 52.19; H, 7.97 Found: C, 51.64; H, 7.66.

\textbf{Melting point} (Mp): 74–76°C (uncorrected).

\textbf{Zirconium bis(tert-butoxide) bis(N,N-diethylacetoacetamide), [Zr(OBu')\(_2\)(deacam)]\(_2\)} (6)

To a solution of 5.82 g of Zr(OPr')\(_4\) (HOPr')\(_4\), (15 mmol) in hexane (30–35 ml), N,N-diethylacetoacetamide ligand (4.74 ml, 30 mmol) was added which immediately resulted in the formation of thick yellow precipitate. The precipitate disappeared once the solution was warmed and the clear solution was refluxed for additional 2 hours. Pale brown viscous oil of [Zr(OPr')\(_2\)(deacam)]\(_2\) was obtained after the solvent was removed completely. 10 ml of toluene and large excess of tert-butanol (40 ml) was added over the viscous product and the solution was further refluxed under vigorous stirring for 4 hours. The solvent and the unreacted tert-butanol were removed under reduced pressure which resulted in the formation of light yellow-brown solid. Yield: 7.50 g (91.0 % based on [Zr(OPr')\(_4\) (HOPr')]\(_4\)).

\( ^1 \text{H} \text{ NMR} \) (room temp., 250 MHz, \( \text{C}_6 \text{D}_6 \)): \( \delta \) (ppm) 1.92 (6H, s, CH\(_3\) deacam), 1.59 (18H, s, OC(CH\(_3\))\(_3\)), 0.71 (6H, bs, NCH\(_2\)CH\(_3\)a), 0.99 (6H, bs, NCH\(_2\)CH\(_3b\)), 2.66 (4H, bs, NCH\(_2a\) CH\(_3\)), 3.09 (4H, bs, NCH\(_2b\) CH\(_3\)), 4.88 (2H, s, CH deacam).

\( ^{13} \text{C} \{^1 \text{H}\} \text{ NMR} \) (room temp., 250 MHz, \( \text{C}_6 \text{D}_6 \)): \( \delta \) (ppm) 41.33 (NCH\(_2a\)CH\(_3\)), 42.43 (NCH\(_2b\)CH\(_3\)), 33.01 (OC(CH\(_3\))\(_3\)), 26.64 (CH deacam), 13.59 (NCH\(_2\)CH\(_3a\)), 13.76 (NCH\(_2\)CH\(_3b\)), 86.03 (CH deacam), 181.54 (COCH\(_3\) deacam), 169.02 (CO deacam), 74.45 (OC(CH\(_3\))\(_3\)).

\textbf{Mass spectrum} (positive-ion El): m/z 549 [Zr(OBu')\(_2\)(deacam)]\(^+\), 393 [Zr(OBu')\(_2\)(deacam)]\(^+\), 320 [Zr(OBu')(deacam)]\(^+\), 476 [Zr(OBu')(deacam)]\(^+\), 477 [Zr(OBu')\(_2\)\{deacam\}_2-N(Et)\(_2\)]\(^+\), 420 [Zr\{OBU'(deacam)\}_2-Bu']\{deacam\}_2-N(Et)\(_2\)]\(^+\).
FT-IR (ν/cm⁻¹, nujol, NaCl): 1601, 1573, 1519 ν(C=O) + ν(C=C); 1163, 1011, 1206 ν(C-O); 534 ν(Zr-O).

Elemental analysis calcd. for C₂₄H₄₆O₈N₂Zr (%): C, 52.44; H, 8.37; N, 5.10 Found: C, 52.28; H, 8.47; N, 4.97.

Melting point (Mp): 48–50°C (uncorrected)

Hafnium bis(tert-butoxide)bis(tert-butylacetoacetate), [Hf(OBu)₂(tbaoac)] (7)

Tert-butylacetoacetate (3.32 ml, 20 mmol) was added to a solution of Hf(OPr)₄ (4.14 g, 10 mmol) in dry hexane (20 ml) at room temperature. The resulting clear solution was refluxed for 90 min after which time the solvent was vacuum evaporated to get a sticky white solid of composition [Hf(OPr)₂(tbaoac)]₂. To the white solid, 10 ml of toluene and large excess of tert-butanol (30 ml) was added and the solution was refluxed for next two hours. Removal of solvent and excess of alcohol under reduced pressure gave white product which was further distilled out at 100°C (10⁻² Torr) and stored as dry crystalline powder. Recrystallisation from minimum amount of saturated hot hexane at −30°C, produced crystals which were measured by single crystal X-ray diffraction. In total, addition of 30 ml of tert-butanol was done four times to push the reaction towards completion. Yield: 6.24 g (98 % based on [Hf(OPr)₄]).

¹H NMR (room temp., 250 MHz, C₆D₆): δ (ppm) 1.74 (6H, s, CH₃ tbaoac), 1.50 (18H, s, C(CH₃)₃ tbaoac), 1.38 (18H, s, OC(CH₃)₃ tbaoac), 5.04 (2H, s, CH tbaoac).

¹³C ¹H NMR (room temp., 250 MHz, C₆D₆): δ (ppm) 28.58 (C(C(CH₃)₃ tbaoac), 25.71 (C(CH₃)₃ tbaoac), 33.02 (OC(CH₃)₃), 90.48 (CH tbaoac), 75.21 (OCCH₃ tbaoac), 173.79 (CO tbaoac), 81.06 (OCH(CH₃)₃ tbaoac).

Mass spectrum (positive-ion EI): m/z 251 [Hf(OC(CH₃)₃)]⁺, 335 [Hf(tbaoac)]⁺, 408 [Hf(OBu)₃(tbaoac)]⁺, 451 [(Hf(OBu)₃(tbaoac))-2C(CH₃)₃]⁺, 508 [(Hf(OBu)₃(tbaoac))-2OC(CH₃)₃]⁺, 566 [Hf(OBu)₃(tbaoac)]⁺, 624 [(Hf(OBu)₃(tbaoac))-2OC(CH₃)₃]⁺, 639 [Hf(OBu)₃(tbaoac)]⁺.

FT-IR (ν/cm⁻¹, nujol, NaCl): 1634, 1608, 1580, 1527, 1415 ν(C=O) + ν(C=C); 1196, 1157, 1054, 1215 ν(C-O); 579, 538 ν(Hf-O).

Elemental analysis calcd. for C₂₄H₄₆O₈N₂Zr (%): C, 52.44; H, 8.37; N, 5.10 Found: C, 52.28; H, 8.47; N, 4.97.

Melting point (Mp): 74–76°C (uncorrected).
Hafnium bis(tert-butoxide)bis(N,N-diethylacetoacetamide), [Hf(OBu')_2(deacam)_2] (8)

To a solution of 4.14 g of Hf(OPr_i)_4, (10 mmol) in hexane (20 ml), N,N-diethylacetoacetamide ligand (3.32 ml, 20 mmol) was added and the resulting clear solution was refluxed for 2 hours. After removal of the solvent, a dark yellow-brown viscous product was obtained. 10 ml of toluene and a large excess of tert-butanol (40 ml) was added over the viscous oil and the solution was further refluxed under vigorous stirring for 4 hours. The solvent and the unreacted tert-butanol were removed under reduced pressure to get a yellow-brown solid. Crystals were obtained by recrystallising the yellow-brown solid in a mixture of hexane:THF and storing the saturated solution at −30°C for about 24 hours. Yield: 5.65 g (89 % based on [Hf(OPr_i)_4]).

^1H NMR (room temp., 250 MHz, C_6D_6): δ (ppm) 1.91 (6H, s, CH_3 deacam), 1.61 (18H, s, OC(CH_3)_3), 0.70 (6H, bs, NCH_2CH_3a), 0.99 (6H, bs, NCH_2CH_3b), 2.64 (4H, bs, NCH_2a CH_3), 3.08 (4H, bs, NCH_2b CH_3), 4.85 (2H, s, CH deacam).

^13C{^1H} NMR (room temp., 250 MHz, C_6D_6): δ (ppm) 41.40 (NCH_2aCH_3), 42.49 (NCH_2bCH_3), 33.33 (OC(CH_3)_3), 26.75 (CH_3 deacam), 13.54 (NCH_2CH_3a), 13.74 (NCH_2CH_3b), 86.34 (CH deacam), 181.85 (COCH_3 deacam), 169.08 (CO deacam), 74.08 (OC(CH_3)_3).

Mass spectrum (positive-ion EI): m/z 480 [Hf(OBu')_2(deacam)]^+, 407 [Hf(OBu')(deacam)]^+, 563 [Hf(OBu')(deacam)_2]^+, 564 [Hf(OBu')_2{deacam-N(Et)_2}]^+, 507 [Hf{(OBu'}_2-Bu')_2{deacam}_2-N(Et)_2}]^+.

FT-IR (ν/cm^-1, nujol, NaCl): 1602, 1572, 1519, ν(C=O) + ν(C=C); 1164, 1086, 1011, 1207, ν(C-O); 596 ν(Hf-O).

Elemental analysis calcd. for C_{24}H_{46}O_6N_2Hf (%): C, 45.25; H, 7.23; N, 4.40 Found: C, 44.69; H, 7.50; N, 4.34.

Melting point (Mp): 63–65°C (uncorrected).
2.3.3 Modified alkylamide and mixed isopropoxide/aminoalcohol complexes of zirconium

Zirconium bis(diethylamide)bis(Di-tert-butylmalonate), \([\text{Zr(NEt}_2\text{)}_2\text{(dbmal)}_2]\) (9)

To 20 ml of hexane, 1.85 ml (5 mmol) \(\text{Zr(NEt}_2\text{)}_4\) and 2.24 ml (10 mmol) di-tert-butylmalonate ligand was added and the resulting pale yellow solution was refluxed for 2 hours with vigorous stirring. After completion of the reaction, the solvent was removed and pale yellow crystalline product was isolated. The product was recrystallised from saturated solution in pentane and storing the schlenk at \(-30^\circ\text{C}\) for about 24 hours. Yield: 2.97 g (89 % based on \([\text{Zr(NEt}_2\text{)}_4]\)).

\[^1\text{H}\text{ NMR}\) (room temp., 250 MHz, \(\text{CD}_6\text{D}_6\)): \(\delta\) (ppm) 1.37 (18H, s, \(\text{CH}_3\text{a dbmal})\), 1.50 (18H, s, \(\text{CH}_3\text{b dbmal})\), 1.18 (12H, t, \(\text{NCH}\text{CCH}_3\), \(^1\text{J}=6.93\) Hz), 3.68 (8H, q, \(\text{NCH}_2\text{CH}_3\), \(^1\text{J}=6.23\) Hz), 4.89 (2H, s, \(\text{CH}\text{ dbmal})\).

\[^{13}\text{C}\{^1\text{H}\}\text{ NMR}\) (room temp., 250 MHz, \(\text{CD}_6\text{D}_6\)): \(\delta\) (ppm) 15.73 (\(\text{NCH}\text{CCH}_3\)), 42.67 (\(\text{NCH}_2\text{CH}_3\)), 29.35 (\(\text{CH}_3\text{a dbmal})\), 29.56 (\(\text{CH}_3\text{b dbmal})\), 80.14 (\(\text{OCOCH}_3\)), 72.85 (\(\text{CH}\text{ dbmal})\), 176.18 (\(\text{OCOCH}_3\)).

**Mass spectrum** (positive-ion EI): \(m/z\) 664 \([\text{Zr(NEt}_2\text{)}_2\text{dbmal)}]^+\), 592 \([\text{Zr(NEt}_2\text{)}_2\text{dbmal)}_2\text{N(Et)}_2]^+\), 536 \([\{\text{Zr(NEt}_2\text{)}_2\text{dbmal)}_2\text{N(Et)}_2\}\text{-isobutene}]^+\), 480 \([\{\text{Zr(NEt}_2\text{)}_2\text{dbmal)}_2\text{N(Et)}_2\}\text{-2 \times isobutene}]^+\), 424 \([\{\text{Zr(NEt}_2\text{)}_2\text{dbmal)}_2\text{N(Et)}_2\}\text{-3 \times isobutene}]^+\), 368 \([\{\text{Zr(NEt}_2\text{)}_2\text{dbmal)}_2\text{N(Et)}_2\}\text{-4 \times isobutene}]^+\).

**Elemental analysis** calcd. for \(\text{C}_{30}\text{H}_{58}\text{O}_{8}\text{N}_2\text{Zr}\): C, 54.07; H, 8.71; N, 4.20 Found: C, 53.69; H, 8.50; N, 3.98.

Zirconium bis(isopropoxide)bis(N,N-diethylaminoethanol), \([\text{Zr(OPr}_i\text{)}_2\text{(deae)}_2]\) (10)

The compound \(\text{Zr(OPr}_i\text{)}_4\text{(HOPr)}\) (1.94 g, 5 mmol) was dissolved in 20 ml of hexane and (N,N-diethylaminoethanol) (1.33 ml, 10 mmol) was added. The solution was stirred at reflux for 2 hours after which time all the volatiles were removed under vacuum to yield a colourless viscous liquid. Yield: 1.77 g (80 % based on \([\text{Zr(OPr}_i\text{)}_4\text{(HOPr)}]\)).
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$^1$H NMR (room temp., 250 MHz, $CD_2Cl_2$): $\delta$ (ppm) 1.04 (12H, t, $NCH_2CH_3$, $^1$J = 7.11 Hz), 1.44 (12H, d, $CH_3$ OPr$^i$, $^1$J = 5.99 Hz), 2.76 (12H, m, $NCH_2 + NCH_2CH_3$), 4.57 (2H, m, OPr$^i$), 4.34 (4H, t, OCH, $^1$J = 6.69 Hz).

$^{13}$C $\{^1$H$\}$ NMR (room temp., 250 MHz, $CD_2Cl_2$): $\delta$ (ppm) 11.57 (NCH$_2CH_3$), 27.71 (CH$_3$ OPr$^i$), 70.25 (CH OPr$^i$), 67.16 (OCH$_2$), 47.90 (NCH$_2CH_3$), 56.95 (NCH$_2$).

Mass spectrum (positive-ion EI): m/z 441 [Zr(OPr$^i$)$_2$(deae)$_2$]$^+$, 324 [Zr(OPr$^i$)$_2$(deae)]$^+$, 381 [Zr(OPr$^i$)(deae)$_2$]$^+$.

FT-IR ($\nu$/cm$^{-1}$, nujol, NaCl): 1175, 1190 $\nu$(C-N); 1035–1070, $\nu$(C-O); 451, 420, 437 $\nu$(Zr-O).

Elemental analysis calcd. for C$_{18}$H$_{44}$O$_4$N$_2$Zr (%): C, 48.95; H, 9.52; N, 6.35 Found: C, 47.84; H, 9.05; N, 6.46.

2.3.4 Mixed silinolate/$\beta$-ketoester complexes of zirconium & hafnium

Zirconium bis(trimethylsilinolate)bis(tert-butylacetoacetate), [Zr(OSiMe$_3$)$_2$(tbaoac)$_2$] (11)

To a clear solution of 3.88 g (10 mmol) zirconium(IV)isopropoxide in hexane (40 ml), 3.32 ml (20 mmol) of bidentate ligand tert-butylacetoacetate was added. The solution was refluxed for 90 min and solvent was removed under reduced pressure to get sticky white solid of composition [Zr(OPr$^i$)$_2$(tbaoac)$_2$] (16). The resulting solid was redissolved in 10 ml of toluene and large excess of trimethylsilylacetate (30 ml) was added through cannula and the solution was allowed to reflux for further 7 h. The solvent and the excess of silyl ester were removed under vacuum and a pale yellow solid was obtained which was purified by distilling at 110°C under reduced pressure (10$^{-2}$ torr) to get white crystalline product. In total addition of trimethylsilyl ester was done three times in order to push the reaction towards completion. Recrystallisation from hexane at -30°C yielded crystals which were measured by single crystal X-ray diffractometer. Yield: 4.80 g (82 % based on [Zr(OPr$^i$)$_4$ (HOPr$^i$)]).

$^1$H NMR (room temp., 250 MHz, $CD_2Cl_2$): $\delta$ (ppm) 1.68 (6H, s, CH$_3$ tbaoac), 1.35 (18H, s, C(CH$_3$)$_3$ tbaoac), 0.34 (18H, s, OSi(CH$_3$)$_3$), 5.04 (2H, s, CH tbaoac).

$^{13}$C $\{^1$H$\}$ NMR (room temp., 250 MHz, $CD_2Cl_2$): $\delta$ (ppm) 28.48 (C(CH$_3$)$_3$ tbaoac), 25.13 (CH$_3$ tbaoac), 2.53 (OSi(CH$_3$)$_3$), 91.09 (CH tbaoac), 185.27 (OCCH$_3$ tbaoac), 174.07 (CO tbaoac), 81.62 (OC(CH$_3$)$_3$ tbaoac).
Mass spectrum (positive-ion EI): m/z 584 [Zr(OSiMe$_3$)$_2$(tbaoac)$_2$]$^+$, 495 [Zr(OSiMe$_3$)(tbaoac)$_2$]$^+$, 427 [Zr(OSiMe$_3$)$_2$(tbaoac)]$^+$, 338 [Zr(OSiMe$_3$)(tbaoac)]$^+$, 412 [Zr(OSiMe$_3$)(OSiMe$_2$H)(tbaoac)]$^+$, 84 [C$_4$H$_4$O$_2$]$^+$, 58 [C$_3$H$_6$O]$^+$, 75 [SiMe$_2$OH]$^+$, 45 [SiOH]$^+$, 43 [SiMe]$^+$.

Elemental analysis calcd. for C$_{22}$H$_{44}$O$_8$Si$_2$Zr (%): C, 45.25; H, 7.54 Found: C, 45.71; H, 7.75.

Melting point (Mp): 60–62°C (uncorrected).

Hafnium bis(trimethylsilinolate)bis(tert-butylacetoacetate), [Hf(OSiMe$_3$)$_2$(tbaoac)$_2$] (12)

To a clear solution of 4.14 g (10 mmol) hafnium(IV)isopropoxide in hexane (40 ml), 3.32 ml (20 mmol) of bidentate ligand tert-butylacetoacetate was added. The reaction conditions and workup were as for compound 1. Efforts in obtaining crystals measurable by single crystal X-ray diffractometer were not successful. Yield: 5.39 g (80.4 % based on [Hf(OPr$_3$)$_4$]).

$^1$H NMR (room temp., 250 MHz, C$_6$D$_6$): δ (ppm) 1.68 (6H, s, C(CH$_3$)$_3$ tbaoac), 1.34 (18H, s, C(CH$_3$)$_3$ tbaoac), 0.34 (18H, s, OSi(CH$_3$)$_3$), 5.01 (2H, s, CH tbaoac).

$^{13}$C {$^1$H} NMR (room temp., 250 MHz, C$_6$D$_6$): δ (ppm) 28.46 (C(CH$_3$)$_3$ tbaoac), 25.37 (CH tbaoac), 2.75 (OSi(CH$_3$)$_3$), 91.19 (CH tbaoac), 185.96 (OCCH$_3$ tbaoac), 174.13 (CO tbaoac), 81.88 (OC(CH$_3$)$_3$ tbaoac).

Mass spectrum (positive-ion EI): m/z 670 [Hf(OSiMe$_3$)$_2$(tbaoac)$_2$]$^+$, 581 [Hf(OSiMe$_3$)(tbaoac)$_2$]$^+$, 513 [Hf(OSiMe$_3$)$_2$(tbaoac)]$^+$, 424 [Hf(OSiMe$_3$)(tbaoac)]$^+$, 499 [Hf(OSiMe$_3$)(OSiMe$_2$H)(tbaoac)]$^+$, 84 [C$_4$H$_4$O$_2$]$^+$, 58 [C$_3$H$_6$O]$^+$, 75 [SiMe$_2$OH]$^+$, 45 [SiOH]$^+$, 43 [SiMe]$^+$.

Elemental analysis calcd. for C$_{22}$H$_{44}$O$_8$Si$_2$Hf (%): C, 39.36; H, 6.56 Found: C, 39.90; H, 6.86.

Melting point (Mp): 63–65°C (uncorrected).
2.4 Results and discussion

2.4.1 Mixed isopropoxide/β-ketoester and β-ketoamide complexes of zirconium

2.4.1.1 Synthesis and characterisation

The reaction of homoleptic alkoxide, \([\text{Zr(Pr}^\text{III}])_4(\text{HPr}^\text{IV})]\) with β-ketoester and β-ketoamide ligands specifically, tert-butylacetoacetate (tbaoac) and N,N-diethylacetoacetamide (deacam) resulted in the formation of desired complexes in quantitative yield (> 80%). Mixed isopropoxide/β-ketoester complexes were obtained by varying the amount of β-ketoester ligand in a stoichiometric manner (scheme A). Large colourless crystals suitable for X-ray single crystal measurement were observed at −30°C in the schlenk flask containing saturated solution of zirconium bis(isopropoxide)bis(tert-butylacetoacetate) (1) in hexane after about two weeks. As a part of the purification process, 1 was repeatedly distilled out quantitatively at 90°C under 10⁻² torr pressure for about two hours. After about 50% of the distillation was complete, compound 1 from the mother flask was measured for proton NMR and the spectrum was found identical to the room temperature ¹H NMR spectrum of pure compound 1. This gave an indication that 1 does not decompose or oligomerise at the set CVD vaporiser temperature (90°C) when maintained for long periods of time. After third distillation however, the precursor in the mother flask turned orange in colour and the ¹H NMR obtained showed additional signals than that of compound 1. Compound 2 namely, zirconium tris(isopropoxide)(tert-butylacetoacetate) was highly soluble in hexane and transparent X-ray quality crystals were obtained by dissolving it in minimum amount of hot hexane and allowing the solution to stand undisturbed at −30°C for 48 hours. During the reaction, zirconium tetrakis(tert-butylacetoacetate) (3) remained insoluble in hexane. The insolvibility of [Zr(tbaoac)]₄ can be attributed to the extremely bulky zirconium centre with four sterically bulky tbaoac ligands forming a saturated eight coordinated metal complex. It was found to be soluble in a 1:1 mixture of methanol/toluene but efforts in obtaining X-ray quality crystals from the same were not successful. Reaction of [Zr(Pr}^\text{III}])_4(\text{HPr}^\text{IV})] with N,N-diethylacetoacetamide in 1:2 equivalent gave a pale brown viscous oil of zirconium bis(isopropoxide)bis(N,N-diethylacetoacetamide) (4) which crystallised at 4°C as pale yellow
crystals after about 24 hours. The compounds, 1, 2 and 4 were highly soluble in common organic solvents making them particularly suitable for LI-MOCVD in addition to CVD process. When compared to the parent alkoxide, the compounds 1–4 showed relatively less reactivity for air and moisture which may be due to the saturated Zr(VI) and Zr(VIII) metal centre.

**Mass spectrometry and Infrared spectroscopy**

Mass spectrometric analysis (electron impact mode) performed on compounds 1, 2, 3 and 4 showed ion fragments corresponding to $[\text{M(OPr}^\text{iP})_2(L)]^+$, $[\text{M(OPr}^\text{iP})(L)_2]^+$, $[\text{M}_2(\text{OPr}^\text{iP})_2(L)]^+$, $[\text{M(OPr}^\text{iP})_3]^+$, $[\text{M}(L)_x]^+$, ($\text{M} = \text{Zr}$, $x = 1, 2, 3$ and $L$: tbaoac or deacam). The IR spectra of all newly synthesised compounds were recorded in the range 4000–400 cm$^{-1}$ as nujol mulls between NaCl windows. Tentative assignment of the IR absorption frequencies are based on the basis of data of previously characterised compounds having similar key structures.$^{[11, 17, 32]}$

Vibrational stretching frequencies for alkoxide and ester C-O absorptions were observed in the region 1300–1050 cm$^{-1}$. Sharp bands in the carbonyl region 1630–1400 cm$^{-1}$ were observed but it was not possible to differentiate between $\nu$(C=O) and $\nu$(C=C) vibrational modes due to the coupling between various modes. Metal-oxygen bands were seen at the lower frequency region between 650–500 cm$^{-1}$.

**NMR studies**

Room temperature $^1$H and $^{13}$C NMR spectra of compound 1 in benzene-$d_6$ are structurally significant without any dynamic solution behaviour. Sharp singlets observed at $\delta$ 1.76, $\delta$ 5.09 and $\delta$ 1.40 are assigned to the protons of methyl, tertiary butyl and methine of the tbaoac ligand. A septet at $\delta$ 4.59 (2H) as well as a doublet at $\delta$ 1.39 (12H) refer to the isopropoxide ligands. The $^{13}$C NMR is in good agreement with the proposed monomeric structure. The $^1$H NMR of compound 3 is also in good agreement with a simple monomeric and homoleptic chemical structure and shows sharp resonances at $\delta$ 5.15 (4H), $\delta$ 1.81 (12H) and $\delta$ 1.53 (36H), associated with the tbaoac ligand. The solution behaviour of 2 is however far more complex. Dissolving the crystalline compound in benzene-$d_6$ shows the expected signals for the symmetric dimeric species at $\delta$ 5.18 (s, $CH$ tbaoac), $\delta$ 4.61 (m, $CH$ OPri), $\delta$ 1.80 (s, $CH_3$...
tbaoac), δ 1.52 (s, C(CH₃)₃ tbaoac) and δ 1.41 (bs, CH₃ OPr'). The two broad signals at δ 4.61 and δ 1.41 indicate a fluxional process, exchanging bridging and terminal isopropoxide groups. When the spectrum is recorded at −80°C, decoalescence of these broad signals could be observed giving separate peaks at δ 4.80 (bs, 2H), δ 4.47 (bs, 4H), δ 1.60 (bs, 4CH₃) and δ 1.33 (bs, 8CH₃). The ¹³C spectrum at the same temperature shows broad peaks for all C atoms except for the ketonic CO and CH (tbaoac) which were not detected.

In addition, the room temperature spectra of 2 exhibit characteristic signals of compound 1. The intensity of these signals was found to increase when the solution of compound 2 was allowed to stand at room temperature up to a final ratio of 1 (2):1.30 (1) after 24 hours. Thus, it is supposed that on dissolving crystals of 2, an equilibrium is established between 2, 1 and [Zr(OPr')₄] (equation 9).

Scheme A: Chemical synthesis route for compounds 1, 2, 3 and 4.
The formation of $[\text{Zr(OPr^i)}_4]_x$ is not found in the $^1\text{H}$ NMR spectrum directly, instead a broad peak at 1.48 ppm is observed (OCH(CH$_3$)$_2$), the integral equalling the sum of 2 and $[\text{Zr(OPr^i)}_4]_x$. This observation suggests a fluxional process exchanging the isopropoxide ligands of 2 and $[\text{Zr(OPr^i)}_4]_x$. In contrast, the signals for the isopropoxide ligands of 1 formed in the course of this reaction are not changed in comparison to the pure solution of 1.

\[ \text{Zr}_2(\text{OPr}^i)_6(\text{tbaoac})_2 \rightarrow \text{Zr}(\text{OPr}^i)_2(\text{tbaoac})_2 + \text{Zr}(\text{OPr}^i)_4 \] (9)

The reaction presented above refers to an equilibrium which is substantiated by the observation that $^1\text{H}$ NMR of a 1:1 mixture of Zr(OPr$^i$)$_4$ and 1, giving a mixture of compound 2 and 1 in a ratio 1:1.35. However variable concentration and variable temperature studies on 2 revealed the solution behaviour is much more complex than that represented in equation 9. Noteworthy NMR studies by R. J. Errington$^{[25]}$ and A. C. Jones$^{[11]}$ on similar titanium and zirconium compounds have also shown complex solution behaviour. Jones et al. reported quantitative disproportionation of $[\text{Zr(OPr}^i)_2(\text{thd})_2]$ to the symmetrical dimer $[\text{Zr(OPr}^i)_6(\text{thd})_2]$, tetrakis-thd, and the parent alkoxide. Interestingly, on distillation of 2 a similar process is observed to take place. The $^1\text{H}$ NMR spectra of the distilled product shows the presence of both, compound 1 and 2 with differing ratios. Detailed analysis of the integrals reveal insufficient amount of isopropoxide ligands relative to tbaoac for 2 thus suggesting that the sublimed product contains 1 and $[\text{Zr(OPr}^i)_4]$ in a ratio less than 1:1. Signals from room temperature $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compound 4 in benzene-d$_6$ are in good agreement with the proposed monomeric structure. The integration of each peak was as expected. Sharp singlet at $\delta$ 1.90 (6H) and a doublet at $\delta$ 1.47 (6H, $^1J = 5.97$ Hz) due to CH$_3$ of respective decam and OP$^i$ ligands are identified in the $^1\text{H}$ NMR spectrum. The two ethyl groups of the decam ligand show four different environment corresponding to methyl ($\delta$ 0.70, $\delta$ 0.96) and methylene ($\delta$ 2.66, $\delta$ 3.09) protons. Similarly two signals for the methyl (13.03, 13.06 ppm) as well as the methylene (41.28, 42.38 ppm) carbon of the diethylamide group of the $\beta$-ketoamide moiety have been observed in the $^{13}\text{C}$ NMR. Broad signal at $\delta$ 4.69 and a singlet at $\delta$ 4.76 are assigned to the methine proton of the isopropoxide and $\beta$-ketoamide.
2.4.1.2 Crystal structures of 1, 2 and 4

The overall molecular geometries with atomic labelling are illustrated in figures 1, 2 and 3 respectively and the relevant crystallographic details are summarised in table 1. In case of compound 1, disorder was found in the isopropoxide group. The positions of the involved atoms C21a and C21b are disordered with site occupancy factor of 0.271 and 0.728 respectively. Crystal of [Zr₂(OPr)i₆(tbaoac)₂] (2) was found to be of weak quality and one of the terminal isopropoxide group had disorder which could not be refined anisotropically. Mononuclear complexes namely [Zr(OPr)i₂(tbaoac)₂] (1) (Figure 1) and [Zr(OPr)i₂(deacam)₂] (4) (Figure 3) are formed by replacing two alkoxy groups of zirconium tetra-isopropoxide with bidentate β-ketoester and β-ketoamide ligands respectively. Formation of metal-oxygen bond in the complex involves delocalisation of \( \pi \) bonds in the acetylacetonate ring, which helps in stabilising the ring in solid state. Compound 1 crystallises in the monoclinic space group C2/c forming a distorted six coordinated environment at the zirconium centre. The two β-ketoester ligands as well as the two isopropoxy ligands are arranged cis to each other, with both tert-butoxy (OBu⁴) groups being trans to the isopropoxide ligands. The structure is isomorphous with its Ti and Hf analogues, [Ti(OPr)i₂(tbaoac)₂]\(^{[26]}\) & [Hf(OPr)i₂(tbaoac)₂]\(^{[27]}\). Important bond lengths and angles are listed in table 2. The Zr1-O bond lengths for the β-ketoester range from 2.095 Å to 2.233 Å (Avg. 2.16 Å) and are comparable with the reported similar monomeric and dimeric zirconium compounds as well as compound 2.\(^{[11, 27]}\) The average Zr1-O bond length for the isopropoxide groups is 1.908 Å which is shorter compared to the average Zr1-O bond length for the tbaoac ligands. The C-O bond distance in the alkoxy substituent is 1.337 Å which is comparable with [Ti(OPr)i₂(tbaoac)₂] & [Hf(OPr)i₂(tbaoac)₂].\(^{[25, 26]}\) All (O-Zr1-O) bond angles strongly deviate from the ideal octahedral angles of 90° varying from 78.33 (15)° (O1-Zr1-O2) to 103.0 (3)° (O6-Zr1-O6A). The small bite angles of the two β-ketoester ligands (78.33 (15)° for O1-Zr1-O2) enlarge the external angle of the alkoxy oxygens (103.0 (3)° for O6-Zr1-O6A).
In the solid state, \([\text{Zr}_2(\text{OPr})_6(\text{tbaoac})_2]\) exists as a six coordinate dimer in which each zirconium atom is surrounded by two oxygen atoms of chelating \(\beta\)-ketoester moiety in \(\eta^2\) fashion; oxygen of the two terminal isopropoxide groups and by two \(\mu\)-oxo atoms of bridging isopropoxide groups. A perspective view of the molecule is illustrated in figure 2. The chelating ligands on each Zr atom are trans to each other. The geometry around each zirconium centre is distorted octahedron and the distance of the two metals is non bonding at 3.4891 Å which is comparable with the values published for similar compounds.\(^{11, 28}\) Selected bond lengths and angles are given in table 3.

The bridging \(\mu\)-oxo bond length is 2.098 Å for Zr2-O26 and 2.231 Å for Zr2-O26A and the average bond distance matches well with the compounds \([\text{Zr}_2(\text{OPr})_6(\text{thd})_2]\)\(^{11}\) and \([\text{Zr}_2(\text{OPr})_8(\text{HOPr})_2]\)\(^{29}\). The average bond distances for the terminal OPr\(^1\) group is 1.932 Å which are at the short end among the three sets of (Zr-O) bonding namely, involving the terminal and bridging isopropoxide groups and the tbaoac ligands. The longer tbaoac (Zr-O) distance (Avg. 2.184 Å) reflects greater trans influence of the terminal alkoxides compared with the \(\beta\)-ketoester ligand.
Chapter 2

Table 1: Crystallographic data for [Zr(OPrP_iP_i)B_2B_2(tbaoac)B_2B_2] (1), [ZrB_2B_2OPrP_iP_iB_6B_2(tbaoac)B_2B_2] (2), [Zr(OPrP_iP_i)B_2B_2B_2(deacam)B_2B_2] (4).

[Zr(OPrP_iP_i)B_2B_2(deacam)B_2B_2] (compound 4) also exist as a monomer and is isomorphous with compound 1. It crystallises in the monoclinic space group P2(1)/c. The overall geometry as well as all the features is very similar to those of compound 1. Selected bond lengths and angles for compound 4 are listed in table 4. The two β-ketoamide ligands as well as the two isopropoxy ligands are arranged cis to each other with the amide groups of both chelating ligands being in trans position to the isopropoxide ligands. It has a slightly distorted octahedral geometry around the zirconium metal centre i.e. all (O-Zr-O) bond angles show a slight deviation from the ideal octahedral angles of 90°. The (O-Zr-O) angles vary from 78.13 (6)° (O11-Zr1-O15) to 102.38 (7)° (O30-Zr1-O11). The small bite angles of the ketoamides of 78.13 (6)° (O11-Zr1-O15) and 78.40 (6)° (O21-Zr1-O25) respectively lead to an opening of the external angle of two alkoxy oxygens O30-Zr1-O40 to 98.59 (7)°.
Table 3: Selected bond distances (Å) and bond angles (deg) for [Zr$_2$(OPr$i$)$_6$(tbaoac)$_2$] (2).

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<th>Bond/Distance/Angle</th>
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Figure 2: Molecular structure of [Zr(OPr$i$)$_4$(tbaoac)$_2$] (2).  

Figure 3: Molecular structure of [Zr(OPr$i$)$_2$(deacam)$_2$] (4).
Table 4: Some selected bond distances (Å) and bond angles (deg) for [Zr(OPr\textsuperscript{i})\textsubscript{2}(deacam)]\textsubscript{2} (4).

2.4.1.3 Thermal analysis

All TG/DTA measurements on compounds 1, 2, 3 and 4 were performed using high purity (99.9999 %) nitrogen at ambient pressure employing a heating rate of 10°C min\textsuperscript{−1} from room temperature to 600°C. During isothermal measurements, the sample amount was about 10 mg and samples were heated under high purity nitrogen with a heating rate of 10°C min\textsuperscript{−1} over a period of 4 hours. TG/DTA curve of [Zr(OPr\textsuperscript{i})\textsubscript{2}(tboaouc)\textsubscript{2}] is presented in figure 4a.
The onset of volatilisation begins at temperatures as low as 140°C and an endothermic peak at around 45°C in the DTA, marks the melting of compound 1. The prevailing process towards decomposition of 1 indicates a one step weight loss which starts at about 240°C and is complete at temperatures around 300°C with 9% residue (theoretical amount of ZrO$_2$ is 23.5%) left behind in the crucible. Compared to the original weight % of ZrO$_2$, lower amounts of residue can be attributed to quantitative vaporisation of 1. Almost complete vaporisation of [Zr(Pr$_3$)$_2$(tbaoac)$_2$] is expected when the TG/DTA is measured under vacuum.

Due to the tendency of [Zr$_2$(Pr$_3$)$_6$(tbaoac)$_2$] to disproportionate into 1 and [Zr(Pr$_3$)$_4$] even during the vaporisation process, TG/DTA analysis was carried out from the crystalline solid of compound 2. As observed for compound 1, 2 also begin to vaporise at lower temperatures of 130°C (Figure 4b). The onset of vaporisation of [Zr$_2$(Pr$_3$)$_6$(tbaoac)$_2$] was found lower than [Zr(Pr$_3$)$_2$(tbaoac)$_2$]. The onset of decomposition temperature of 2 is similar to 1 (~
240–245°C). DTA curve shows a very sharp endothermic peak at 114°C thus indicating melting of 2 and the melting was in full agreement with the melting point measured in sealed glass capillary. Till the temperature reached at about 205°C, compound 3 display no weight loss and after that large portion of 3 vaporises (Figure 4c). However, during actual sublimation experiment, almost no condensation of 3 was observed on the cold finger even when the oil bath temperature was held at 200°C under 10^{-2} torr pressure for 2–3 hours. After about two hours, the compound eventually turned yellow and gradually decomposed. TG/DTA plot of compound 4 (Figure 4d) indicates that the precursor is a low melting solid at 60°C and that a major weight portion of it evaporates below 250°C. The decomposition onset of 4 is marked at 310°C and is higher compared to compounds 1 and 2. The residue left after decomposition is around 11 % which is much less than the theoretical ZrO$_2$ amount of 23.61 %. When the TG/DTA measurements on these new compounds namely 1, 2 and 4 are performed under vacuum, the residual amount after complete decomposition of the compounds is expected to reduce significantly, thus implying quantitative and clean vaporisation. It is worthwhile to note here that during actual MOCVD experiments performed under low pressure of 10 mbar and bubbler temperature of 90°C, clean vaporisation with no colour change of the precursor left in the bubbler was observed.

To show the potential of the new compounds as MOCVD precursors than the conventional precursors for ZrO$_2$ film deposition, the thermogravimetric curve of compounds 1, 2 and 4 is compared with [Zr(thd)$_4$] (reference compound) and is shown in figure 5. [Zr(thd)$_4$] was synthesised according to the literature procedure. It is apparent from the plot that 1, 2 and 4 begin to volatilise at relatively low temperatures (~ 150°C) compared to [Zr(thd)$_4$] (~ 275°C). The new compounds are low melting solids and the decomposition temperature is comparable to those reported for [Zr(OPr$_i$)$_2$(thd)$_2$] and much lower when compared to that of [Zr(thd)$_4$]. Also when compared with the parent alkoxide, [Zr(OPr$_i$)$_4$] the onset of decomposition is shifted to higher side of the temperature window.

Thermal characteristics of compound 1 were found very similar to that of its Ti congener. The amount of residue left behind after complete decomposition of compounds 1 (~ 9 %), 2 (~ 6 %) and 4 (~ 11 %) is slightly higher than [Zr(thd)$_4$] which vaporises with almost zero residue being left in the crucible. Lowering the onset of volatilisation temperature for compound 1 by about 100°C compared to [Zr(thd)$_4$] (the benchmark precursor for obtaining ZrO$_2$ films), is expected to make 1 more compatible with [Pb(thd)$_2$] (~ 170°C) during the growth of PZT thin films.
Figure 5: Comparative TG plots of [Zr(OPrP)B₂B₂(tbaoac)B₂] (1), [Zr₂(OPrP)₆(tbaoac)] (2), [Zr(OPrP)₂(deacam)] (4) and reference compound [Zr(thd)₄] under nitrogen flow rate 300 ml min⁻¹ with heating rate of 10°C min⁻¹.

Figure 6: Isothermal pattern for [Zr(OPrP)₂(tbaoac)] at 150°C and 175°C with a heating rate of 10°C min⁻¹.

Close matching of thermal window (volatileisation and decomposition) between individual precursors will be an added advantage in the case of CVD of multicomponent materials. Isothermal studies carried out on compounds 1, 2 and 4 revealed that the compounds vaporise at a constant and appreciable rate for long periods of time (> 200 min) in the temperature range 150–175°C, which is an essential requirement for a CVD precursor so as to ensure reproducibility by having a constant precursor vapour transport. As an example, isothermal studies (atmospheric pressure) performed on compound 1 at two different temperatures (150 and 175°C) are illustrated in figure 6. It is seen that there is a positive slope and no distinct
steps observed in the TG curves implying that there is quantitative and relatively unchanged volatilisation at moderate temperatures (below 200°C).

2.4.1.4 Summary

In summary, two monomeric low melting mixed alkoxides of Zr, namely [Zr(OPr)2(tbaoac)2] (1) and [Zr(OPr)2(deacam)2] (4) and a dimer [Zr2(OPr)6(tbaoac)2] (2) have been synthesised and structurally characterised. The new complexes exhibited improved thermal properties suitable for MOCVD applications. The thermal characteristics of the complexes showed reasonable temperature window between melting, volatilisation and decomposition as desired for a CVD process. Compound 1, specifically has thermal behaviour which matches closely to that of [Ti(OPr)2(tbaoac)2] and [Pb(thd)2] making it more suitable than [Zr(thd)4] for growing multicomponent oxides like PZT thin films. Appreciable solubility of the monomers, 1 and 4 in common organic solvents like THF, hexane, toluene etc makes them attractive precursors for LI-MOCVD as well. Applicability of [Zr(tbaoac)4] (3) to be used as a CVD precursor was ruled out due to its insoluble and involatile nature. Generally metal alkoxides are known for undergoing transesterification reactions which was not observed in the case of newly synthesised complexes. From the present work it can be inferred that mononuclear complexes can be stabilised by using stronger donating ligands (such as esters or amide) and that it is possible to fine tune the thermal properties of CVD precursors by incorporating small but distinct changes (like esters and amides) as targeted cleavage points in the ligand sphere of established key structures.

2.4.2 Mixed tert-butoxide/β-ketoester and β-ketoamide complexes of zirconium and hafnium

2.4.2.1 Complex synthesis and spectroscopic characterisation

Extensive studies carried out by Bradley and Mehrotra have shown that alkoxides of zirconium and hafnium readily exchange their alkoxy groups with other alcohols. In case of tert-butyl derivatives, transesterification reactions are more convenient and are preferred mainly due to
the difference in boiling points of tert-butylacetate and the isopropyl acetate (formed during the reaction), which gives broad temperature window for their separation by fractional distillation.\cite{9,31} Further, transesterification reactions have shown to be more facile than the corresponding alcohololysis reactions. However, the new mixed tert-butoxide/β-ketoester and β-ketoamide complexes of zirconium and hafnium were synthesised via alcoholysis route without any difficulty in high yields. Two equivalent each of tert-butylacetoacetate (tbaoac) and N,N-diethylacetoacetamide (deacam) ligands were reacted with metal (IV) isopropoxide to give expected stochiometry of [M(OPr\text{P}^\text{t})_2(tbaoac)_2] and [M(OPr\text{P}^\text{t})_2(deacam)_2], (M: Zr and Hf) respectively. In the next step, large excess of tert-butanol was added to the resulting metal mixed isopropoxide complexes in order to obtain the final desired products namely, [Zr(OBu\text{P}^\text{t})_2(tbaoac)_2] (5), [Zr(OBu\text{P}^\text{t})_2(deacam)_2] (6), [Hf(OBu\text{P}^\text{t})_2(tbaoac)_2] (7) and [Hf(OBu\text{P}^\text{t})_2(deacam)_2] (8). Large excess of tert-butanol was required to push the reaction towards completion. Synthesis of compounds 5–8 was one-pot synthesis and the new complexes were easy to prepare and scale-up. The overall synthesis is shown in scheme B (compounds 5 and 6) and scheme C (compounds 7 and 8).

The new compounds were found to be low melting volatile solids and hence were distilled in quantitative yields under reduced pressure at low temperatures between 100–110°C. High volatility exhibited by these compounds indicates their suitability as MOCVD precursors. The products were also moderately soluble in hydrocarbon solvents such as hexane, pentane and showed exceptionally good solubility in toluene and THF making them highly suitable for liquid injection MOCVD (LI-MOCVD) in addition to chemical vapor deposition (CVD). Compounds 5–8 showed relatively less reactivity towards air and moisture than the parent alkoxide. This reduced reactivity may be due to the saturated Zr(VI) and Hf(VI) metal centre compared to highly electrophilic M(IV) centre in case of parent zirconium and hafnium alkoxides.

Infrared spectra of all the synthesised compounds showed C=O and C=C stretching vibrations in the region 1400–1630 cm\(^{-1}\) as two strong bands. Due to the expected coupling between the various modes, it was difficult to differentiate between the ν(C=O) and ν(C=C) vibrational modes. The C-O absorptions of the modified β-diketonate ligands were seen in the region 1300–1050 cm\(^{-1}\). Formation of M-O bond where M is zirconium and hafnium is indicated by appearance of bands in the IR region 650–500 cm\(^{-1}\). The assignment of the bands is mainly
based on the spectra of free $\beta$-ketoester, $\beta$-ketoamide and tert-butoxide ligands as well as on the literature reported compounds with similar key structures.$^{[5,11,25,32]}$

Scheme B: Chemical synthesis route for compounds 5 and 6.

The mass spectrometric analysis was performed on all the four compounds in the electron impact mode employing low ionisation energy of 15–20 eV. The molecular ion peak was seen in very low intensity in case of all the compounds. The mass data for compounds 5 and 7 showed major fragments corresponding to $[\text{M(OBu})^\text{III}(\text{tbaoac})_{2}]^+$, $[\text{M(OBu})^\text{III}(\text{tbaoac})]^{+}$ and $[\text{M(tbaac)}]^{+}$ (where M: Zr and Hf). For compounds 6 and 8 intense peaks due to $[\text{M(OBu})^\text{III}_{2}(	ext{deacam})]^{+}$, $[\text{M(OBu})^\text{III}(	ext{deacam})]^{+}$, and $[\text{M(OBu})^\text{III}(	ext{deacam})_{2}]^{+}$ fragments (where M: Zr and Hf), were observed. Room temperature NMR data obtained in $C_{6}D_{6}$, indicates the formation of respective species in right stoichiometry. Room temperature $^1$H and $^{13}$C NMR spectra of compound 5 and the analogous compound 7 are consistent with the proposed mononuclear structure. Characteristic sharp singlets observed at (6H), $\delta$ 1.49 & $\delta$ 1.39 for compound 5 and $\delta$ 1.50 & $\delta$ 1.38 for compound 7 are assigned to the methyl protons of tbaoac and OBu$^\text{III}$ ligands respectively. Sharp singlet from the six methyl protons of the $\beta$-ketoester ligands are observed at 1.75 (1) and 1.74 (2) ppm. The methine (CH) protons of the tbaoac ligands are seen at $\delta$ 5.07 for 5 and $\delta$ 5.04 for 7 and are shifted up field compared to the CH singlet in $[\text{Zr(Pr}^\text{III})_{2}($tbaoac)$]_{2}$ ($\delta$ 5.09) and $[\text{Hf(Pr}^\text{III})_{2}($tbaoac)$]_{2}$ ($\delta$ 5.06) complex.

The NMR spectra of $[\text{M(OBu})_{2}($deacam)$]_{2}$ [M = Zr, Hf] also gives striking confirmation of the presence of two different types of ligands in right proportions. Sharp resonances in the $^1$H spectra, at $\delta$ 1.92 (6H), $\delta$ 1.91 (6H) are associated with the methyl protons of the deacam.
ligands for 6 and 8 respectively whereas $\delta$ 1.59 and $\delta$ 1.61 are assigned to the protons of tert-butoxide ligands. The diethylamide group of the $\beta$-ketoamide gives individual NMR signals, a well resolved triplet for each methyl protons and a broad signal for each methylene protons.

```
Hf(OPr')_4
  /       \
2 H-tbaoac  Hf(OPr')_2(tbaoac)_2 + 2 Pr'OH
  \       / 2 H-deacam
    [Hf(OPr')_2(L)_2] + 2 Bu'OH
    \       / 2 Hf(OPh)_2(deacam)_2 + 2 Pr'OH
```

**Scheme C:** Chemical synthesis route for compounds 7 and 8.

Similarly two signals for the methyl (13.03, 13.06 ppm) as well as the methylene (41.28, 42.38 ppm) carbon of the diethylamide group of the $\beta$-ketoamide moiety is observed in the $^{13}$C NMR. NMR on the new compounds gave no indication of *trans* esterification phenomenon which is otherwise very common in the metal alkoxide system. Variable temperature $^1$H NMR studies performed on compounds 5–8 in the temperature range 40–70°C revealed characteristic resonances for the individual monomeric compounds and thus gave no hint to the formation of dimeric or decomposed species (Figure 7).

### 2.4.2.2 Crystal structures of 5, 7 and 8

Recrystallisation of compounds 5 and 7 from saturated solution of hexane at $-30^\circ\text{C}$ for about a week yielded crystals which were measured by single crystal X-ray analysis. Compound 8 namely, [Hf(OBu')_2(deacam)_2] crystallised from a 1:1 mixture of hexane:THF at $-30^\circ\text{C}$ in 24 hours. Compound 5 crystallises in the monoclinic space group P2(1)/c and comprises of two tert-butoxide units and two chelating tert-butylacetoacetate units forming a distorted octahedron. Important crystallographic details are listed in table 6.
The zirconium atom is octahedrally surrounded by six oxygen atoms and the monomeric structure and selected bond angles and bond lengths are shown in figure 8 and table 5 respectively. Two sets of Zr-O bonding are identified. The Zr1-O bond lengths for the β-ketoester range from 2.123 Å to 2.224 Å which are comparable with the isopropoxide analogue [Zr(OPr\text{P}t\text{P})_2(bbaoac)_2] and with the reported similar monomeric [Zr(acac)_4] complex. The Zr-O bond lengths of the tert-butoxide groups range from 1.887 Å to 1.909 Å which are shorter compared to those found in the complex [Zr(OBu\text{P}t\text{P})_2(mmp)_2]. The Zr-O(Bu\text{P}) bonds in [Zr(OBu\text{P}t\text{P})_2(bbaoac)_2] are also shorter than the Zr-O bonds of the cheating β-ketoester ligands. The O-Zr-O bond angles fall into three groups namely the bite angles of the alkoxides, bite angles of the chelating bbaoac ligand and the trans O-Zr-O angles between the alkoxide and the bbaoac ligands. All O-Zr-O bond angles significantly deviate from the ideal octahedral angles of 90° varying from 102.5(4) (O31-Zr 1-O41) to 80.4 (3) (O11-Zr1-O15). The trans O-Zr-O bond angles also deviate strongly from linearity, with O-Zr1-O ranging from 164.0(4)° (O41-Zr1-O25) to 168.5(4)° (O31-Zr1-O15).

[Hf(OBu\text{P}t\text{P})_2(bbaoac)_2] also crystallises in monoclinic P2(1)/c space group which is isomorphous with its zirconium analogue [Zr(OBu\text{P}t\text{P})_2(bbaoac)_2] and hence the structural features of 7 are very similar to compound 5. Important crystallographic details are listed in table 6. The two β-ketoester ligands are arranged cis to the two tert-butoxide ligands enabling a distorted six coordinated octahedron with the oxygen atoms surrounding the Hf centre. In the complex the Hf-O bond lengths of the cheating β-ketoester ligands range from [2.009 (16) (Hf1-O4) to 2.238 (9) (Hf1-O1)] and are comparable with that reported in [Hf(OPr\text{P}t\text{P})_2(bbaoac)_2] complex.
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The Hf-O bond lengths of the tbaoac ligand are longer than the Hf-O(Bu') bond distance which ranges from [1.965 (10) (Hf1-O8) to 1.973 (9) (Hf1-O7)]. The average bond distance for the Hf-O(Bu') is 1.969 Å which is longer in length than found in [Hf(OBu')2(mmp)2] (1.932 Å)[32]. The O-Hf-O bond angles expected to be 90° in an ideal octahedron vary from 79.2(4)° (O2-Hf1-O1) to 101.5(5)° (O8-Hf1-O7) while those expected to be 180° vary in the range 165.0(4)° (O7-Hf1-O1) to 171.4(4)° (O8-Hf1-O4).

Figure 8: Molecular structure of [Zr(OBu')2(tbaaoe)2] (5).

Table 5: Some selected bond distances (Å) and bond angles (deg)

for [Zr(OBu')2(tbaaoe)2] (5).

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Molecular structure of [Hf(OBu')2(deacam)2] (8) in the solid state is depicted in figure 10. The crystallographic data is summarised in table 6 and selected bond lengths and angles are given in table 7. The structural features of 8 are very similar to compound 5. [Hf(OBu')2(deacam)2] crystallises in the monoclinic space group and the two β-ketoamide moieties are arranged cis to the two tert-butoxide moieties. The two diethyl amide groups of the β-ketoamide are trans to the tert-butoxide ligands. The overall molecule is a distorted six coordinated octahedron with the oxygen atoms surrounding the Hf metal centre. All O-Hf-O bond angles show a slight deviation from the ideal octahedral angles of 90°. The cis O-Hf-O angles vary from 81.6 (4)° (O15-Hf1-O25) to 100.2 (4)° (O40-Hf1-O30). The trans O-Hf-O angles also deviate significantly from the ideal 180° with O30-Hf1-O15 showing the largest deviation at 168.8 (4)°. The Hf-O bond lengths of the ketoamide ligands are longer than the tert-butoxide ligands. C-O bond distance in the alkoxy substituent is 1.49 (2) Å which is comparable with [Zr(OPr)2(deacam)2].
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Table 6: Crystallographic data for [Zr(OBu)₃(PtP)B₂B₂(tbaoac)B₂] (5), [Hf(OBu)₃(PtP)B₂B₂(deacam)B₂] (8).

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<td>0.0662</td>
<td>0.1264</td>
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<td>bwr₂</td>
<td>0.3474</td>
<td>0.2053</td>
<td>0.2324</td>
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aR₁ = Σ(∥F₀∥ - ∥Fc∥) / Σ∥F₀∥.

bwR₂ = [Σw(F₀² - Fc²)² / Σw(F₀²)²]¹/².

Figure 9: Representative molecular structure of [Hf(OBu)₃(tbaoac)₂] (7).

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
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<td>C(3)-C(1)</td>
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<td>O(8)-Hf(1)-O(2)</td>
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2.4.2.3 Thermal analysis

Simultaneous TG/DTA of mixed tert-butoxide complexes of Zr and Hf is illustrated in figure 11. Compounds 5–8 begin to volatilise at relatively low temperatures (\( \sim 150^\circ C \)) and the compounds are low melting solids (5: \( \sim 75^\circ C \), 6: \( \sim 51^\circ C \), 7: \( \sim 78^\circ C \), 8: \( \sim 66^\circ C \)). Compound 5 is found to be relatively more volatile than its isopropoxide analogue \([\text{Zr(OPr}^i\text{)}_2\text{tbaoc)}_2]\) (1) primarily due to the presence of sterically bulky tert-butoxide groups which are known to enhance the volatility. But the decomposition temperature is much lower when compared to

![Molecular structure of [Hf(OBu$^t$P$^t$P)B$_2$(deacam)B$_2$] (8).](image)

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Table 7: Some selected bond distances (Å) and bond angles (deg) for [Hf(OBu$^t$P$^t$P)B$_2$(deacam)B$_2$] (8).
that of [Zr(thd)$_4$] which can be clearly taken from the comparative TG plots illustrated in figure 12. In the case of compound 7 however an opposite behaviour was seen with [Hf(OPr$_i$)$_2$(tbaoac)$_2$] being more volatile than its tert-butoxide analogue [Hf(OBu)$_2$(tbaoac)$_2$].

As determined from the DTA measurements, the temperature onset of decomposition for metal mixed alkoxide/β-ketoamide (~ 320°C) is higher than metal mixed alkoxide/β-ketoester (~230°C). Compounds 5 and 7 are particularly more suitable for MOCVD applications for growing individual and multicomponent oxides such as ZrO$_2$ or HfO$_2$ or PZT due to the low temperature onset of volatilisation and decomposition compared to [Zr(thd)$_4$].

**Figure 11:** TG/DTA plot of a: [Zr(OBu)$_2$(tbaoac)$_2$] (5), b: [Zr(OBu)$_2$(deacam)$_2$] (6), c: [Hf(OBu)$_2$(tbaoac)$_2$] (7), and d: [Hf(OBu)$_2$(deacam)$_2$] (8) employing a heating rate of 10°C min$^{-1}$. 
Low melting mixed tert-butoxide/β-ketoester and ketoamide complexes of zirconium and hafnium have been synthesised and characterised by NMR, IR and Mass spectrometry. NMR data indicates no solution dynamics and the characteristic resonances obtained for compounds 5–8 suggests the presence of monomer in the solution. The crystal structure of [Zr(OBu)₂(tbaoac)] (5), [Hf(OBu)₂(tbaoac)] (7) and [Hf(OBu)₂(deacam)] (8) confirm the monomeric structure in solid state. Thermal analysis performed on the compounds 5 and 7 in particular, showed improved thermal properties and these compounds hold promise as a CVD precursor.


Chapter 2

2.4.3 Modified alkyamide and mixed isopropoxide/aminoalcohol complexes of zirconium

2.4.3.1 Synthesis and characterisation

Reaction of zirconium tetrakis ethylamide with two equivalents of di-tert-butylmalonate as the chelating ligand yielded pale yellow zirconium bis(diethylamido)bis(di-tert-butylmalonate) complex in high yields. Suitable single crystals for X-ray analysis were obtained after recrystallising the crude product from saturated hexane at \(-30^\circ\text{C}\). \(^1\text{H}\) and \(^{13}\text{C}\) NMR data indicate the formation of the complex. Elemental analysis was consistent with the molecular formula \(\text{C}_{30}\text{H}_{58}\text{O}_8\text{N}_2\text{Zr}\) of the compound. The room temperature \(^1\text{H}\) NMR spectrum reveals sharp singlet at 4.89 ppm corresponding to \(\text{CH}\) (tbaoc). The two tertiary butyl groups of the di-tert-butyl-malonate ligand are not chemically equivalent and two separate signals at 1.37 and 1.49 ppm are observed. No splitting of the diethylamido group is observed and well resolved quartet at 3.68 ppm is assigned to the \(\text{CH}_2\) group. The room temperature \(^{13}\text{C}\) NMR is also in good agreement with the molecular structure of compound 9. The mass spectrum of \([\text{Zr} (\text{NEt}_2)_2(\text{dbmal})_2]\) showed a very low intense molecular peak at \(m/z\) 664. Other intense characteristic peaks at \(m/z\) 592, 536 and 424 attributable to \(\text{M}^+\)-\(\text{NEt}_2\), \(\text{M}^+\)-[\(\text{NEt}_2\)-(isobutene)], \(\text{M}^+\)-[\(\text{NEt}_2\)-(2 isobutene)] were observed.

Reaction of \([\text{Zr}(\text{OPr}_i)_4(\text{HOPr}_i)]\) with 2 equivalents of \(\text{N,N-diethylaminoethanol}\) in refluxing hexane led to the formation of viscous \([\text{Zr}(\text{OPr}_i)_2(\text{deae})_2]\) (10) in high yield (> 80%). However, efforts in crystallising the complex were not successful. Compound 10 have been characterised by means of NMR, Mass, IR and by elemental analysis. The room temperature \(^1\text{H}\) and \(^{13}\text{C}\) NMR are consistent with the chemical structure of compound 10. The \(^1\text{H}\) NMR spectrum reveal characteristic resonances at 1.04 and 1.44 ppm for the \(\text{CH}_3\) group of deae and the isopropoxide ligand respectively. A multiplet corresponding to \(\text{CH}\) (OPr\(^i\)) is observed at 4.57 ppm. The \(\text{CH}_2\) resonances for deae ligands are overlapped at 2.77 ppm corresponding to a total of 12 protons. The representative proton NMR spectrum of 10 is shown in figure13. The mass spectrometry data demonstrate major fragments of \(m/z\) 441, 324 and 381 corresponding to \([\text{Zr}(\text{OPr}_i)_2(\text{deae})_2]\^+, [\text{Zr}(\text{OPr}_i)_2(\text{deae})]\^+ and [\text{Zr}(\text{OPr}_i)(\text{deae})_2]\^+. The infrared spectrum of the complex 10 was studied as nujol mulls between NaCl windows. The bands are tentatively assigned on the basis of data of previously characterised alkofoxides and aminoalcohols.\(^{13, 33}\)

The asymmetric and symmetric \(\nu(\text{C-O})\) stretches were observed in the region 1035–1070 cm\(^{-1}\).
and the ν(C-N) absorption frequencies corresponding to the aminoalcohol region 1175–1190 cm\(^{-1}\). The Zr-O absorption frequencies were detected in the region 400–450 cm\(^{-1}\).

![Chemical shift spectrum](image)

**Figure 13:** Room temperature \(^1\)H NMR of [Zr(OPr\textsubscript{i})\textsubscript{2}(deae)\textsubscript{2}] (10) in benzene-d\(_6\).

### 2.4.3.2 Crystal structure of compound 9

The molecular structure and the single crystal X-ray data of compound 9 is illustrated in figure 14 and table 8 respectively. The interatomic distances and angles are listed in table 9. The complex is a monomer (triclinic, P-1) consisting of two diethylamido ligands and two di-tert-butylmalonate ligands arranged in a distorted octahedral geometry. The two diethylamido ligands and the malonate ligands are cis to each other. The Zr-N bond lengths of the diethylamide groups are in the range of 2.047 (3)–2.061 (3) Å which are comparable with the literature reported Zr-N bonds.\[^{34}\] The Zr-N bonds are however longer than in the case of isomorphous Ti analogue namely [Ti(NEt\textsubscript{2})\textsubscript{2}(dbmal)\textsubscript{2}]. The Zr-O bonds of the chelating malonate ligands vary in the range 2.122 (2)–2.206 (2) Å and are slightly longer than those in [Ti(NEt\textsubscript{2})\textsubscript{2}(dbmal)\textsubscript{2}]. The N-Zr-N bite angle between the diethylamido ligands is 100.11 (11)° which is significantly larger than reported in reference 39 and in analogous [Ti(NEt\textsubscript{2})\textsubscript{2}(dbmal)\textsubscript{2}] complex. The O-Zr-O bond angles of the chelating ligand significantly deviate from the ideal octahedral angles of 90° 78.92 (8)°(Avg.). The trans N-Zr-O bond angles also deviate strongly from linearity, with N-Zr1-O ranging from 168.65 (10)° (N116-Zr1-O16) to 167.37 (9)° (N111-Zr1-O15).
### Compound: [Zr(NEt₂)₂(dbmal)₂] (9)

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</tr>
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</tr>
<tr>
<td>c, Å</td>
<td>17.220 (3)</td>
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<tr>
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<td>b, Å</td>
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<td>γ, deg</td>
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</table>

*<sup>a</sup>R<sub>1</sub> = Σ([F<sub>o</sub>ı] - |F<sub>c</sub>|) / Σ|F<sub>o</sub>ı|.

*b<w>2</w*R = [Σw(F<sub>o</sub>² - F<sub>c</sub>²)² / Σw(F<sub>o</sub>²)]<sup>1/2</sup>.

**Table 8:** Crystallographic data for [Zr(NEt₂)₂(dbmal)₂] (9).

---

![Molecular structure of [Zr(NEt₂)₂(dbmal)₂] (9)](image)

**Figure 14:** Molecular structure of [Zr(NEt₂)₂(dbmal)₂] (9).

**Table 9:** Some selected bond distances (Å) and bond angles (deg) for [Zr(NEt₂)₂(dbmal)₂] (9).

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<td>N(116)-Zr(1)-O(16)</td>
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-89-
2.4.3.3 Thermal analysis

Compounds 9 and 10 were studied by TG/DTA to investigate their suitability for CVD applications. It can be seen from the TG curve of compound 9 (Figure 15, left) that it begins to lose weight at around 175°C and the decomposition is observed at about 250°C. Comparative TG of 9 with the standard [Zr(NEt$_2$)$_4$] is depicted in figure 15 (right). It can be clearly taken from the figure that both the compounds show similar onset of decomposition which is suitable for CVD application. In addition, compound 9 vaporises at relatively higher temperatures compared to the standard amide precursor which makes it relatively more suitable for growing multicomponent oxide films by MOCVD and it also imparts ambient stability to the complex during handling.

![Figure 15: TG/DTA of [Zr(NEt$_2$)$_2$(dbmal)$_2$] (9) (left) and comparative TG of [Zr(NEt$_2$)$_2$(dbmal)$_2$] (a) with [Zr(NEt$_2$)$_4$] (b) as the reference compound (right).](image)

TG/DTA of compound 10 is shown in figure 16. The mixed alkoxide/ aminoalkoxide zirconium complex remains stable up to relatively higher temperatures of 250°C. The prevailing process is decomposition (~370°C) towards ZrO$_2$ which is apparent from the amount of residue (~25 %) left behind in the crucible which was closely matching with the theoretical wt % of ZrO$_2$ (27.5 %) calculated for [Zr(OPr$^i$)$_2$(deae)$_2$]. Inadequate volatility of [Zr(OPr$^i$)$_2$(deae)$_2$] indicates that the compound may not possess such high potential as a MOCVD precursor as other synthesised compounds in this study. However the compound is a viscous liquid and it was found highly soluble in common organic solvents like hexane, toluene, octane etc. which
makes 10 a highly potential precursor for LI-MOCVD where low volatility compounds does not pose a serious problem for film deposition.

![Figure 16: TG/DTA of [Zr(OPrP$^2$P)$_2$(deae)$_2$] (10) measured with a heating rate of 10°C min$^{-1}$ from ambient to 500°C.](image)

**2.4.3.4 Summary**

In summary, two new compounds namely zirconium bis(diethylamido)bis(di-tert-butyl malonate) (9) and zirconium bis(isopropoxido)bis(N,N-diethylaminoethanol) (10) have been synthesised in high yields. Compound 9 crystallises in a triclinic space group where Zr metal has a coordination number of 6. Both the compounds exhibit high solubility in organic solvents such as hexane, toluene, THF etc. Thermal properties the compounds 9 and 10 were evaluated using TG/DTA analysis. Compound 9 was found to be a suitable precursor for CVD applications including LI-MOCVD due to similar decomposition temperature and slightly higher onset of volatilisation compared to the standard [Zr(NEt$_2$)$_4$] precursor for growing ZrO$_2$ films. Compound 10 however was found to be suitable for LI-MOCVD of ZrO$_2$ films due to its high onset of vaporisation.
2.4.4 Mixed silinolate/β-ketoester complexes of zirconium & hafnium

2.4.4.1 Synthesis and characterisation

Synthesis of mixed silinolate/β-ketoester complex of zirconium and hafnium was achieved by transesterification of [Zr(OPr\text{P_{i}P})_{2}B_{2}B(tbaoac)_{2}] and [Hf(OPr\text{P_{i}P})_{2}B_{2}B(tbaoac)_{2}] respectively with excess of trimethylsilylacetate in refluxing toluene. The compounds [Zr(OSiMe_{3})_{2}(tbaoac)_{2}] (11) and [Hf(OSiMe_{3})_{2}(tbaoac)_{2}] (12) were purified by quantitative distillation in the temperature range 100–125°C at 10^{-2} torr. X-ray quality crystals of 11 were obtained after recrystallising the crude product in minimum amount of hot hexane at −30°C for about 7 days. The new compounds showed high solubility in common organic solvents. Compounds 11 and 12 were analysed by NMR, and by elemental analysis. The elemental analysis was found consistent with the formula [C_{22}H_{60}O_{8}Si_{2}M], (M: Zr and Hf).

Multinuclear NMR studies carried out with compounds 11 and 12 reveal that the stoichiometry of the complexes in solution is well preserved as [M(OSiMe_{3})_{2}(tbaoac)_{2}] where M is Zr and Hf respectively. Sharp resonance at 5.04 ppm and 5.01 ppm is observed for the methine protons of 11 and 12 respectively. The protons of the trimethylsilyl groups show sharp resonance at 0.34 ppm in case of both Zr and Hf complex. A sharp singlet corresponding to the protons of tert-butyl group of the chelating ligands is observed at 1.35 ppm (11) and 1.34 ppm (12). The $^{13}$C NMR is also in good agreement with the stoichiometric composition of 11 and 12. The Room temperature proton NMR spectra of compound 11 is depicted in figure 17.

![Figure 17: Room temperature $^1$H NMR of [Zr(OSiMe_{3})_{2}(tbaoac)_{2}] (11) in benzene-d$_6$.](image-url)
2.4.4.2 Crystal structure of compound 11

The mononuclear structure of [Zr(OSiMe$_3$)$_2$(tbaoac)]$_2$ (11) is illustrated in figure 18. The data collection parameters and the interatomic bond distances and angles are given in tables 10 and 11 respectively. The molecule comprises of two units of trimethylsilyl ligands and two units of chelating tbaoac ligands. The complex crystallises in a triclinic structure and the overall geometry around the central Zr atom is a six coordinated distorted octahedron. Two different types of Zr-O bonds are observed in [Zr(OSiMe$_3$)$_2$(tbaoac)]$_2$ complex. Zr-O bonds of the trimethylsilyl groups (Avg. 1.623 (5) Å) are shorter compared to the Zr-O bonds of chelating β-ketoester ligands (Avg. 2.157 (5) Å). The O-Zr-O bond angle between the two trimethylsilyl groups is distorted from the ideal octahedral angles of 90° (101.1 (2)°). The small bite angles of the β-ketoester ligands are also significantly distorted from the ideal octahedral angles of 90° (Avg. 78.53 (18)°). The trans O-Zr-O bond angles also deviate significantly from the ideal 180° angle, with O(31)-Zr(1)-O(15) showing the largest deviation (167.5 (2)°).

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<td>Temperature, K</td>
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<tr>
<td>Wavelength, Å</td>
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<tr>
<td>$\rho$ calcd, g/cm$^3$</td>
</tr>
<tr>
<td>abs. Coeff. µ/mm$^1$</td>
</tr>
<tr>
<td>Refl.coll./uniq.</td>
</tr>
<tr>
<td>$R_{int}$</td>
</tr>
<tr>
<td>$R_1$</td>
</tr>
<tr>
<td>wR$_2$</td>
</tr>
</tbody>
</table>

$^aR_1 = \Sigma(\|F_0\| - |F_c|)/\Sigma |F_0|$.

$^bW_R = \Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2$.$^{1/2}$.

Table 10: Crystallographic data for [Zr(OSiMe$_3$)$_2$(tbaoac)]$_2$ (11).
2.4.4.3 Thermal analysis

Figure 19 (left) displays TG/DTA curve of \([\text{Zr(OSiMe}_3]_2(\text{tbaoac})_2]\) (11) and figure 19 (right) shows the analogous \([\text{Hf(OSiMe}_3]_2(\text{tbaoac})_2]\) (12) compound. TG curve of both compounds show a single step assigned to evaporation at 100°C (11) & 105°C (12) and decomposition occurring at 230°C (11) & 220°C (12). The endothermic dip in the DTA curve at around 60°C (11) and 63°C (12) indicates the melting of the compound. High volatility and moderate thermal stability is expected to make compounds 11 and 12 promising precursors for direct deposition of metal silicate films by MOCVD.

<table>
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<th>Distance/Angstrom</th>
<th>Angle/degree</th>
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<td></td>
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<tr>
<td>Zr(1)-O(31)</td>
<td>1.941 (5)</td>
<td></td>
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<tr>
<td>O(41)-Si(42)</td>
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<tr>
<td>O(31)-Si(32)</td>
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<tr>
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<td>2.105 (5)</td>
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<tr>
<td>Zr(1)-O(25)</td>
<td>2.202 (5)</td>
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<td>O(25)-Zr(1)-O(15)</td>
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<td>O(31)-Zr(1)-O(15)</td>
<td>167.5 (2)</td>
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Figure 18: Molecular structure of \([\text{Zr(OSiMe}_3]_2(\text{tbaoac})_2]\) (11).
Figure 19: TG/DTA of a: [Zr(OSiMe$_3$)$_2$(tbaoac)$_2$] (11) and b: [Hf(OSiMe$_3$)$_2$(tbaoac)$_2$] (12) with a heating rate of 10°C min$^{-1}$.

2.4.4.4 Summary

Two novel mixed silinolate complexes of zirconium and hafnium specifically, [Zr(OSiMe$_3$)$_2$(tbaoac)$_2$] (11) and [Hf(OSiMe$_3$)$_2$(tbaoac)$_2$] (12) have been synthesised and chemically analysed. The single crystal X-ray structure shows compound 11 to be a monomer in solid state. No complex behaviour of the new compounds was observed in the solution phase and from the NMR data available the Hf analogue is also proposed to be mononuclear molecule. The compounds were studied by TG/DTA and they displayed promising thermal properties in terms of vapourisation and decomposition profile suitable for MOCVD applications.
2.5 References

Chapter 2


3 MOCVD of zirconium dioxide and hafnium dioxide thin films from metalorganic precursors

Abstract

Thin films of ZrO$_2$ have been deposited by MOCVD using mixed ligand precursors [Zr(OPr$_i$)$_2$(tbaoac)$_2$] (1) and [Zr(OBu)$_2$(tbaoac)$_2$] (5) (tbaoac = tert-butylacetoacetate). Oxide film growth was studied over wide temperature range between 350-800°C using home-built horizontal cold-wall reactor. In the case of [Zr(OPr$_i$)$_2$(tbaoac)$_2$], the onset of crystallisation was observed at 450°C in absence of additional oxidant and at 400°C in presence of oxygen. Deposition and annealing temperature as well as deposition pressure influenced the film morphology and density. Minimum film growth temperature was 375°C for [Zr(OBu)$_2$(tbaoac)$_2$] and was significantly at the lower range of substrate temperature compared to [Zr(OPr$_i$)$_2$(tbaoac)$_2$]. Growth of HfO$_2$ films using analogous [Hf(OBu)$_2$(tbaoac)$_2$] (7) precursor have also been demonstrated. In addition to metal oxide film deposition, preliminary MOCVD of single source zirconium silicate and hafnium silicate precursors, [Zr(OSiMe$_3$)$_2$(tbaoac)$_2$] (11) and [Hf(OSiMe$_3$)$_2$(tbaoac)$_2$] (12) is shown. Film composition was analysed by RBS spectroscopy which confirmed the presence of Zr, Si and O in ZrSi$_x$O$_y$ films and Hf, Si and O in HfSi$_x$O$_y$ films with varying stoichiometry of silicon and oxygen throughout the films. In the last section, thin zirconia films grown in the state of the art commercial liquid injection MOCVD reactor using n- butylacetate solution of [Zr(OPr$_i$)$_2$(tbaoac)$_2$] have been deposited and the growth rates were studied as a function of substrate temperature and film thickness. Electrical properties of ZrO$_2$ thin films within MIS and MIM structures for gate oxide applications have been emphasised. Low leakage currents were observed in the lower voltage region.
Chapter 3

3.1 Introduction

Zirconia (ZrO$_2$) and hafnia (HfO$_2$) are well known high temperature ceramic materials which has received much attention because of its many interesting and useful applications. As the dimension of electronic devices is decreasing continuously, need for more reliable thin film technique arises. One such reliable technique to grow oxide films is MOCVD and the process requires suitable precursors with appropriate physical properties. Zirconium and hafnium complexes designed by introducing small but specific change in the key structure of β-diketonate ligand, are reported in Chapter 2. The novel compounds namely, [Zr(OPr$i$)(tbaoac)$_2$], [Zr(OBu$i$)$_2$(tbaoac)$_2$] and [Hf(OBu$i$)$_2$(tbaoac)$_2$] showed promising thermal properties and hence their use as MOCVD precursors was appealing. ZrO$_2$ films have been grown from [Zr(OPr$i$)$_2$(tbaoac)$_2$] using a homebuilt MOCVD reactor as well as a production tool by LI-MOCVD. The physical analysis of the films has been correlated to the capacitance and leakage properties of the dielectric.

As a solution to detrimental interface layer formation of metal silicate or SiO$_2$ during high temperature annealing, direct deposition of metal silicate layer on silicon substrate is also attempted. In this chapter, the growth and characterisation of ZrSi$_x$O$_y$ and HfSi$_x$O$_y$ films using single source [Zr(tbaoac)$_2$(OSiMe$_3$)$_2$] and [Hf(tbaoac)$_2$(OSiMe$_3$)$_2$] precursors are also discussed.

3.2 General MOCVD experimental aspects

3.2.1 MOCVD reactor set-up

Thin films of zirconium- and hafnium dioxide as well as zirconium- and hafnium silicates were deposited using a home-built horizontal cold-wall MOCVD reactor operating under low pressure. Figure 1 shows the schematic and a photograph of the MOCVD reactor employed for all film depositions.

The reactor shown here is a 15 cm long quartz tube with an internal diameter of 2.5 cm. The quartz tube is equipped with a 5 cm long cold water jacket at the centre of which a SiC coated graphite susceptor (1.5 cm) is placed. During a typical MOCVD experiment, 1×1 cm$^2$ Si(100) substrates were placed on the susceptor and the substrate heating was accomplished by an
inductive heating set up coupled to a radiation pyrometer for sensing the reactor temperature. The front part of the reactor has a short T-shaped extension through which reactive gas enters (top-end) and the horizontal end of the extension is further connected to the precursor vaporiser reservoir (also called as bubbler). The precursor vaporiser is placed in an air bath which can be used as a heating medium for precursors which needs vaporising temperatures upto 130°C. The gas supply consists of two lines, one connected to the precursor vaporiser unit and the other is used for the supply of diluent gas and/or reactive gas. All gas supply lines contain a mass flow controller to adjust and regulate the gas flow. High purity nitrogen (99.9999 %) was used as the carrier/diluent gas and 99.998 % purity oxygen was used as the reactive gas for deposition purpose. The rear end of the reactor is attached to a nitrogen cold trap where the reaction by-products are collected. The pressure of the reactor is controlled by a motor driven throttle valve. ZrO$_2$ films from compound 1 were also deposited using state of the art, AIXTRON 2600G3 planetary reactor which can handle five 6-inch wafers simultaneously. As shown in figure 2 the wafers are placed on a coated graphite susceptor which rotates typically at 8 rpm and carries five smaller plates (satellites) which rotate by gas foil rotation. The gas inlet is in the centre of the reactor providing a pure horizontal gas flow direction which makes this reactor a radial flow system. The precursor solution is delivered by a micro-pump to the vaporizer placed on top of the reactor. Hot Argon gas at the evaporation temperature carries the evaporated solution through a quartz nozzle to the substrate.
Figure 1: Schematic (up) and actual picture (down) of the horizontal cold-wall MOCVD reactor showing main parts: a) turbomolecular pump, b) pressure control valve, c) and d) pressure gauge, e) inductive heating, f) SiC coated graphite susceptor, g) substrate, h) quartz deposition zone with water cooling jacket, i) air bath, j) precursor reservoir (bubbler), k) bypass line, l) valves and m) mass flow controllers (MFC). The gas supply lines in the actual photograph are not clearly visible as they are connected from behind.
3.2.2 Substrate cleaning

All depositions in the home-built CVD reactor were carried out on p-type Si(100) wafers with approximate dimensions of 1 cm × 1 cm. The substrates were not etched with hydrofluoric acid to remove the native oxide but were thoroughly cleaned prior to film deposition by boiling in deionised water, acetone and finally in 2-propanol. The substrate were weighed and immediately transferred into the reactor chamber which was then evacuated for 10-15 min before starting the deposition. Weighing was necessary for calculating the film thickness from weight gained by the bare silicon substrate after the deposition was complete.

Two different kinds of substrate namely, p-type Si(100) wafers without removing the native oxide layer and platinised wafers, Pt/TiO$_2$/SiO$_2$/Si (denoted as Pt/Ti/Si in this study) were used for depositing ZrO$_2$ films in the commercial AIXTRON 2600G3 planetary reactor.

3.2.3 Thin film characterisation methods

Metal oxide and metal silicate films were characterised with a variety of analytical techniques. X-ray powder diffraction (XRD) of the as-deposited and annealed films was measured on a D8-Advance Bruker AXS diffractometer using Cu-K$_{α}$ radiation. Microstructure of the films
was studied by scanning electron microscopy (SEM) and the micrographs were recorded using LEO 1530 Gemini SEM equipment. Chemical composition of the as-deposited films was analysed using Rutherford back-scattering (RBS) spectroscopy and energy dispersive analysis of X-rays (EDAX). SEM and EDAX analysis was provided by Dr. R. Neuser. The RBS spectra were measured with the 2 MeV single charged He-beam of the 4 MV Dynamitron-Tandem laboratory in Bochum by Dr. H-W Becker. A beam intensity of about 20 nA incident to the sample perpendicular to the surface was used. The back-scattered particles were measured at an angle of 170º by a Si-detector with a resolution of 16 keV. The spectra were analysed with the program RBX.\textsuperscript{[1]}

Analysis of the ZrO$_2$ films grown using Compound 1, in the commercial LI-MOCVD reactor were done in collaboration at the IFF-Institut für Festkörperforchung and CNI-Centre for Nanoelectronic Systems for Information Technology, Forschungszentrum Jülich. Efficiency of the ZrO$_2$ films was deduced from X-ray fluorescence spectroscopy with a XRF RIGAKU ZSX- 100e instrument. Crystal structure analysis of the films was investigated using an Philips Analytical X-ray diffractometer employing grazing incidence and Cu-K$_\alpha$ radiation. Surface morphology of the films was studied with AFM (SIS Picostation). Electrical properties of the films were studied after sputter deposition and patterning of Pt top electrodes. C–V and I–V characteristics of the films in the MIS or MIM configuration were obtained using a HP 8284 LCR meter and a 617 Keithley programmable electrometer respectively. In the case of MIS structures, silicon substrate was the semiconductor and in MIM structure, the bottom metal electrode was platinised silicon (Pt/Ti/Si) substrate, on which the dielectric layer was directly deposited.

3.3 MOCVD of ZrO$_2$ films using [Zr(OPr$^i$)$_2$(tbaoac)$_2$] as precursor

3.3.1 Film growth conditions

3.3.1.1 ZrO$_2$ growth parameters in absence of additional oxidant

Zirconium dioxide films were deposited in a home-built horizontal cold-wall conventional MOCVD reactor (base pressure: $10^{-6}$ mbar) using [Zr(OPr$^i$)$_2$(tbaoac)$_2$] as precursor. Films were grown in the temperature range of 400–900°C on Si(100) substrates. No additional oxygen was
used during actual film deposition because oxygen of the alkoxide ligand and/or the ketoester ligand was expected to act as the oxygen source during film growth. Post annealing on the films was performed with 50 sccm oxygen flow at 800°C for 30 min. Precursor vaporiser temperature was set at 90°C and depositions were carried out employing 10 mbar and 50 mbar as reactor pressure for 90 min. High purity nitrogen with 100 sccm flow rate was used as carrier and diluent gas. For every new deposition, precursor amount of 110 mg was cautiously maintained, which is one of the crucial parameters in determining the accurate thickness of the film after a deposition is complete.

### 3.3.1.2 ZrO$_2$ growth parameters in presence of additional oxidant

In order to observe the influence of reactive gas such as oxygen, on the properties of zirconium dioxide films, depositions were carried out using 100 sccm of oxygen as the oxidant and 100 sccm of nitrogen as the carrier gas. Other deposition characteristics were same as above except that the depositions were conducted only at reactor pressure of 10 mbar in the temperature range 400–800°C.

### 3.3.2 Phase analysis

X-ray diffraction measurements performed on the as-deposited films showed amorphous films at 400°C. The onset of crystallisation was established at 450°C and at temperatures above 450°C polycrystalline films were obtained. The films had tetragonal structure as the only dominant crystal phase of ZrO$_2$, indicated by the reflexes at $2\theta = 30.10^\circ$, 34.83°, 50.08° characteristic of 101, 110 and 200 reflections. Figure 3 shows XRD images of the as-deposited films as a function of deposition temperature. XRD pattern from the annealed films showed better film crystallinity than the as-deposited films measured at same deposition temperatures. No change in the ZrO$_2$ crystal phase was observed for the films annealed in oxygen atmosphere at 800°C for 30 min. Figure 4 shows XRD spectra of oxygen annealed ZrO$_2$ films at three different temperatures of 500°C, 550°C and 600°C.
The monoclinic phase is often predominant in ZrO$_2$ films grown by MOCVD. However, reports exist in the literature where cubic or tetragonal phases of ZrO$_2$ have been stabilised by MOCVD and it was attributed to specific growth kinetics and nucleation effects.$^{[2-6]}$

### 3.3.3 Film microstructure and composition

SEM analysis on the zirconia films shows presence of microcrystalline structures on the surface having irregular grain geometries with average grain size varying between 30 to 100 nm. Well defined grain boundaries were observed in the case of oxygen annealed films but no regular shape of the grains was seen. Cross-sectional SEM view of the ZrO$_2$ samples indicates the films to be dense and as a representative example, as-deposited, annealed and cross-sectional micrographs of ZrO$_2$ film deposited at 550°C are illustrated in figures 5a, 5b and 5c respectively. The presence of Zr and O was confirmed by EDAX analysis. AFM micrograph of the annealed ZrO$_2$ film grown at 550°C showed rough film with root mean square (RMS) of 5.79 nm (last image in figure 5).

RBS spectroscopy was applied to estimate the composition ratio of the thin films and the thickness of the film deposited. Figure 6 shows a RBS spectrum from a ZrO$_2$ film grown on Si (100) at 600°C. The thickness of the layer was approximately 821 nm which is comparable with the 600°C deposited ZrO$_2$ film thickness, calculated from the mass deposited over $1 \times 1$
cm² substrate and considering the density of tetragonal zirconia to be 6.1 g cm⁻³. In the spectrum, the signals from Zr and O in the layer can be clearly identified. The comparison with the simulation (straight line) supported the stoichiometric ratio of Zr and O as 1:2. An atomic carbon content of about ~ 23 % (± 5 %) has to be included for an understanding of the data. As these films are grown without using any additional oxidant, the carbon content can be lowered significantly when the CVD is performed using oxygen as additional oxidant.

3.3.4 Growth rate

Deposition rates of ZrO₂ film as a function of increasing substrate temperatures are summarised in Table 1 and figure 7. In lower deposition regions (400–600°C), the growth rates are found to increase with temperature which may be due to ZrO₂ film growth as a result of reaction kinetics of the precursor molecules on the substrate surface. The growth rate increases from 0.87 nm min⁻¹ at 400°C to 9.17 nm min⁻¹ at 600°C. Considerably weak variation (9.46–9.06 nm min⁻¹) in the

![Figure 5: SEM image of the ZrO₂ films deposited on Si(100) at 550°C, a: as-deposited; b: oxygen annealed; c: cross-sectional view and d: AFM micrograph of the as-deposited film using compound 1.](image-url)
Figure 6: RBS plot of a ZrO\textsubscript{2} film deposited on Si(100) at 600°C using compound 1.

growth rates is observed in the temperature region between 650–750°C probably due to diffusion controlled film growth being the limiting process. At temperatures higher than 750°C, deposition profile decreased with increasing temperatures which may be attributed to decomposition of [Zr(OPr\textsubscript{3})\textsubscript{2}(tbaoac)\textsubscript{2}] in the gas phase or due to the possible pre-reactions that may take place in the gas phase.

<table>
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<th>T\textsubscript{deposition} [°C]</th>
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</tbody>
</table>

Table 1: Observed film thickness and growth rates for ZrO\textsubscript{2} films obtained from [Zr(OPr\textsubscript{3})\textsubscript{2}(tbaoac)\textsubscript{2}] (1).
3.3.5 Influence of deposition pressure on the crystal phase and morphology of ZrO$_2$ films

In order to study the influence of reactor pressure on the quality of ZrO$_2$ films obtained from [Zr(OPr)$_2$(bacoac)$_2$] precursor, depositions were carried out in the temperature range between 400–700°C with 50 mbar deposition pressure in the absence of oxidant.

No change in the crystal structure of ZrO$_2$ was found, and tetragonal phase was the only phase identified by X-ray diffraction. As the deposition temperature increased, the intensity of the most prominent diffraction peak ($2\theta = 29.81^\circ$) corresponding to (101) reflex increased suggesting polycrystalline nature of the films at elevated temperatures. EDAX and RBS measurements performed on the as-deposited films revealed presence of Zr and O in the films. In addition, RBS analysis indicated homogeneous films with $\sim$ 15–20 at % (± 5 %) carbon content in the films. With increasing substrate temperature, the impurity content was found to decrease compared to 10 mbar deposition pressure. Relatively thicker films were obtained with 50 mbar deposition pressure. For example, ZrO$_2$ film grown at 550°C using 10 mbar as deposition pressure was found to be 530 nm thick whereas the film at same substrate temperature grown using 50 mbar as pressure gave 650 nm thick ZrO$_2$ film. Flat and cross-sectional SEM view of a 550°C grown annealed ZrO$_2$ film is shown in figure 8. Well defined oval shaped grains of zirconia with the average grain size varying between 0.4–0.5 µm are obtained and the film is 680 nm thick.

![Figure 8: Flat (left) and cross-sectional (right) SEM micrograph of a 550°C grown ZrO$_2$ film.](image-url)
3.3.6 Influence of reactive gas on the ZrO$_2$ films

Since about 23 atomic % of carbon was detected in the ZrO$_2$ films obtained without using any reactive gas, depositions were carried out under oxygen atmosphere with an aim to achieve carbon free zirconia films at lower deposition temperature. Thin films of ZrO$_2$ were grown in the temperature region of 400–800°C and employing 100 sccm of oxygen as additional oxidation source. Unlike tetragonal phase of ZrO$_2$ films obtained in absence of oxygen, monoclinic phase which is the low temperature stable phase was analysed as the predominant ZrO$_2$ phase in presence of oxygen. As the deposition temperature increased, intensity of the most prominent peaks increased suggesting improvement in the crystallinity. Small diffraction peak around $2\theta = 30.3^\circ$, corresponding to the tetragonal and/or cubic (111) reflection was observed at all deposition temperature. Onset of crystallisation was found at 400°C which is 50 degrees lower than films grown in absence of oxygen. SEM images of the as-deposited ZrO$_2$ films at various deposition temperatures revealed dense and homogeneous surfaces as shown in Figure 9. Almost similar oval shaped grains (average grain size: 400 nm) with rough surfaces were observed at 550°C. The grain shape was not significantly changed in the temperature range between 600–700°C but the average grain size varied between 225–430 nm at 600°C to 200–375 nm at 700°C. At temperatures above 650°C, mixed grain shapes were obtained. AFM roughness of 5.83 nm was obtained at growth temperature of 550°C using compound 1. EDAX analysis revealed presence of elemental Zr and O and the stoichiometric composition was obtained from RBS spectroscopy. RBS analysis carried out on different ZrO$_2$ films indicated the films to be very homogeneous and confirmed presence of Zr to O ratio as 1:2.3 throughout the films. Within the detection limits of RBS spectroscopy (approximately 2 at. %), no carbon content was observed. Figure 10 shows the RBS spectra of ZrO$_2$ film grown at a substrate temperature of 600°C. The straight line in the figure indicates the modelled spectra of the formula ZrO$_2$. From the RBS data it seems apparent that oxygen significantly helps in achieving clean decomposition and producing high-quality films. Figure 11 shows the variation of growth rate as a function of substrate temperature. Minimum growth rate of 3.75 nm min$^{-1}$ was obtained at 400°C and the maximum of 11.95 nm min$^{-1}$ was calculated at 600°C. Growth rate of 3.75 nm min$^{-1}$ is significantly high compared to the growth rate of 0.87 nm min$^{-1}$ obtained at 400°C for ZrO$_2$ films deposited in the absence of oxygen. Therefore growth rate results obtained using compound 1 in the presence and in the absence of oxygen indicate that
oxygen has an apparently positive effect on the rate of ZrO$_2$ film growth. It is worthwhile to mention here that the growth rate results are presented independent of the effects of feed rate.

Figure 9: SEM images of ZrO$_2$ films at substrate temperatures of a: 550°C, b: 600°C, c: 650°C and d: 700°C on Si(100).

Figure 10: RBS plot of a ZrO$_2$ film grown on Si(100) at 600°C using compound 1 under 100 sccm oxygen flow.

Figure 11: Growth rate as a function of increasing substrate temperature.
3.3.7 Summary

ZrO$_2$ films were successfully grown using $[\text{Zr(OPr}^3\text{)}_2(\text{tbaoac})_2]$ as precursor in the absence of oxygen and in the presence of oxygen as additional oxidation source. Influence of reactor pressure on the films deposited in absence of oxygen was also studied. The precursor was liquid at the operating vaporiser temperature of 90°C. While threshold temperature for film deposition was 400°C, reports exists in literature where using $[\text{Zr(OPr}^3\text{)}_2(\text{thd})_2]$, film deposition was possible at 350°C by LI-MOCVD. Growth rates were significantly higher in the case of oxygen deposited zirconia films and the maximum growth rates with and without oxygen were found at 600°C. No change in the ZrO$_2$ crystal phase was found with increasing deposition pressure of and tetragonal phase was the only crystal phase detected. However, in the presence of oxygen as reactive gas, monoclinic phase of ZrO$_2$ was found to be the predominant phase. SEM analysis showed the films to be dense and uniform. RBS spectroscopy indicated formation of carbon free ZrO$_2$ films (RBS detection limit is $\sim$ 2 at. %) at temperatures as low as 400°C using oxygen as the reactive gas.

3.4 MOCVD of ZrO$_2$ films using $[\text{Zr(OBu}^1\text{)}_2(\text{tbaoac})_2]$ as precursor

3.4.1 Film growth conditions

Thin films of ZrO$_2$ were deposited over wide temperature range of 350–700°C using a home-built horizontal cold-wall CVD reactor (base pressure: $10^{-6}$ mbar). All depositions were carried out on 1 x 1 cm$^2$ Si(100) substrates which were thoroughly cleaned prior to film deposition. Although, it was possible to grow oxide films without using any external oxidant, CVD was performed under oxygen (100 sccm) to reduce the carbon incorporation into the films. For a typical ZrO$_2$ film deposition experiment, 110 mg precursor (compound 5) was heated upto a set vaporiser temperature of 90°C in an air bath and films were deposited over a period of 90 min as a function of substrate temperature employing 10 mbar deposition pressure and high purity nitrogen (99.9999 %, 100 sccm) as the carrier gas.
3.4.2 Phase analysis

The crystallinity of the as-deposited films were studied by X-ray diffraction. No film growth was observed on the Si substrate at deposition temperature of 350°C and therefore XRD analysis was performed on the films grown between 375–700°C. Amorphous ZrO$_2$ film was obtained at 375°C, while polycrystalline films were obtained at higher temperatures. Reflexes corresponding to the monoclinic ZrO$_2$ were detected over the whole deposition range and hence the monoclinic phase was attributed as the predominant zirconia phase. At temperatures above 550°C, ZrO$_2$ films showed textured growth in the 020 ($2\theta = 34.1$) direction as can be seen in figure 12. The onset of film growth was marked at 375°C which is lower compared to the ZrO$_2$ films obtained from [Zr(OPr$_3$)$_2$(tbaoac)$_2$] at minimum deposition temperature of 400°C.

![XRD pattern of ZrO$_2$ films grown on Si(100) displaying 020 as the preferred orientation at temperatures above 550°C using compound 1. * indicate reflex from the Si(100) substrate.](image)

3.4.3 Morphology and film composition

The surface morphology of the ZrO$_2$ films was probed by scanning electron microscopy (SEM). The films adhered strongly to the underlying substrate and it can be seen from figure 13 that the films display a granular morphology with the average grain size varying between 80–100 nm. The grains are elongated in shape with rough grain edges and the cross section view shows dense ZrO$_2$ film at 600°C (Figure 13 (d)). Surface roughness of the film was
studied with atomic force microscopy (AFM) and figure 14 shows the AFM pictures of a 600 °C deposited ZrO$_2$ film on Si substrate. The RMS roughness of ZrO$_2$ films was found to increase with increasing film crystallinity at higher substrate temperatures. For example, RMS roughness of a 450°C deposited ZrO$_2$ film was 3.4 nm whereas the roughness at 600°C was 15.7 nm. EDAX analysis showed the presence of Zr and O in the films deposited. The composition and the thickness of the films was checked regularly by RBS spectroscopy and the analysis, revealed signals from Zr as well as from O in the layer. The experimental curve fitted well with the simulated curve for ZrO$_2$. As an illustrative example, RBS spectrum of a ZrO$_2$ film deposited at substrate temperature of 550°C is shown in figure 15. Stoichiometric ratio of Zr:O in the figure as well as in rest of the ZrO$_2$ film samples obtained at different deposition temperatures, was found to be 1:2 and no hints for carbon contamination within the detection limit of RBS spectroscopy was observed.Thickness of the ZrO$_2$ film at deposition temperature of 550°C was 420 nm.

Figure 13: SEM images of ZrO$_2$ films deposited at, a: 500°C, b: 550°C, c: 600°C and d: 600°C (cross section).
Figure 14: AFM micrograph (topographical and cross-sectional) of ZrO$_2$ film deposited on Si(100) substrate displaying RMS value of 15.7 nm at 600°C.

3.4.4 Growth rate

The variation in ZrO$_2$ growth rate, calculated from the thickness obtained by RBS experiments as a function of substrate temperature for [Zr(OBu$_t^1$)$_2$(tbaoac)$_2$] is shown in figure 16 (left). The growth rates were also calculated from the mass deposited over 1 by 1 cm$^2$ Si(100) substrates assuming the ZrO$_2$ density of 5.6g cm$^{-3}$ (monoclinic) and were found comparable with the results obtained from RBS spectroscopy. It should be noted that the growth rate results presented here are irrespective of the effects of feed rate. The growth rate increased in the temperature range 375–600°C. At higher temperatures (650°C and above) the growth rate were found to decrease and this may be attributed to the decomposition of the precursor in the gas phase. A systematic comparison is made between the growth rates obtained for ZrO$_2$ films grown using [Zr(OBu$_t^1$)$_2$(tbaoac)$_2$] and [Zr(OPr$_i^1$)$_2$(tbaoac)$_2$] under equivalent growth conditions in the same reactor (Figure 16 (right)). The results indicated that, relatively thinner ZrO$_2$ films were deposited using compound 5. Maximum growth rate obtained for [Zr(OBu$_t^1$)$_2$(tbaoac)$_2$] was of the order 5 nm min$^{-1}$ at 600°C and for [Zr(OPr$_i^1$)$_2$(tbaoac)$_2$] was 12.0 nm min$^{-1}$. Nevertheless, growth rates for compound 5 are comparable with the growth rates obtained using the standard [Zr(thd)$_4$] and other literature reported mixed alkoxide zirconium precursors for ZrO$_2$, although the rates are significantly lower than that of [Zr(OPr$_i^1$)$_4$][7]. For example, at deposition temperature of 500°C, growth rates obtained for [Zr(thd)$_4$], [Zr(acac)$_4$] and [Zr(OBu$_t^1$)$_2$(tbaoac)$_2$] were 3–4 nm min$^{-1}$, 6–7 nm min$^{-1}$ and 3.4 nm min$^{-1}$ respectively. [8]
Figure 15: RBS spectrum of a ZrO$_2$ film grown on Si(100) at 550°C using compound 5.

The growth rates for [Zr(OBu)$(t^{i}Pr)_{2}$(tbaoac)$_{2}$] were also comparable with that obtained for [Zr(OBu)$_{2}$(thd)$_{2}$] by LI-MOCVD at 500°C (growth rate: 1.25 nm min$^{-1}$).$^{[9]}$

Figure 16: Variation in the ZrO$_2$ growth rate as a function of substrate temperature. Left: [Zr(OBu)$_{2}$(tbaoac)$_{2}$] and right: comparison of the ZrO$_2$ growth rates for ■ [Zr(OPr)$_{2}$(tbaoac)$_{2}$] and ▲ [Zr(OBu)$_{2}$(tbaoac)$_{2}$].

3.4.5 Summary

Thin films of ZrO$_2$ have been deposited by MOCVD using a mixed ligand precursor [Zr(OBu)$_{2}$(tbaoac)$_{2}$]. Film growth results were compared with the results obtained from [Zr(OPr)$_{2}$(tbaoac)$_{2}$]. The [Zr(OBu)$_{2}$(tbaoac)$_{2}$] precursor deposited ZrO$_2$ films at lower growth
temperatures than \([\text{Zr(OPr} \cdot \text{Pr)}_2 \text{tbaoac)}_2]\), but the growth rate was significantly lower in the case of former precursor. Within the detection limit of RBS spectroscopy, no carbon contamination was found in the films. Compound 5 was found to provide comparable growth rates with the standard and literature reported precursors for deposition of ZrO\(_2\) films.

3.5 MOCVD of HfO\(_2\) films using \([\text{Hf(OBu} \cdot \text{Bu)}_2 \text{tbaoac)}_2]\) as precursor

3.5.1 Film growth conditions

HfO\(_2\) films were grown from \([\text{Hf(OBu} \cdot \text{Bu)}_2 \text{tbaoac)}_2]\), compound 7, over a wide temperature range of 375–700\(^\circ\)C in a horizontal cold-wall reactor operating under base pressure of 10\(^{-6}\) mbar. Hafnia films were deposited at 10 mbar pressure and employing carrier gas (nitrogen) and reactive gas (oxygen) flow of 100 sccm. Pre-weighed 1 \(\times\) 1 squares of Si(100) were used as substrate without removing the native oxide. During every experiment 110 mg precursor was held at a bubbler temperature of 100\(^\circ\)C for 90 min.

3.5.2 Phase analysis

MOCVD from \([\text{Hf(OBu} \cdot \text{Bu)}_2 \text{tbaoac)}_2]\) resulted in polycrystalline HfO\(_2\) films in the monoclinic crystal structure. The films were amorphous below 450\(^\circ\)C and increasing the substrate temperature showed increase in crystallinity of the films. Textured growth of HfO\(_2\) films with 002 (2\(\theta\) = 35.5\(^\circ\)) as the preferred orientation was observed at higher temperatures of 650\(^\circ\)C and above (figure 17). No diffraction peaks attributable to crystalline hafnium silicate were observed even at high deposition temperatures of 700\(^\circ\)C.
3.5.3 Morphology and film composition

Morphology as studied by SEM indicated dense and uniform HfO$_2$ films. Figure 18 (left) shows irregular microstructures of HfO$_2$ on the Si(100) deposited at 600°C with the average size varying between 40–80 nm. HfO$_2$ films grown from compound 7 were subjected to RBS analysis. In the spectra depicted in figure 18 (right) the signal from Hf and O can be seen clearly. A carbon content of 10 at. % (± 5%) needs to be included for understanding of the spectra. Slight mismatch between the observed and simulated curve at the Hf interface may be attributed to change in the stoichiometry at the surface or to the channelling effects.

Figure 17: XRD pattern of HfO$_2$ films grown at 550°C, 600°C and 650°C using compound 7. * indicates textured growth of HfO$_2$ in 002 direction.

Figure 18: SEM image (left) of a HfO$_2$ film deposited at 600°C and RBS spectrum (right) of a HfO$_2$ film deposited at 500°C from compound 7.
3.5.4 Growth rate

Table 2 lists the HfO$_2$ thickness and average growth rates calculated and that obtained from the RBS measurements. Growth rates were calculated from the weight gain of the silicon wafers and calculating the film thickness using density as 9.8 g cm$^{-3}$ for monoclinic HfO$_2$. Sharp increase in the HfO$_2$ growth rate (figure 19) was observed till 550°C after which the growth rate began to decrease. This may be due to lower thermal stability of the precursor leading to decomposition of the complex. Compared to analogous Zr-complex, [Hf(OBu)$_3$(tbaoac)$_2$] is thermally less stable in the gas phase as can be inferred from the MOCVD results obtained.

<table>
<thead>
<tr>
<th>$T_{\text{deposition}}$ [°C]</th>
<th>ZrO$_2$ thickness [nm]</th>
<th>Growth rate [nm min$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>RBS</td>
</tr>
<tr>
<td>400</td>
<td>148.49</td>
<td>157.50</td>
</tr>
<tr>
<td>500</td>
<td>187.32</td>
<td>177.30</td>
</tr>
<tr>
<td>550</td>
<td>338.33</td>
<td>284.0</td>
</tr>
<tr>
<td>600</td>
<td>188.54</td>
<td>152.83</td>
</tr>
<tr>
<td>650</td>
<td>150.81</td>
<td>176.0</td>
</tr>
<tr>
<td>700</td>
<td>129.64</td>
<td>137.0</td>
</tr>
</tbody>
</table>

Table 2: HfO$_2$ film thickness and growth rate calculated and growth as-obtained from the RBS experiments.

Figure 19: Dependence of HfO$_2$ film rate on the substrate temperature.

3.5.5 Summary

Monoclinic HfO$_2$ films were deposited by MOCVD in the temperature range 375–700°C from [Hf(OBu)$_3$(tbaoac)$_2$]. A carbon content of ~10 at. % (±5 %) was detected in the films by RBS spectroscopy. The onset of film growth was 400°C and is significantly lower compared to the conventional [Hf(thd)$_3$] precursor which requires higher substrate temperature of 500°C and above for HfO$_2$ film growth.
3.6 Deposition of zirconium-and hafnium silicate films by MOCVD

3.6.1 MOCVD experiments

Preliminary CVD experiments were conducted using the newly synthesised \([\text{Zr(OSiMe}_3\text{B}_2\text{B}_2\text{B}_{\text{tbaoac}}\text{B}_2\text{B}_{\text{acac}}}] (11)\) and analogous \([\text{Hf(OSiMe}_3\text{B}_2\text{B}_2\text{B}_{\text{tbaoac}}\text{B}_2\text{B}_{\text{acac}}}] (12)\) precursors to test their suitability for CVD applications. Films were deposited at substrate temperatures between 450-800°C employing 100 sccm of oxygen as the reactive gas and 200 sccm of nitrogen as the carrier gas which was passed through the precursor bubbler. Deposition pressure of the cold-wall reactor was set to 10 mbar and the precursors were kept at 125°C during 90 min of deposition time. No film deposition was observed at 1 mbar pressure with the above deposition parameters till 600°C. Before every deposition experiment, the base pressure was recorded which was of the order of $10^{-6}$ mbar.

3.6.2 Film characterisation

Zirconium and hafnium silicate films were successfully deposited using novel \([\text{Zr(OSiMe}_3\text{B}_2\text{B}_{\text{tbaoac}}\text{B}_2\text{B}_{\text{acac}}}]\) and \([\text{Hf(OSiMe}_3\text{B}_2\text{B}_{\text{tbaoac}}\text{B}_2\text{B}_{\text{acac}}}]\) precursors respectively. The metal silicate films deposited adhered strongly to the underlying silicon substrate. The threshold temperature for film deposition was 450°C using both precursors. Growth rates in the case of ZrSi$_x$O$_y$ films were of the order of 2.75 nm min$^{-1}$ at 600°C (film thickness was calculated using the weighted average density 5.4 g cm$^{-3}$ of zirconia and zircon. For binary ZrO$_2$–SiO$_2$ alloys deposited by MOCVD technique using \([\text{Zr(OSiMe}_3\text{B}_2\text{B}_{\text{acac}}\text{B}_2\text{B}_{\text{acac}}}]\) as precursor, Zürcher et al. obtained amorphous films till 525°C but no zircon (ZrSiO$_4$), tetragonal zirconium dioxide, or monoclinic zirconium dioxide phase was observed by XRD. However above 525°C, broad diffraction peaks of cubic ZrO$_2$ were noticed. Therrien et al. deposited binary ZrO$_2$–SiO$_2$ alloys with low silicon content by rapid plasma enhanced (RPE) CVD and found cubic zirconia in a matrix of amorphous ZrSi$_x$O$_y$ after rapid thermal annealing of the films.$^{[9]}$ In our case, amorphous as-deposited films were obtained at substrate temperatures of 400, 450 and 500°C. At 550°C, small reflexes which could be assigned to cubic ZrO$_2$ (111, 200, 222) started to appear which increased with increasing substrate temperatures but no particular texturing was observed. Also, reflexes due to cubic HfO$_2$ were seen at the substrate temperatures above
500°C in the HfSi$_x$O$_y$ films grown using [Hf(OSiMe$_3$)$_2$(tbaoc)$_2$]. SEM images of ZrSi$_x$O$_y$ and HfSi$_x$O$_y$ films showed homogeneous but featureless structures and the cross-sectional SEM images revealed dense nature of the films. Elemental composition and chemical stoichiometry was determined using RBS spectroscopy. The RBS analysis confirmed the presence of Zr, Si and O in ZrSi$_x$O$_y$ films (figure 20 (a)) and Hf, Si and O in HfSi$_x$O$_y$ films with varying stoichiometry of silicon and oxygen at different deposition temperatures. Within the detection limit of RBS experiment (approximately 2 at. %) no carbon content was found in the films except for a HfSi$_x$O$_y$ film deposited at 600°C which showed ~ 10 at. % (± 5 %) carbon content. The silicon content of the deposited silicate film was found to increase with increasing substrate temperatures which can be clearly seen in the HfSi$_x$O$_y$ films obtained at 550, 650 °C (figure 20 (b)).

![RBS plot of (a): ZrSi$_x$O$_y$ film grown at 600°C and (b) HfSi$_x$O$_y$ film grown at 550°C & 650°C.](image)

Figure 20: RBS plot of (a): ZrSi$_x$O$_y$ film grown at 600°C and (b) HfSi$_x$O$_y$ film grown at 550°C & 650°C.
3.6.3 Summary

Preliminary MOCVD results of Zirconium silicate and hafnium silicate films from single source \([\text{Zr(OSiMe}_3\text{)}_2(tbaoac)_2]\) and \([\text{Hf(OSiMe}_3\text{)}_2(tbaoac)_2]\) precursors using oxygen as oxidiser have been reported. Composition of the resulting film was dependent on the deposition temperature and the Si content in the films was found to increase with increasing substrate temperature. Crystallinity of the metal silicate films improved with increasing deposition temperature. From RBS spectroscopy, Zr- and Hf silicate films were analysed for no carbon content except for one hafnium silicate film deposited at 600°C which showed ~10 at. % carbon.

3.7 LI-MOCVD of ZrO\(_2\) films using \([\text{Zr(OPr}_i\text{)}_2(tbaoac)_2]\) as precursor

3.7.1 Film growth conditions

As mentioned before, the preliminary CVD experiments using the test MOCVD reactor (home-built) showed the potential of \([\text{Zr(OPr}_i\text{)}_2(tbaoac)_2]\) (1) for CVD applications. Therefore it was interesting to test compound 1 in an actual industrial tool. Thus accordingly, ZrO\(_2\) film depositions using \([\text{Zr(OPr}_i\text{)}_2(tbaoac)_2]\) were performed in state of the art commercial AIXTRON 2600G3 planetary reactor located at Institut für Festkörperforchung Jülich, equipped with a TRIJET liquid injection system, which allows deposition on 5 × 6 inch wafers simultaneously. Deposition parameters are summarised in table 3. The length of the injection pulses was kept at 0.8 ms, which corresponds to 5 µl/pulse and the period of the pulses was 0.32 seconds. From the total amount of precursor injected into the reactor the efficiency of the precursor incorporation into the film was determined from XRF by measuring the areal mass of the films. The efficiency of the precursor is defined as the ratio of the amount (moles) of respective element in the film deposited on all the five wafers (6 inch each) to the amount (moles) of element in the consumed precursor. Film depositions were carried out as a function of substrate temperature and also as a function of film thickness at 400, 500 and 600°C by varying the number of pulses.

Electrical properties of the films were studied after sputter deposition and patterning of Pt top electrodes with an electrode area of 0.0491 mm\(^2\). All measurements were carried out at room
temperature but in order to check the effect of heat-treatment, the MOS structures were annealed under nitrogen and oxygen at 550°C for 20 min.

### 3.7.2 Phase analysis

Crystalline structures of the as-deposited ZrO\(_2\) films on Si(100) and Pt/Ti/Si substrates were studied by X-ray diffraction with grazing angle X-ray and Bragg-Brentano geometries. The grazing angle XRD pattern of the zirconia films on silicon and platinum coated silicon substrates are shown in figure 21. On both substrate types, the films deposited at 400°C were amorphous and the onset of crystallisation was marked at 450°C.

<table>
<thead>
<tr>
<th>Precursor concentration</th>
<th>0.05 M in n-butylacetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor pressure</td>
<td>1.5 mbar</td>
</tr>
<tr>
<td>Evaporator temperature</td>
<td>110−225°C</td>
</tr>
<tr>
<td>Precursor injection rate</td>
<td>5(\mu)l/pulse</td>
</tr>
<tr>
<td>Pulse period</td>
<td>0.32 s</td>
</tr>
<tr>
<td>Carrier gas flow rate</td>
<td>Argon, 1000 sccm</td>
</tr>
<tr>
<td>Reactive gas flow rate</td>
<td>Oxygen, 200 sccm</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>400−700°C</td>
</tr>
</tbody>
</table>

**Table 3:** ZrO\(_2\) film deposition parameters for [Zr(OPr\(_3\))\(_3\)(thaoac)]\(_2\), (1).

At temperatures above 450°C, crystalline reflexes started to appear and the intensity of these reflex increased thereafter, suggesting improvement in the crystalline phase. The diffraction peak around 2\(\theta\) = 30.3° may correspond either to the tetragonal or to the cubic (111) reflex. But as the temperature of deposition increased, broad reflexes around 2\(\theta\) = 35° and 50° were seen in the XRD pattern. The broadness of these diffraction peaks is due to the overlap of (002) & (200) and (202) & (220) reflexes and hence tetragonal structure of ZrO\(_2\) was assigned as the predominant crystal phase in the films. It should be noted here that ZrO\(_2\) films grown using compound 1 in horizontal cold-wall reactor in presence of oxygen however, showed predominant reflexes of monoclinic ZrO\(_2\). This difference in the crystal phases may be due to the different reactor geometries and deposition techniques. Interestingly, at higher deposition temperature of 650°C and above, no reflex appeared for the ZrO\(_2\) films grown on Pt substrate. Therefore in order to check the orientation of the films, 0-20 scan was performed on the films.
and it was observed that the ZrO$_2$ films on Pt substrate at higher substrate temperatures (650°C and above) were strongly textured in the (111) direction as depicted in Figure 22. X-ray diffraction analysis was done on ZrO$_2$ films grown on silicon and platinised silicon substrates at 500°C and 600°C as a function of increasing film thickness. As expected the film crystallinity of ZrO$_2$ increased with the increasing film thickness at the two different deposition temperatures (figure 23 (a-d)).

![Grazing angle XRD pattern of ZrO$_2$ films deposited at 500°C (a and b) and 600°C (c and d) as a function of varying film thickness on Si and Pt/Ti/Si substrates respectively.]

**Figure 23:** Grazing angle XRD pattern of ZrO$_2$ films deposited at 500°C (a and b) and 600°C (c and d) as a function of varying film thickness on Si and Pt/Ti/Si substrates respectively.

### 3.7.3 Morphology

Surface morphology and roughness of the ZrO$_2$ films was studied with atomic force microscopy (AFM). The AFM micrographs and the RMS values plotted as a function of
substrate temperature are shown in figure 24 and figure 25. With the increasing deposition temperature, the measure of film roughness was found to increase on silicon as well as on platinum coated silicon substrate. However, the films grown on platinised silicon substrate were found to be relatively more rough than those deposited on the silicon substrate. It can be clearly taken from figure 25 that ZrO$_2$ films grown on Si substrate showed very slight variation in the film roughness of approximately 1 nm. This may be due to higher roughness of platinum coated silicon surface compared to the bare silicon surface. Granular but random microstructures between 200–500 nm in size were seen on the platinised silicon substrate and resulting in high film roughness of 8 nm at 700°C.

![AFM micrographs](image)

**Figure 24:** AFM micrographs (5 µm × 5 µm) of ZrO$_2$ films deposited on Si and Pt/Ti/Si substrate as a function of substrate temperature.

Comparison between the RMS roughness of amorphous (400°C) and crystalline (600°C) ZrO$_2$ films grown on Si substrate indicated relatively smoother surface in case of amorphous ZrO$_2$ film (RMS: 0.40 nm) than crystalline ZrO$_2$ film (RMS: 0.53 nm).
Surface morphology of ZrO$_2$ films on silicon substrate was also studied as a function of film thickness at 400, 500 and 600°C. The roughness was found to increase with increasing ZrO$_2$ film thickness which may be due to the enhanced grain growth with thickness. As a representative example, AFM micrographs of ZrO$_2$ film as a function of thickness series at 600°C are depicted in figure 26.

![AFM surface roughness of ZrO$_2$ films grown on Pt/Ti/Si and Si substrates as a function of deposition temperature.](image)

**Figure 25:** AFM surface roughness of ZrO$_2$ films grown on Pt/Ti/Si and Si substrates as a function of deposition temperature.

### 3.7.4 Growth rate

Thin film depositions were carried out as a function of increasing substrate temperatures and varying ZrO$_2$ film thickness at various deposition temperatures and the corresponding precursor efficiency (ZrO$_2$ growth rate) was studied. Growth rates were calculated from the thickness obtained by XRF measurements of ZrO$_2$ films grown on silicon as well as platinum coated silicon substrates. Table 4 and figure 27 lists the growth rate of ZrO$_2$ films deposited as a function of substrate temperature on Si and Pt/Ti/Si substrate. From figure 27, the growth rate was found to be strongly dependent on the susceptor temperature in the low and high temperature growth region. In the middle region of 500–600°C, growth rate remained independent of the substrate temperature. Highest growth rate was obtained in this region and the films in this temperature regime were crystalline as indicated by XRD. Compared to Si, the growth rates were higher on platinised silicon substrates which may be due to the lower activation energy of platinum (0.56 eV) substrate than the silicon substrate (0.75 eV).
Figure 26: AFM micrographs and RMS plot of ZrO$_2$ films grown on silicon substrate as a function of varying film thickness at 600°C.

As mentioned above the film growth rates were also calculated as a function of film thickness and systematic comparison is made between amorphous and crystalline ZrO$_2$ films deposited on Si and Pt/Ti/Si substrate. Figure 28 depicts thickness and precursor efficiency of a 400°C grown amorphous ZrO$_2$ films as a function of varying number of pulses and figure 29 depicts thickness and precursor efficiency of a 600°C grown crystalline ZrO$_2$ films as a function of varying number of pulses.

Film thickness was found to increase linearly with increasing number of pulses, thus indicating film uniformity. Significant variation in the film thickness was observed in the case of amorphous films than in the case of crystalline ZrO$_2$ films with increasing number of pulses, but in either case thicker films were deposited on platinum coated silicon substrate. In the kinetically controlled region, the temperature difference on the Pt/Ti/Si and Si substrate can cause such kind of variation.
Table 4: ZrO$_2$ film thickness and the growth rate as a function of substrate temperature obtained from compound 1. SA and PA stands for silicon (Si) and platinum coated silicon (Pt/Ti/Si) substrate respectively, near the edge of 6 inch wafer mask.

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Number of pulses</th>
<th>Deposition temperature [°C]</th>
<th>XRF thickness [nm]</th>
<th>% Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>SA</td>
<td>PA</td>
</tr>
<tr>
<td>Z_657</td>
<td>1000</td>
<td>400</td>
<td>3.8</td>
<td>6.4</td>
</tr>
<tr>
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<td>1000</td>
<td>450</td>
<td>9.3</td>
<td>15.3</td>
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<tr>
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<td>1000</td>
<td>500</td>
<td>18.2</td>
<td>21.8</td>
</tr>
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<td>Z_653</td>
<td>1000</td>
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</tr>
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<td>650</td>
<td>8.2</td>
<td>8.3</td>
</tr>
<tr>
<td>Z_659</td>
<td>1000</td>
<td>700</td>
<td>5.2</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Figure 27: Temperature dependence of growth rate of ZrO$_2$ films deposited on Si and Pt/Ti/Si substrate.

Unlike the film thickness trend observed for amorphous as well as crystalline ZrO$_2$ films, no systematic conclusion could be drawn from the precursor efficiency plots at 400 and 600°C. For amorphous films, in the lower pulse region the precursor efficiency reduced very slightly and later saturation in the precursor efficiency was observed with increasing number of pulses. In the case of crystalline films, efficiency of precursor incorporation increased significantly in the lower pulse region and slight variation occurred at higher pulses.
Figure 28: Thickness (a) and efficiency (b) of amorphous ZrO$_2$ grown at 400°C as a function of number of pulses. (SM and PM stands for silicon (Si) and platinum coated silicon (Pt/Ti/Si) substrate respectively, in the middle of 6 inch wafer mask.)

Figure 29: Thickness and efficiency of crystalline ZrO$_2$ grown at 600°C as a function of number of pulses on Si and Pt/Ti/Si substrates respectively. (SM and PM stands for silicon (Si) and platinum coated silicon (Pt/Ti/Si) substrate respectively, in the middle of 6 inch wafer mask.)

3.7.5 Electrical properties of ZrO$_2$ films

Metal oxide semiconductor capacitors were fabricated with platinum metal as the top electrode to evaluate the electrical properties in terms of capacitance–voltage (C–V) and current–voltage (I–V) characteristics of ZrO$_2$ films deposited from [Zr(OPr$_3$)$_2$(tbaoc)$_2$], (1) because of their
potential application as gate oxides. Electrical properties of ZrO$_2$ films were also studied for MIM structures employing platinum as the top and bottom electrode and the dielectric sandwiched between them. Results obtained from MIS [Pt/ZrO$_2$/p-Si(100)] and MIM [Pt/ZrO$_2$/Pt] capacitors are discussed separately. C–V measurements provide the equivalent oxide thickness (EOT) which is the thickness that the high-$\kappa$ layer would have if its dielectric constant were that of SiO$_2$ (3.9). In addition, from these measurements value of flatband voltage ($V_{fb}$) can be obtained and comparing the measured $V_{fb}$ with the one theoretically calculated, charge in the dielectric layer can be known. Figure 30 demonstrates C–V curves for a 31 nm (sample: Z_653 SA and thickness obtained from XRR) thick crystalline ZrO$_2$ film in MIS capacitor and effect of post annealing of Pt top electrode is examined. It is noteworthy that C–V curve measured on as-deposited and annealed films show significant hysteresis ($\Delta V_{fb}$ ~100 mV) which can be attributed to the charging and de-charging of interface traps when bias is swept between positive to negative voltages and backwards. However, for as-deposited ZrO$_2$ film (figure 30 a), a small hump in the C–V curve in the accumulation region is observed which disappears upon annealing under oxygen and nitrogen atmosphere at 550°C for 20 min (figure 30 b). The corresponding current–voltage (I–V) behaviour for the [Pt/ZrO$_2$/p-Si(100)] structures is shown in figure 31. For as-deposited ZrO$_2$ film the leakage current density was of the order of $10^{-7}$ A cm$^{-2}$ at bias voltage of 1 V whereas significant reduction in the leakage current ($10^{-8}$ A cm$^{-2}$) across the gate stack was observed after post annealing of the top Pt electrode.

The dielectric constant calculated from the accumulation capacitance considering simple parallel-plate capacitor was in the range 17.5–19.8 (bulk $\kappa$ for ZrO$_2$ is ~ 25) with 600°C deposited ZrO$_2$ films under different annealing conditions and the values are summarised in table 5. The largest value of measured capacitance in accumulation is 280 pF for nitrogen annealed MOS structure, which corresponds to $\kappa$: ~ 19.8, or EOT of 6.05 nm.

The C–V and I–V behaviour was also examined for the [Pt/ZrO$_2$/Pt] (MIM) structures with the ZrO$_2$ films grown at 600°C (figure 32). The C–V curve was flat thus indicating no voltage dependence. Almost symmetric current–voltage characteristics with leakage current of the order of $10^{-10}$ A cm$^{-2}$ at 1 volt was obtained which is much less than that obtained for the MIS structures. Dielectric constant values on the MIM structures were approximately 25 which are comparable with the bulk ZrO$_2$ effective permittivity. Since Si with native oxide is used as
substrate for MIS structures, formation of interfacial layer may cause reduction in the effective $\kappa$.

Figure 30: C–V curves for MIS structures on p-Si(100) demonstrating post-annealing effect of top electrode with ZrO$_2$ film grown at 600°C using compound 1.

Figure 31: I–V curves for MIS structures on p-Si(100) with ZrO$_2$ film grown at 600°C using compound 1.

<table>
<thead>
<tr>
<th>Area: 0.0491 mm$^2$</th>
<th>$C_{\text{accumulation}}$ [pF]</th>
<th>Current density [A cm$^{-2}$]</th>
<th>Dielectric constant [$\kappa$]</th>
<th>EOT [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{deposition}}$: 600°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As deposited</td>
<td>248</td>
<td>$2.4 \times 10^{-7}$</td>
<td>17.5</td>
<td>6.83</td>
</tr>
<tr>
<td>O$_2$ ann at 350°C/20 min</td>
<td>229</td>
<td>$2.02 \times 10^{-7}$</td>
<td>16.1</td>
<td>7.40</td>
</tr>
<tr>
<td>O$_2$ ann at 550°C/20 min</td>
<td>244</td>
<td>$4.38 \times 10^{-8}$</td>
<td>17.3</td>
<td>6.94</td>
</tr>
<tr>
<td>N$_2$ ann at 550°C/20 min</td>
<td>280</td>
<td>$2.60 \times 10^{-8}$</td>
<td>19.8</td>
<td>6.05</td>
</tr>
<tr>
<td>O$_2$ &amp; N$_2$ ann at 400°C/20 min</td>
<td>258</td>
<td>$8.5 \times 10^{-9}$</td>
<td>18.3</td>
<td>6.56</td>
</tr>
</tbody>
</table>

Table 5: Dielectric constant and EOT measured for the Pt/ZrO$_2$-p-Si(100) capacitor structures.
Figure 32: C–V, I–V and dielectric constant curves for the [Pt/ZrO$_2$/Pt] (MIM) structures with 68 nm thick ZrO$_2$ film grown on platinum coated silicon substrate at 600°C using compound 1.

### 3.7.6 Summary

Deposition characteristics have been investigated in a state of the art LI-MOCVD production tool and the ZrO$_2$ thin films were characterised by XRD, SEM and XRF. While the threshold temperature for film deposition was 400°C using compound 1, reports exists in the literature where using [Zr(OR)$_2$(thd)$_2$]$^{[10]}$, film deposition was possible at 350°C. The growth of PZT films by LI-MOCVD using [Pb(thd)$_2$], [Zr(thd)$_4$] and [Ti(OPr$_i$)$_2$(thd)$_2$] as precursors is often critical because of the high thermal stability of [Zr(thd)$_4$] which needs temperatures > 500°C for film growth in comparison to [Pb(thd)$_2$] (450–500°C)$^{[11]}$. This clearly indicates that
[Zr(OPr^i)₂(tbaoac)_2] is a more suitable precursor than [Zr(thd)_4] for growing PZT films by MOCVD. The electrical properties for MIS and MIM capacitor structures with ZrO₂ films have been investigated and the values for permittivity and leakage currents seem promising for gate oxide applications.

### 3.8 Summary of Chapter 3

The following precursors were successfully used for depositing metal oxide and metal silicate films by MOCVD and the results are summarised in table 6.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Film &amp; deposition conditions</th>
<th>Evaporator temp. [°C]</th>
<th>Deposition temp. [°C]</th>
<th>Crystal phase</th>
<th>Carbon content [RBS at. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zr(OPr^i)₂(tbaoac)_2]</td>
<td>ZrO₂, 10 mbar</td>
<td>90</td>
<td>400–900</td>
<td>tetragonal</td>
<td>20–23</td>
</tr>
<tr>
<td>[Zr(OPr^i)₂(tbaoac)_2]</td>
<td>ZrO₂, 50 mbar</td>
<td>90</td>
<td>400–700</td>
<td>tetragonal</td>
<td>15–20</td>
</tr>
<tr>
<td>[Zr(OPr^i)₂(tbaoac)_2]</td>
<td>ZrO₂, 10 mbar, O₂</td>
<td>90</td>
<td>400–800</td>
<td>monoclinic</td>
<td>ND</td>
</tr>
<tr>
<td>[Zr(Obu^t)₂(tbaoac)_2]</td>
<td>ZrO₂, 10 mbar, O₂</td>
<td>90</td>
<td>350–700</td>
<td>monoclinic</td>
<td>ND</td>
</tr>
<tr>
<td>[Hf(OBu^t)₂(tbaoac)_2]</td>
<td>HfO₂, 10 mbar, O₂</td>
<td>100</td>
<td>375–700</td>
<td>monoclinic</td>
<td>10</td>
</tr>
<tr>
<td>[Zr(OSiMe₃)x₂(tbaoac)_2]</td>
<td>ZrSi₃O₇, 10 mbar, O₂</td>
<td>125</td>
<td>450–800</td>
<td>cubic (ZrO₂)</td>
<td>ND</td>
</tr>
<tr>
<td>[Hf(OSiMe₃)x₂(tbaoac)_2]</td>
<td>HfSi₃O₇, 10 mbar, O₂</td>
<td>125</td>
<td>450–800</td>
<td>cubic (HfO₂)</td>
<td>ND</td>
</tr>
</tbody>
</table>

**Table 6:** MOCVD results obtained from novel organometallic precursors reported in Chapter 2. ND stands for ‘not detected’.
3.9 References

4 Evaluation of thermal properties of novel Zr and Hf complexes as precursors for MOCVD

Abstract

Properties of novel mixed ligand complexes of zirconium and hafnium have been studied in detail by means of thermogravimetry (TG) and differential thermal analysis (DTA) in order to investigate their suitability as MOCVD precursors. From TG/DTA and the evaporation rate at different temperatures, the mixed alkoxide/β-ketoester, mixed alkoxide/β-ketoamide and mixed silinolate/β-ketoester complexes of zirconium and hafnium were found as potential MOCVD precursors for depositing metal oxide and metal silicate thin films. Thermal properties of the novel precursors have also been compared with the thermal properties of literature known compounds employed as MOCVD precursors for obtaining ZrO$_2$ and HfO$_2$ films.

4.1 Introduction

It is well known that volatile metalorganic precursors play a vital role in achieving desired thin films by chemical vapor deposition (CVD). CVD process require precursors possessing suitable inherent properties such as sufficient volatility, long-term stability, moderate temperature window between precursor vaporisation and decomposition, high purity and low toxicity.$^{[1]}$

Noteworthy efforts have been directed towards the designing of metalorganic precursors for group IVb metal oxides and silicates.$^{[2]}$ Before testing the compound for MOCVD, it becomes necessary to know the precursor vaporisation and decomposition temperature and also whether the precursor is able to deliver constant mass transport over long periods of time which later helps in optimising the bubbler temperature during actual MOCVD experiments.

To evaluate a metal complex as a CVD precursor, thermal analysis (TA) serves as a very informative tool.$^{[3]}$ TA comprises a group of techniques like TGA, DTA, DSC, EGA etc. TGA is a technique in which the mass of a substance is measured either as a function of controlled
temperature or as a function of time at a set temperature (isothermal measurements). DTA involves measurement of the temperature difference that develops between a sample and a reference material when both are subjected to identical heat treatments. Usually, wealth of information is obtained by coupling both, thermogravimetry and differential thermal analysis and is often called as simultaneous TG/DTA. DSC relies on differences in energy required to maintain the sample and an inert reference material at an identical temperature. Information such as temperature of phase transition (for example, solid-solid, liquid-solid, temperature of crystallisation etc), heat of formation, heat capacity, reaction enthalpies etc are revealed by DSC. The effect of substitution of the chemical groups in the ligand sphere of the complex and thereby the changes in the volatility can be systematically studied by examining a thermogram. Temperature onset of vaporisation, melting point, temperature at which the complex under study decompose are some of the information revealed by TG/DTA. TA also provides information on the sublimation rates or evaporation rates (in case of a liquid or a low melting solid precursor) at a set temperature over long periods of time (isothermal studies). This is of particular importance to optimise the precursor vapouriser temperature at which the bubbler is maintained during CVD. In addition, TG/DTA gives reliable comments on the long-term stability of the precursor and also the purity of the sample from each precursor synthesis batch can be interpreted by analysing the TG profile. In this chapter detailed thermogravimetric analyses are performed on the newly synthesised zirconium and hafnium metalorganic complexes from Chapter 2 to assess their suitability as CVD precursors.

4.2 Experimental aspects

Synthesis of compounds namely [Zr(OPr)i2(tbaoac)2] (1), [Zr(OPr)i2(thd)2] (2), [Zr(OBu)2(tbaoac)2] (5), [Hf(OBu)2(tbaoac)2] (7), [Zr(OSiMe3)2(tbaoac)2] (11) and [Hf(OSiMe3)2(tbaoac)2] (12) is reported in Chapter 2. For comparison, the known zirconium and hafnium precursors namely [Zr(thd)4], [Zr(OPr)i2(thd)2] and [Hf(Pr)i2(tbaoac)2] were prepared by literature procedures and are also reported in Chapter 2.\cite{4, 5} All compounds were characterised by elemental analysis, NMR, Mass and IR spectroscopy before analysing for TG/DTA. Thermal analyses were performed using an EXSTAR TG/DTA 6200 SII thermogravimetric analyser from Seiko and employing a heating rate of 10°C min⁻¹. All TG/DTA analyses were carried out under flowing atmosphere of nitrogen (99.9999 %) and
keeping flow rate of 300 ml min\(^{-1}\). In order to study the reactivity of the newly synthesised complexes towards moisture, 99.999 % purity nitrogen (containing 5.0 ppm H\(_2\)O) was used. Evaporation rates of Zr and Hf compounds were measured as a function of time at constant temperature. For a typical isothermal experiment, 10 mg of finely ground sample was heated to a set temperature employing heating rate of 10°C min\(^{-1}\) and maintained constant at the set temperature for 250 min.

Gaseous fragments present in the exhaust gases during simultaneous TG/DTA measurement of compound 1 were detected by a ThermoStar 200 quadrupole mass spectrometer from Balzers coupled to a thermogravimetric analyser from Netzsch. About 20 mg of sample was filled in a ceramic crucible under argon atmosphere and the sample was heated from ambient to 600°C employing a heating rate of 5°C min\(^{-1}\) and argon (99.9999 %) flow of 100 sccm.

### 4.3 Results and discussion

Thermogravimetric analysis was carried out on the synthesised complexes to get detailed insight of their physical characteristics and thus evaluate them as MOCVD precursors. For systematic interpretation of the results, the zirconium and hafnium complexes are categorised according to the modified \(\beta\)-diketone, namely \(\beta\)-ketoester and \(\beta\)-ketoamide ligands used.

#### 4.3.1 Mixed alkoxide/\(\beta\)-ketoester complexes of zirconium and hafnium

Compounds studied in this section are mixed \(\beta\)-ketoester/isopropoxide or tert-butoxide complexes of Zr and Hf obtained by reacting one equivalent of zirconium isopropoxide with two equivalents of \(\beta\)-ketoester ligand.

Simultaneous TG/DTA of \([\text{Zr(OPr}^i\text{)}_2\text{(tbaoac)}_2]\) (1) at room temperature is displayed in figure 1. As seen from the TG curve, compound 1 begins to vaporise at temperatures as low as 120°C with maximum weight loss occurring at about 170–175°C. In addition, the TG/DTA curve indicates decomposition of compound 1 to be a one step process which is completed at around 300°C. Significantly lower amount of residue (9.3 %) was left behind after decomposition of \([\text{Zr(OPr}^i\text{)}_2\text{(tbaoac)}_2]\) compared to the theoretical weight % of ZrO\(_2\) (23.6 %) thus indicating
almost quantitative vaporisation. It is strongly expected that TG/DTA measurements performed under vacuum will lead to complete vaporisation of compound 1 with almost zero residue. A broad endothermic peak at around 45°C in the DTA marks the melting of 1 which was confirmed by melting point measurement in sealed glass capillary. High volatility and adequate temperature window between evaporation and decomposition makes compound 1 a potential precursor for depositing ZrO\(_2\) films by CVD. In order to observe reactivity and stability of 1 against moisture, thermal analysis was carried out under flowing atmosphere of nitrogen, containing 5 ppm water.

**Figure 1:** Simultaneous TG/DTA of [Zr(OPr\(_i\)P\(_2\))]\(_2\)(tbaoac)\(_2\)] employing a heating rate of 10°C min\(^{-1}\) under atmospheric pressure.

**Figure 2:** Comparative TGA plots of [Zr(OPr\(_i\)P\(_2\))]\(_2\)(tbaoac)\(_2\]. (a) freshly prepared, (b) after storing in glove box for about 365 days and (c) with 5 ppm of water.

Compound 1 revealed moderate reactivity towards moisture which can be understood from high amount of residue left after the decomposition was complete. Thus in presence of water, the prevailing process is certainly decomposition towards ZrO\(_2\) with an excellent match in the residue left in the crucible (23.9 %) and that of theoretically calculated ZrO\(_2\) amount of 23.6 wt % (Figure 2 (b)). This makes compound 1 highly suitable also as an ALD precursor for growing ZrO\(_2\) films with alternating pulsing of precursor solution and water. In addition, figure 2 (c) illustrates the thermogram measured after storing the precursor in glove box for about 365 days. Almost no change in the thermal behaviour was observed except for slight increase (~ 3 wt %) in the residue compared to the freshly prepared sample, thus suggesting optimal precursor ‘shelf-life’ and run-to-run reproducibility for CVD.
The main aim of synthesising mixed ligand complexes of Zr and Hf by introducing specific variations in the ligand sphere was to tune the precursor thermal properties to ensure stable and easy handling together with decomposition at lower temperatures compared to the standard precursors. In figure 3, thermogram of I is compared with standard literature known precursors for ZrO$_2$ films. Onset of evaporation temperature for I is comparable to [Zr(OPr$_3$)$_2$(thd)$_2$] and is higher than [Zr(OPr$_3$)$_4$]. Compound I volatilises at relatively low temperatures (∼150°C) compared to [Zr(thd)$_4$] (∼275°C). Lowering the onset of volatilisation temperature for compound I by about 100°C compared to [Zr(thd)$_4$], is expected to make the precursor more compatible with [Pb(thd)$_2$] (∼170°C) during the growth of PZT thin films. Close matching of thermal window (volatilisation and decomposition) between individual precursors will be an added advantage in the case of CVD of multicomponent materials.

![Figure 3](image_url)

**Figure 3**: Comparative TGA plots of (a) [Zr(OPr$_3$)$_2$(thaoac)$_2$] (1), (b) [Zr(OPr$_3$)$_4$], (c) [Zr(thd)$_4$] and (d) [Zr(OPr$_3$)$_2$(thd)$_2$] as reference compounds.

Isothermal studies carried out on compound I (figure 4) revealed that the compound vaporise at a constant and appreciable rate for long periods of time (>200 min) in the temperature range 150–175°C, which is an ideal requirement for a CVD precursor so as to ensure reproducibility by having a constant precursor vapour transport. At isothermal temperature of 200°C, saturation of mass transport is observed probably due to the beginning of decomposition. Evaporation rates calculated at isothermal temperatures of 125, 150 and 175°C (figure 5) exhibits highest evaporation rate of $4.46 \times 10^{-2}$ mg min$^{-1}$ at 175°C.
Figure 4: Weight loss as a function of time (isothermal plot) at (a) 125°C, (b) 150°C and (c) 175°C for \([\text{Zr(OPr}^i\text{P}^i\text{P}^i]_2\text{tbaoac}_2]\) with heating rate of 10°C min\(^{-1}\) and \(N_2 = 300\) ml min\(^{-1}\).

Figure 5: Evaporation rate as a function of reciprocal temperature obtained for \([\text{Zr(OPr}^i\text{P}^i\text{P}^i]_2\text{tbaoac}_2]\) employing a heating rate of 10°C min\(^{-1}\) and \(N_2 = 300\) ml min\(^{-1}\).

Thermogravimetry coupled with mass spectrometry is a useful technique to detect components in the exhaust gases which are produced as a result of precursor decomposition. This may give significant hints in formulating plausible precursor decomposition pathways which further helps in getting useful insights into the actual CVD process.

\([\text{Zr(OPr}^i\text{P}^i\text{P}^i]_2\text{tbaoac}_2]\) was subjected to TG-MS analysis and the major fragments detected in the exhaust gases are shown in table 1. The major fragments detected with maximum intensity were that of 2-methylpropene (a.m.u.: 56), acetone (a.m.u.: 58) and acetylketene (a.m.u.: 84) in addition to carbon monoxide, ethyl and carbon dioxide species. In figure 6, intense peak corresponding to 2-methylpropene at a.m.u. 56 can be clearly identified.

Interestingly, the above species were also detected in the FTIR spectra obtained after thermolysis of the \(\beta\)-ketoester (tert-butylacetocetate) ligand and analogous \([\text{Ti(OPr}^i\text{P}^i\text{P}^i]_2\text{tbaoac}_2]\) complex studied by Matrix-isolation technique.\(^6\) Thus in the case of \([\text{Zr(OPr}^i\text{P}^i\text{P}^i]_2\text{tbaoac}_2]\) too the decomposition mechanism is expected to occur, liberating acetylketene and acetone. Matrix-isolation FTIR spectroscopy is a complementary method to mass spectroscopy and is a very informative technique for understanding the molecular decomposition mechanisms in the gas phase during a CVD process.
Simultaneous TG/DTA of \([\text{Zr(OBu)}_2(\text{tbaoac})_2]\) (5) is depicted in figure 7a and a comparative thermogram of the same with 5.0 and 0.5 ppm of water is represented in figure 7b. TG/DTA curve indicates the precursor to be a low melting solid at 75°C and that it vaporises almost quantitatively in the region 150–200°C. Compound 5 begins to decompose at around 230°C and completion of the decomposition process is observed at about 300°C.

**Figure 7:** (a) Simultaneous TG/DTA of \([\text{Zr(OBu)}_2(\text{tbaoac})_2]\) and (b) comparative TGA plot of \([\text{Zr(OBu)}_2(\text{tbaoac})_2]\) in presence of 0.5 and 5.0 ppm of water.
Chapter 4

A residue of 8.9 % which could not be assigned to the theoretical ZrO\textsubscript{2} content of 22.3 % was obtained and hence it is anticipated that TG/DTA measurements of 5 carried out in vacuum would give clean and quantitative evaporation. Compound 5 showed some reactivity against moisture which could be understood from the high amount of residue left behind by 5 when TG/DTA was performed under nitrogen containing 5.0 ppm of water. As in the case of compound 1, [Zr(OBu)\textsubscript{2}(tbaoc)\textsubscript{2}] was analysed isothermally at four different temperatures of 75, 100, 125 and 150°C for more than 240 min to determine the evaporation rate. According to the isothermal curves presented in figure 8, [Zr(OBu)\textsubscript{2}(tbaoc)\textsubscript{2}] showed low vaporisation profile between 75–125°C and maximum vapour transport at 150°C. The corresponding evaporation rates are calculated and depicted in figure 9. As concluded from figure 8, highest evaporation rate of $4.8 \times 10^{-2}$ mg min\textsuperscript{-1} is obtained at 150°C.

Figure 8: Weight loss as a function of time (isothermal plot) at (a) 75°C, (b) 125°C, and (c) 150°C for [Zr(OBu)\textsubscript{2}(tbaoc)\textsubscript{2}] employing heating rate of 10°C min\textsuperscript{-1} and N\textsubscript{2} = 300 ml min\textsuperscript{-1} under atmospheric pressure.

Thus from the simultaneous TG/DTA and isothermal studies performed indicate that [Zr(OBu)\textsubscript{2}(tbaoc)\textsubscript{2}] (5), shows promise as a CVD precursor and in order to obtain sufficient and constant mass transport during a CVD process, the precursor vaporiser temperature should be set at a temperature higher than 125°C. It is important to note that since the thermal analyses were performed at normal temperature pressure (NTP), the bubbler temperature is significantly lowered when actual CVD is performed under reduced pressure. Therefore, in the case of CVD experiments performed using 5 reported in chapter 3, the ZrO\textsubscript{2} films, which were deposited under 10 mbar pressure, the precursor bubbler was maintained at 90°C.
Figure 9: Evaporation rate as a function of reciprocal temperature obtained for [Zr(OBu\textsubscript{i})\textsubscript{2}(tbaoac)\textsubscript{2}] employing a heating rate of 10°C min\textsuperscript{-1} and N\textsubscript{2} = 300 ml min\textsuperscript{-1} under atmospheric pressure.

To study the effect of ligand variation on the precursor volatility and decomposition temperature, TG profile of compounds 1 and 5 and the reference compound [Zr(thd)\textsubscript{4}] were compared and are illustrated in figure 10a. The onset of evaporation is lowered in the case of [Zr(OBu\textsubscript{i})\textsubscript{2}(tbaoac)\textsubscript{2}] by about 20–25°C compared to [Zr(OPr\textsubscript{i})\textsubscript{2}(tbaoac)\textsubscript{2}] and by about 125°C than [Zr(thd)\textsubscript{4}]. Higher volatility of 5 may be due to the sterically demanding tert-butoxide groups present on the Zr metal centre. Among the pure alkoxides of zirconium, the metal tert-butoxides are more volatile than their corresponding isopropoxide analogues due to more steric bulk present in the former case and have been employed in the past to limit oligomerisation. The decomposition temperatures of 5 (~ 230°C) and 1 (~ 245°C) are comparable but the decomposition temperature of compound 5 is significantly less when compared to [Zr(thd)\textsubscript{4}] which decomposes at temperatures greater than 350°C. Isothermal measurement at 150°C (Figure 10b) also indicate [Zr(OBu\textsubscript{i})\textsubscript{2}(tbaoac)\textsubscript{2}] to be more volatile than the analogous [Zr(OPr\textsubscript{i})\textsubscript{2}(tbaoac)\textsubscript{2}].

From the TG analysis it can be inferred that inclusion of small but systematic variation in the ligand sphere such as replacing isopropoxide ligand with tert-butoxide group in the mixed isopropoxide/\(\beta\)-ketoester complex of zirconium gave rise to potential MOCVD precursor with significant improvement in the thermal properties.

<table>
<thead>
<tr>
<th>Isothermal temp. [°C]</th>
<th>1000/T [K\textsuperscript{-1}]</th>
<th>Evaporation rate [mg min\textsuperscript{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>2.87</td>
<td>2.5 \times 10\textsuperscript{-2}</td>
</tr>
<tr>
<td>125</td>
<td>2.51</td>
<td>3.9 \times 10\textsuperscript{-2}</td>
</tr>
<tr>
<td>150</td>
<td>2.36</td>
<td>4.8 \times 10\textsuperscript{-2}</td>
</tr>
</tbody>
</table>
Figure 10: Comparative plots of; a: TGA of \([\text{Zr(OBu}^t\text{P}^t\text{P})_2\text{B}_2\text{(tbaoac)}_2] (5)\), \([\text{Zr(OPr}^i\text{P}^i\text{P})_2\text{B}_2\text{(tbaoac)}_2] (1)\), with \([\text{Zr(thd)}_4]\) and b: isothermal curve of compound 1 & 5 at 150°C. ER stands for evaporation rate.

Figure 11 shows the TG/DTA plot of \([\text{Hf(OBu}^t\text{P}^t\text{P})_2\text{(tbaoac)}_2] (7)\) measured employing a heating rate of 10°C min\(^{-1}\) and 300 ml min\(^{-1}\) nitrogen flow from ambient to 500°C. The onset of weight loss is observed at around 145°C and maximum weight loss occurred till 230°C. From 230°C, the compound begins to decompose and the decomposition is completed at around 280°C after which temperature a residue of 16.9% was observed in the crucible. The residual amount is found lower than the theoretical HfO\(_2\) amount of 32.9%, thus indicating some evaporation. The initial sharp endothermic peak in the DTA curve at around 78°C indicates the melting of compound 7.

Compound 7 showed some reactivity towards water which is apparent from the high amount of residue (22.3%) left behind by \([\text{Hf(OBu}^t\text{P}^t\text{P})_2\text{(tbaoac)}_2]\) in presence of 5 ppm water (Figure 12). However, the residual amount does not fit to the theoretical amount of HfO\(_2\) calculated when the prevailing process is decomposition towards HfO\(_2\). Nevertheless reactivity towards water makes \([\text{Hf(OBu}^t\text{P}^t\text{P})_2\text{(tbaoac)}_2]\) a suitable precursor for growing HfO\(_2\) films by ALD process. Isothermal analysis was performed on compound 7 as a function of time and the plots are depicted in figure 13. \([\text{Hf(OBu}^t\text{P}^t\text{P})_2\text{(tbaoac)}_2]\) shows lower degree of vaporisation in the isothermal temperature range between 75–125°C. Since maximum vapour transport is observed at 150°C, bubbler should be maintained at a temperature higher than 150°C to ensure sufficient mass transport to the deposition zone during actual CVD experiment. During MOCVD of \([\text{Hf(OBu}^t\text{P}^t\text{P})_2\text{(tbaoac)}_2]\) the bubbler temperature was set to 100°C and HfO\(_2\)
depositions were carried out under 10 mbar pressure and employing 100 sccm oxygen as external oxidant.

**Figure 11:** Simultaneous TG/DTA of [Hf(OBu)_{2}(tbaoac)_{2}] employing heating rate of 10°C min$^{-1}$ and 300 ml min$^{-1}$ nitrogen flow.

**Figure 12:** Comparative TGA plot of [Hf(OBu)_{2}(tbaoac)_{2}] in presence of 0.5 and 5.0 ppm of water and employing heating rate of 10°C min$^{-1}$ under atmospheric pressure.

**Figure 13:** Weight loss as a function of time (isothermal plot) at (a) 75°C, (b) 100°C, (c) 125°C and (d) 150°C for [Hf(OBu)_{2}(tbaoac)_{2}] employing a heating rate of 10°C min$^{-1}$ and N$_2$ = 300 ml min$^{-1}$ under atmospheric pressure.

Effect of ligand substitution on the thermal properties of the precursor was investigated by comparing the TG as well as the isothermal plots of [Hf(OBu)_{2}(tbaoac)_{2}] and the known [Hf(OPr$^i$)_{2}(tbaoac)_{2}] as the reference compound (figures 14 and 15 respectively).
The onset of volatilisation and decomposition from the TG plot was marked at 145 and 220°C respectively for [Hf(OBu)\(_2\)(tbaoac)\(_2\)] which is slightly higher than [Hf(OPr\(_i\)\(_2\)(tbaoac)\(_2\)] (130 and 210°C respectively). At an isothermal temperature of 150°C, evaporation rate of [Hf(OPr\(_i\)\(_2\)(tbaoac)\(_2\)] is \(5.6 \times 10^{-2}\) mg min\(^{-1}\) and of [Hf(OBu)\(_2\)(tbaoac)\(_2\)] was \(5.2 \times 10^{-2}\) mg min\(^{-1}\) which can be clearly seen in figure 15 (marked in red circle).

Thus from thermal analysis it is apparent that unlike in the case of mixed alkoxide complexes of zirconium, [Hf(OPr\(_i\)\(_2\)(tbaoac)\(_2\)] is relatively more volatile than its analogous
[Hf(OBu')_2(tbaaoac)_2], although both the compounds show great potential as CVD precursors for depositing HfO_2 films. Isothermal plots of [Hf(OBu')_2(tbaaoac)_2] and [Zr(OBu')_2(tbaaoac)_2] at 150°C are shown in figure 16. It can be taken from the figure that at isothermal temperature of 150°C, compound 5 shows higher mass transport than compound 7 for long time periods of time (> 200 min).

### 4.3.2 Mixed alkoxide/β-ketoamide complexes of zirconium

Simultaneous TG/DTA curve of [Zr(OPr')_2(deacam)_2] (4) is shown in figure 17. From the TG, monotonic weight loss of compound 4 occurs between 185–310°C after which temperature the compound begins to decompose leaving behind a residue of 11% which is much lower than the theoretical amount of ZrO_2 (23.6 wt%) thus indicating some evaporation. [Zr(OPr')_2(deacam)_2] melts at a low temperature of around 60°C which is indicated by the sharp endothermic dip in the DTA.

**Figure 17:** Simultaneous TG/DTA of [Zr(OPr')_2(deacam)_2] employing a heating rate of 10°C min^{-1} and 300 ml min^{-1} of nitrogen flow rate.

**Figure 18:** Comparative TGA plots of [Zr(OPr')_2(deacam)_2] in presence of 0.5 ppm and 5.0 ppm water and employing a heating rate of 10°C min^{-1} and 300 ml min^{-1} of nitrogen flow rate.

The melting point of 4 was also confirmed by the capillary melting point determination method. As observed in the case for compounds 1, 5 and 7, compound 4 also showed reactivity towards water and about 22.3% of the original weight corresponding to theoretical ZrO_2 was
left behind in the crucible (figure 18). Isothermal studies performed on 4 at 140 and 150°C (figure 19) showed a positive slope with no distinct steps in the TG curves implying relatively unchanged volatilisation profile for long length of time which is a typical important parameter for a thin film deposition experiment. However compared to [Zr(OPr)2(tbaao)2], compound 4 required higher vaporisation temperature and the rate of evaporation calculated at isothermal temperature of 140°C for [Zr(OPr)2(deacam)2] was $3.24 \times 10^{-2}$ mg min$^{-1}$ and at 150°C was $3.43 \times 10^{-2}$ mg min$^{-1}$. TG/DTA and evaporation rate studies carried out on [Zr(OPr)2(deacam)2] (4) thus indicates that the precursor is a low melting solid and possess thermal properties that are suitable for MOCVD and ALD of ZrO$_2$. Figure 20 compares the TG profile of [Zr(OPr)2(deacam)2] with [Zr(OPr)2(tbaao)2] and related literature known zirconium complexes to determine the effect of ligand variation on the precursor thermal properties. It is inferred that [Zr(OPr)2(tbaao)2] and [Zr(OPr)2(thd)2] has lower onset of vaporisation (~ 150°C) than [Zr(OPr)2(deacam)2] due to the presence of bulky OC(CH$_3$)$_3$ and C(CH$_3$)$_3$ groups in the β-ketoester and β-diketone ligand moiety respectively.

![Figure 19: Weight loss as a function of time at (a) 140°C and (b) 150°C for [Zr(OPr)2(deacam)2] employing a heating rate of 10°C and nitrogen flow of 300 ml min$^{-1}$.](image)

However, compared to the volatility of [Zr(thd)$_4$], the benchmark precursor for MOCVD of ZrO$_2$, compound 4 significantly demonstrates higher volatility (~ 175°C). It can therefore be inferred that by combining the advantages of alkoxide precursors with β-diketonates, it is possible to design zirconia precursors with improved thermal characteristics. Apart from high volatility, another factor which is equally important for CVD applications is the moderate
temperature window between evaporation and precursor decomposition. [Zr(OPrP)B_2B(deacam)B_2] showed reasonable window between vaporisation and decomposition than [Zr(thd)_4] which makes it suitable especially for multicomponent oxide growth.

Figure 20: Comparative TGA plots of; a: [Zr(OPrP)B_2B(tbaoac)B_2] (1), b: [Zr(OPrP)B_2B(deacam)B_2] (4), with known c: [Zr(OPrP)B_2B(thd)B_2] and d: [Zr(thd)_4] compounds illustrating the effect of ligand variation on the thermal properties of the precursors.

4.3.3 Mixed silinolate/β-ketoester complexes of zirconium and hafnium

Mixed silinolate/β-ketoester complexes namely [Zr(OSiMe_3)B_2B(tbaoac)B_2] (11) and [Hf(OSiMe_3)B_2B(tbaoac)B_2] (12) were synthesised with the purpose to serve as potential precursors for MSi_xO_y, (M: Zr and Hf) thin film deposition by CVD. To investigate their suitability as CVD precursors they were subjected to thermal analysis and the simultaneous TG/DTA of compounds 11 and 12 is shown in figure 21. It is observed from the TG/DTA data that both [Zr(OSiMe_3)B_2B(tbaoac)B_2] and [Hf(OSiMe_3)B_2B(tbaoac)B_2] are low melting at 60 and 63°C respectively. Both the compounds shows similar TG profile except for the different weight percentage of the residue obtained after decomposition. The onset temperature of volatilisation is recorded at around 100°C for [Zr(OSiMe_3)B_2B(tbaoac)B_2] (figure 21 left)where as for its hafnium analogue, the temperature onset of volatilisation is also about 105°C. Decomposition of 11 occurred at around 230°C after which the TG curve remains constant with a residue of 11.6 % which is much lower than the initial ZrSiO_4 content (31.4 wt. %). This clearly indicates high volatility of the complex [Zr(OSiMe_3)B_2B(tbaoac)B_2] (11).
Chapter 4

Figure 21: Simultaneous TG/DTA of a: [Zr(OSiMe$_3$)$_2$(tbaoac)$_2$] (11) and b: [Hf(OSiMe$_3$)$_2$(tbaoac)$_2$] (12) employing a heating rate of 10°C min$^{-1}$ and nitrogen flow rate of 300 ml min$^{-1}$.

On similar lines, decomposition of 12 occurs at slightly lower temperature of about 220°C (figure 21 right) and a residual amount of 20.5 % is left behind in the crucible. The residual amount in the TG crucible did not match with the initial wt % of hafnium silicate (40.3 %) thus indicating some vaporisation of [Hf(OSiMe$_3$)$_2$(tbaoac)$_2$]. Thus from the TG/DTA results it can be concluded that compounds 11 and 12 successfully fulfil the criteria of high volatility and moderate stability required for a MOCVD process.

As mentioned before, actual mass transport of the precursor to the reactor is one of the few parameters that determine the quality of the resulting thin films in a CVD process. Using TG analyser, detailed study regarding the rate of evaporation can be obtained. Figure 22 shows isothermal studies performed on [Zr(OSiMe$_3$)$_2$(tbaoac)$_2$] at three different isothermal temperatures of 75, 100 and 125°C. It was observed that at isothermal temperature of 125°C, [Zr(OSiMe$_3$)$_2$(tbaoac)$_2$] had the highest evaporation rate of $6.52 \times 10^{-2}$ mg min$^{-1}$ over long periods of time of about 250 min. Therefore during actual CVD experiment, for sufficient precursor delivery to the reactor zone the bubbler temperature should be kept about 125°C. Similarly at isothermal temperature of 125°C, [Hf(OSiMe$_3$)$_2$(tbaoac)$_2$] displayed unchanged volatilisation and had highest evaporation rate calculated as 5.0 mg min$^{-1}$. Thus in the case of [Hf(OSiMe$_3$)$_2$(tbaoac)$_2$] too the vapouriser temperature must be maintained at about 125°C to achieve an efficient CVD process. Figure 24 shows the comparative study of vaporisation of [Zr(OSiMe$_3$)$_2$(tbaoac)$_2$] and [Hf(OSiMe$_3$)$_2$(tbaoac)$_2$] plotted as a function of inverse
temperature. From the evaporation rates it is observed that [Zr(OSiMe₃)₂(tbaoac)₂] is more volatile than [Hf(OSiMe₃)₂(tbaoac)₂].

![Graph](image)

**Figure 22:** Weight loss as a function of time at (a) 75, (b) 100 and (c) 125°C for [Zr(OSiMe₃)₂(tbaoac)₂] employing a heating rate of 10°C and nitrogen flow of 300 ml min⁻¹ under atmospheric pressure.

![Graph](image)

**Figure 23:** Weight loss as a function of time at (a) 75, (b) 100, (c) 125°C for [Hf(OSiMe₃)₂(tbaoac)₂] employing a heating rate of 10°C and nitrogen flow of 300 ml min⁻¹ under atmospheric pressure.

Thus, TG/DTA and isothermal studies carried on compound 11 and 12 revealed that they can be used as potential precursors for metal silicate MOCVD.
4.4 Summary and conclusions

Thermal analysis has been employed as a very informative tool in evaluating the suitability of the synthesised complexes as CVD precursors. It was shown that by introducing small changes in the established key structures of the existing precursors, it is possible to tune the thermal properties. The mixed alkoxide and mixed silinolate complexes of zirconium and hafnium demonstrated improved thermal properties in terms of reasonable temperature onset of volatilisation and decomposition suitable for MOCVD applications for individual oxide and silicates. From the TG/DTA data it was inferred that the [Zr(OBu)₂(tboaoc)₂] complex was more volatile than [Zr(OPr)₂(tboaoc)₂] analogous, essentially due to the presence of bulky tert-butoxy groups. However in case of hafnium mixed alkoxide/β-ketoester complexes, the isopropoxide analogue was found to be more volatile than its tert-butoxide counterpart. From TG/DTA and isothermal analysis [Zr(OSiMe)₂(tboaoc)₂] was investigated as a more volatile precursor than [Hf(OSiMe)₂(tboaoc)₂]. Table 2 lists the physical characteristics of the novel precursors. In addition, the precursors possess a narrow temperature window for decomposition, which is particularly relevant for multicomponent oxide films deposition. For example, thermal characteristics of [Zr(OPr)₂(tboaoc)₂] matches closely to those of
[Ti(OPr$^i$)$_2$(tbaoac)$_2$]$^7$ or [Ti(OPr$^i$)$_2$(thd)$_2$] and [Pb(thd)$_2$]$^8$ making it more suitable than [Zr(thd)$_4$] for growing multicomponent oxides like PZT thin films.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting point [°C]</th>
<th>Quantitative temperature of vaporisation [°C]</th>
<th>Decomposition temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zr(OPr$^i$)$_2$(tbaoac)$_2$] 1</td>
<td>~ 45</td>
<td>~ 170</td>
<td>~ 245</td>
</tr>
<tr>
<td>[Zr(OPr$^i$)$_2$(deacam)$_2$] 4</td>
<td>~ 60</td>
<td>~ 185</td>
<td>~ 310</td>
</tr>
<tr>
<td>[Zr(OBu$^t$)$_2$(tbaoac)$_2$] 5</td>
<td>~ 75</td>
<td>~ 150</td>
<td>~ 230</td>
</tr>
<tr>
<td>[Hf(OBu$^t$)$_2$(tbaoac)$_2$] 7</td>
<td>~ 78</td>
<td>~ 145</td>
<td>~ 220</td>
</tr>
<tr>
<td>[Zr(OSiMe$_3$)$_2$(tbaoac)$_2$] 12</td>
<td>~ 60</td>
<td>~ 100</td>
<td>~ 230</td>
</tr>
<tr>
<td>[Hf(OSiMe$_3$)$_2$(tbaoac)$_2$] 13</td>
<td>~ 63</td>
<td>~ 105</td>
<td>~ 220</td>
</tr>
<tr>
<td>[Zr(thd)$_4$] as reference</td>
<td>–</td>
<td>~ 275</td>
<td>~ 350</td>
</tr>
<tr>
<td>[Zr(OPr$^i$)$_2$(thd)$_2$] as reference</td>
<td>~ 110</td>
<td>~ 160</td>
<td>~ 300</td>
</tr>
<tr>
<td>[Hf(OBu$^t$)$_2$(tbaoac)$_2$] as reference</td>
<td>~ 44</td>
<td>~ 130</td>
<td>~ 210</td>
</tr>
</tbody>
</table>

Table 2: Physical properties of the new Zr and Hf containing compounds interpreted from thermal analysis data. All the measurements were performed under atmospheric pressure.

Isothermal studies carried out as a function of time at different temperatures on the precursors showed a quantitative and unchanged volatilisation at high rates over a long periods of time (> 200 min). Reactivity of [Zr(OPr$^i$)$_2$(tbaoac)$_2$] (1), [Zr(OPr$^i$)$_2$(deacam)$_2$] (4), [Zr(OBu$^t$)$_2$(tbaoac)$_2$] (5) and [Hf(OBu$^t$)$_2$(tbaoac)$_2$] (7), towards water makes them highly suitable for metal oxide ALD applications as well.
4.5 References

5 Characterisation of ZrO$_2$ nanoparticles synthesised from a modified organometallic precursor

Abstract

ZrO$_2$ particles with diameters in the 2–3 nm range have been synthesised by the pyrolysis of organometallic precursor namely, [Zr(OPr$_i$)$_2$(deae)$_2$] (10) in tri n-octylphosphine oxide (TOPO) as capping agent. The nanoparticles were synthesised via non hydrolytic route and the X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDAX) and selected area electron diffraction (SAED) studies were consistent with particles of tetragonal zirconia. Transmission electron microscopy (TEM) detected monodispersed ZrO$_2$ nanoparticles with average size of 2–3 nm determined by assuming the particles to posses relatively spherical shape. UV-Vis spectroscopy showed absorption maxima at 281 nm and a broad photoluminescence band at 345 nm.

5.1 General introduction

Particles with structural dimensions between 1-100 nm occupy a state of matter somewhere between those of atoms and bulk materials and are referred to as nanoparticles. Through his frequently-cited lecture entitled “There is plenty of room at the bottom”, physicist Richard Feynman in 1959 pointed out the potential nanotechnology offers to the field of advance materials.[1] The fundamentals of nanotechnology is miniaturisation which relies on the challenge to sustain Moore’s law. There has been tremendous growth in the field of nanotechnology in the past few years essentially due to the availability of new routes for nanoparticle synthesis and sophisticated characterisation tools like electron microscopy, diffraction methods, scanning probe microscopies.

The potential applications of nanoparticles are due to the quantum size effect and their extremely high surface areas.[2-5] In other words, bandgap (especially for semiconductors), magnetic moments, specific heats, melting point, surface chemistry are some of the properties associated with materials that change in the nanoregime.[6-8] For example in the case of InP or...
GaAs semiconductors used in solid-state lasers, the characteristic wavelength at which the emission occurs depends on the size of the particles.

Group IVb oxides are of increasing interest because of their importance as gate oxides in CMOS technology and as ferroelectric ceramics (PZT, BST etc) in memory applications. ZrO$_2$ in particular is an interesting material due to its large band gap of 5.0 eV, high refractive index, and relatively high dielectric constant of ~ 25. Apart from its physical properties, zirconia is an interesting support material for heterogeneous catalysis including hydrogenation of CO$[9]$, olefins$[10]$ and dienes$[11]$ and much effort has been directed towards the controlled synthesis of high surface area ZrO$_2$ as well as nanodisperse powders or colloids$[12, 13]$. Due to its mechanical and thermal properties relevant for ceramics, much of the earlier work on the precursor chemistry of ZrO$_2$ and related ferroelectric oxides was focused towards understanding and optimisation of sol-gel processes involving zirconium alkoxides$[14, 15]$. The oxide nanoparticles have been synthesised by various specific routes such as precipitative methods usually by water, thermolysis, metathesis involving reactions of metalorganic compounds in high boiling solvents, gas phase reactions as occuring in CVD, or thermolysis reactions involving formation of nano scale particles by either utilising polymers, micelles and coordinative ligands as stabilising agent. Capping the nanoparticles with stabilising agents, renders the molecule to be easily soluble which opens up a number of possibilities such as size-selective precipitation, permitting monodispersed preparation of nanoparticles$[16]$

5.2 **Zirconium dioxide nanoparticles**

Metal oxide nanoparticles have attracted considerable interest in various fields such as optics$[17, 18]$ , biological labelling$[19]$, catalysis$[20, 21]$ , advance ceramics$[22]$ because of their size and shape dependent physico-chemical properties. In view of these vast areas of application, intense research has been focused on the synthesis of well-defined uniform nanocrystals of semiconductors of group II-VI and nobel metals. Relatively less work has been done on the synthesis of transition metal oxide nanoparticles in particular ZrO$_2$ and HfO$_2$ despite their many potential applications$[23-25]$. ZrO$_2$ nanoparticles have been synthesised by various methods such as sol-gel process$[26]$, spray pyrolysis$[27]$, carbon nanotube-template method$[28]$, CVD$[29]$. However, these methods suffer from lack of producing particles with narrow size distribution. Among the above mentioned methods, sol-gel approach to obtain zirconia
nanoparticles is the most extensively used but the problems associated with water based synthesis is fast hydrolysis, low concentration of the reactants and difficulty in removing the residue (by-products) after synthesis.\(^{[30]}\) The non-hydrolytic sol-gel approach is an alternative solution and has been employed in obtaining good quality nanoparticles of titania.\(^{[24, 31]}\) However, this synthesis route also resulted in broad particle size distribution. Fischer and coworkers employed non-hydrolytic pyrolysis approach and obtained monodispersed TOPO-capped titania nanocrystals from a modified alkoxide precursor.\(^{[32]}\) Unlike the titanium (IV) alkoxides which are difficult to handle due to their highly moisture sensitive nature, the modified precursor displayed ambient reactivity against moisture because of the coordinatively saturated Ti(VI) metal centre.

We further extended this non-hydrolytic route to produce zirconia nanoparticles by thermal decomposition of a mixed alkoxide/aminoalkoxide precursor, \([Zr(OPr\text{\textsubscript{i}})_2(\text{deae})_2]\) at high temperatures.

\section*{5.3 Experimental}

\subsection*{5.3.1 Starting materials}

All manipulations were carried out in moisture free atmosphere using glove box and standard schlenk techniques. Tri n-octylphosphine oxide (TOPO) (Aldrich) was dried under vacuum at 120°C for 2 h and degassed prior to use. The solvents, methanol and toluene used for synthesis were dried, distilled and stored under argon.

Synthesis and characterisation of mixed alkoxide/aminoalkoxide precursor, \([Zr(OPr\text{\textsubscript{i}})_2(\text{deae})_2]\) (10) is described in § 2.3.3 of Chapter 2. The precursor was synthesised by reacting \([Zr(OPr\text{\textsubscript{i}})_4(HOPr\text{\textsubscript{i}})]\) with N,N-diethylethanolamine in an alcohol-exchange procedure.

\subsection*{5.3.2 Synthesis procedure for ZrO\textsubscript{2} nanoparticles}

In a typical synthesis of ZrO\textsubscript{2} nanoparticles, 1.0 mmol (0.44 g) of \([Zr(OPr\text{\textsubscript{i}})_2(\text{deae})_2]\) was injected into 10 g of dry and degassed TOPO at 50°C in an argon atmosphere. The temperature of the mixture was raised slowly to 410°C and held at this temperature for 2 h with vigorous
stirring. Yellow-green flocculates were obtained at the end of the reaction and the reaction mixture was allowed to cool to about 50°C. The reaction mixture was then treated with dried and degassed methanol to precipitate the resulting zirconia nanoparticles. The precipitate was retrieved by centrifugation and washed three times with methanol to remove excess of TOPO, producing white coloured ZrO$_2$ nanoparticles which could be easily re-dispersed in non polar solvents like toluene or hexane.

### 5.3.3 Characterisation methods

The particles were analysed by various analytical techniques. XRD measurements were carried out employing a D8-Advance Bruker AXS diffractometer using Cu-K$_\alpha$ radiation. Optical absorption of ZrO$_2$ nanocrystals was obtained using a Perkin Elmer Lambda 9 UV/VIS/NIR spectrometer. The samples were dispersed in toluene and were placed in special optical glass cuvettes. Photoluminescence measurements were performed on a Fluoro-Max 2 instrument equipped with a continuous ozone-free xenon lamp (150 W) and a R928P photomultiplier tube. A Hitachi H-8100 scanning and transmission electron microscope operating at accelerating voltages up to 200 KeV was used for obtaining TEM images. Elemental composition of the ZrO$_2$ nanoparticles was obtained from an attached EDAX system (Oxford Link with Si (Li) crystal and ultrathin window ATW2). TEM samples were prepared by placing a small drop of dilute solution of the sample dispersed in toluene on a copper grid and was allowed to dry at room temperature.
5.4 Results and discussion

Thermal decomposition of [Zr(OPr\textsubscript{i}P\textsubscript{i}P\textsubscript{i})\textsubscript{2}B\textsubscript{2}B\textsubscript{2}B\textsubscript{2}] in tri n-octylphosphine oxide at 410°C for 2 h resulted in ZrO\textsubscript{2} nanoparticles.

5.4.1 Thermal characterisation

The pyrolysis temperature was decided from the TG/DTA analysis (figure 1) obtained for [Zr(OPr\textsubscript{i}P\textsubscript{i}P\textsubscript{i})\textsubscript{2}B\textsubscript{2}B\textsubscript{2}B\textsubscript{2}] under flowing atmosphere of nitrogen (300 ml min\textsuperscript{-1}) and employing a heating rate of 10°C min\textsuperscript{-1}. The TG curve of [Zr(OPr\textsubscript{i}P\textsubscript{i}P\textsubscript{i})\textsubscript{2}B\textsubscript{2}B\textsubscript{2}B\textsubscript{2}] indicates that the quantitative weight loss occurs at about 280°C and the temperature onset of decomposition is around 355°C.

![Figure 1: TGA plot of [Zr(OPr\textsubscript{i}P\textsubscript{i}P\textsubscript{i})\textsubscript{2}(deae)\textsubscript{2}] employing a heating rate of 10°C min\textsuperscript{-1} and nitrogen flow rate of 300 ml min\textsuperscript{-1}.](image)

5.4.2 Phase analysis

X-ray diffraction analyses were performed on the powder sample supported on a flat sample holder to investigate the crystal structure of ZrO\textsubscript{2} nanoparticles. The representative XRD pattern is depicted in figure 2. Based on the broad reflexes observed at 2\texttheta = 29.49° and 42.49°,
tetragonal crystal structure was assigned to the ZrO$_2$ nanoparticles. However, since the tetragonal phase is only slightly distorted from the cubic phase and that the observed reflexes were broadened due to small particle size, it was difficult to distinguish between the two crystal phases of zirconia. Consequently, SAED analysis (figure 4 (right)) supported the presence of tetragonal ZrO$_2$ crystal structure as the predominant phase. The distance 2.99 Å of the most prominent 101 (2$\theta$ = 29.49°) reflex of tetragonal ZrO$_2$ matched more closely with the calculated distance from SAED data of 3.04 Å.

![Figure 2: X-ray diffraction pattern of ZrO$_2$ nanoparticles.](image)

### 5.4.3 UV-Vis and photoluminescence spectroscopy

The optical properties of the resulting ZrO$_2$ nanoparticles were studied by UV-Vis and photoluminescence spectrometry. UV-Vis spectrum (figure 3 (left)) of the TOPO-capped zirconia nanoparticles was obtained by dispersing the sample in toluene. A strong absorption peak was observed at $\lambda$ = 281 nm. The profile of the absorption band indicates narrow size distribution of the ZrO$_2$ particles. Absorption wavelength of 281 nm resulted in ZrO$_2$ band gap of 4.4 eV which is comparable to the reported band gap of 4.6 eV for TOPO-stabilised 4 nm zirconia nanoparticles.$^{[33]}$

In general, the band gap can be tuned by varying the particle size, with smaller particles having larger band gaps than the bulk material. Band gap of bulk ZrO$_2$ is about 5 eV and it is apparent from the band gap calculated from the present study and from reference 17 that the values lies on the lower side of the energy. This result most likely indicates that there exist transitions
involving extrinsic states such as surface trap states or defect states. Photoluminescence studies were carried out with various excitation wavelengths and figure 3 (right) displays a emission fluorescence spectrum obtained with excitation wavelength of 295 nm. A sharp peak at a wavelength of around 324 nm is expected due to the scattered incident light. It is however possible to block the scattered incident light by using appropriate cutoff filter.

The emission spectra of ZrO\textsubscript{2} nanoparticles shows a broad fluorescence band centred around 345 nm. A red-shift is observed in the peak position compared to the bulk band gap which also indicates that the fluorescence involves contribution from extrinsic states.

5.4.4 TEM and EDAX analysis

The morphology and size of the nanoparticles were examined by TEM. Figure 4 (left) shows a TEM micrograph of TOPO-capped ZrO\textsubscript{2} nanoparticles. ZrO\textsubscript{2} nanoparticles were detected all over the copper grid. From the data it was inferred that the nanoparticles were quite faceted and monodisperse. Due to their faceted shape it was difficult to estimate the accurate particle size. But if the particle shape was assumed to be relatively spherical, particle size distribution of 2–3 nm was obtained.
Composition of the nanoparticles was studied by EDAX which revealed strong absorption features for elemental Zr and O in addition to the signals from elemental C and P of TOPO and Cu from the grid used to prepare the samples. Results from SAED micrograph are interpreted in § 5.4.2.

Figure 4: TEM image (left) and SAED image (right) of ZrO$_2$ nanoparticles.

Figure 5: EDAX analysis of TOPO-capped ZrO$_2$ nanoparticles.
5.5 Summary and conclusions

In summary, thermal decomposition of \([\text{Zr(OPr^iP_iP}_2B_2B_2(\text{deae})B_2}\]) at high temperatures in TOPO yielded monodispersed \(\text{ZrO}_2\) nanoparticles with particle size distribution between 2–3 nm. EDAX analysis on the particles confirmed the presence of elemental Zr and O. UV-Vis spectrum showed strong absorption around 281 nm and photoluminescence spectrum of the \(\text{ZrO}_2\) particles with excitation at 295 nm showed a broad fluorescence emission band around 345 nm.

5.6 References

Publications and Presentations

Articles

Conference Proceedings

Oral Presentation
1. “Metalorganic zirconium and hafnium precursors for gate oxide application”
DFG-CVD-Schwerpunktprogramm 1119, Dingden, October 2003.
Publications and Presentations

Conference and Poster

1 Sonderforchungsbereiche (SFB) 558 Meeting

2 Deutsche Forschungsgemeinschaft (DFG) Schwerpunktprogramm
   Poster: “Rational development of metalorganic precursors of Ti and Zr used for
   MOCVD of ferroelectric oxides”, Ruhr-Universität Bochum, June 2002.

3 Gesellschaft für Thermische Analyse (GEFTA) Jahrestagung
   Ruhr-Universität Bochum, September 2002.

4 14th European Conference on chemical vapor deposition EUROCVD 14 & CVD-XVI
   Poster: “MOCVD of TiO$_2$ films using a new class of metalorganic precursors”, Palais

5 DFG-CVD-Schwerpunktprogramm
   Poster: “MOCVD of HfO$_2$ and ZrO$_2$ ultra-thin films using novel precursors: High-κ

6 From Molecules to Materials: Materials Discussion 7
   Poster: “Metalorganic precursors of zirconium and hafnium for gate oxide
Curriculum Vitae

Personal Information

Name               Urmila Patil
Date of birth      13.02.1977
Place of birth     Bombay, India
Nationality        Indian

Education

1992               Secondary School Examination (CBSE Board)
1992-94            Higher Secondary School Examination (CBSE Board)
1994-1997          Bachelor of Science (B.Sc.), Chemistry
                    University of Bombay, India
1997-1999          Master of Science (M.Sc.), Inorganic Chemistry
                    University of Bombay, India
June 1999-June 2000 Research assistant at the Indian Institute of Technology, Bombay (I.I.T)
                    Supervisor: Prof. H. B. Singh
                    “Synthesis and characterisation of single source precursor
                    for preparation of semiconductor material using MOCVD.”
July 2000-March 2001 Research assistant at the Indian Institute of Technology, Bombay (I.I.T)
                    Supervisor: Prof. A. Q. Contractor
                    “Inductively coupled plasma-Atomic emission spectroscopy (ICP-AES) analysis”
April 2001-February 2005 Pursuing Doctoral degree (Ph.D.) in Organometallic and Materials Chemistry at the Ruhr-University Bochum, Germany
                    Supervisor: Prof. Dr. R. A. Fischer
                    “Metalorganic precursors for metal organic chemical vapor deposition (MOCVD) of ZrO_{2} and HfO_{2} thin films as gate dielectrics in complementary metal-oxide-semiconductor (CMOS) devices”