MOCVD of Electroceramic Oxides: A Precursor Manufacturer's Perspective**

By Anthony C. Jones*

Thin films of metal oxides are finding an increasing application in electronic devices and components in both civil and defense-related areas. These materials can be deposited by a number of methods, each of which has its merits. However, metal organic chemical vapor deposition (MOCVD) offers the most flexible approach to the growth of metal oxides. Key to the success of this technology is the manufacture and supply of suitable precursors with sufficient volatility and stability, as well as adequate purity. In this article a number of manufacturing issues are discussed, as well as the development of new precursors with improved physical properties and enhanced MOCVD performance.

Keywords: Metal organic chemical vapor deposition, Metal oxide thin films, Precursors

1. Introduction

Thin films of metal oxides are finding a rapidly growing application in advanced materials technology. Multi-component metal oxides exist in a variety of compositions and crystal structures, and their properties vary widely, from insulators to superconductors, leading to a vast range of potential applications, as shown in Figure 1. In particular, electroceramic oxide films have important applications in microelectronics and telecommunications, including computer memories, infrared detectors, optical waveguides, and electrooptic storage,[1] see Table 1.

The various techniques that have been used for the deposition of electroceramic metal oxide films can be divided into three general categories:
- Physical vapor deposition (radio-frequency and magnetron sputtering, ion beam sputtering, molecular beam epitaxy, and laser ablation).[2–5]
- Solution deposition (sol-gel, metal organic decomposition).[6,7]
- Chemical vapor deposition (atomic layer epitaxy and MOCVD, involving halide or metal organic precursors).[8–12]

Of these techniques, MOCVD, which uses vapor mixtures of metal alkoxides or β-diketonate precursors, offers the most flexible approach to the deposition of metal ox-

ides, and has the advantages of large area deposition capability, excellent composition control and film uniformity, high film densities and deposition rates, and excellent conformal step coverage at device dimensions <2 μm, which is particularly important in microelectronics applications.

An essential requirement in the commercialization of the MOCVD technique is the availability of suitable precursors with sufficient volatility and stability, as well as adequate purity. Production-scale MOCVD requires multi-kilogram quantities of reproducibly pure precursors, so that precursor synthesis must be scaled up by approximately three orders of magnitude from bench scale to kilogram scale. The various application areas of metal oxides involve a wide variety of elements (see Table 1) and consequently a large range of precursor chemistries must be employed during precursor manufacture, with an equivalent range of scale-up problems. Although, historically, some of these precursors were available commercially for other applications (e.g., TiO_2 precursors have a bulk application in paints), they were frequently poorly characterized and of insufficient purity for electronic applications. It is only recently that metal oxide precursors designed and manufactured specifically for the MOCVD process have become available.

Issues involved in the development and commercial manufacture of precursors for the MOCVD of a range of electroceramic oxides, including $(Ba,Sr)TiO_3$, $Pb(Zr,Ti)O_3$, $Pb(Mg,Nb)O_3$, $SrBi_2Ta_2O_9$, Ta_2O_5, TiO_2, and (Ni,Zn)-Fe_2O_4, are discussed in this article.

2. Precursor Selection

2.1. Precursor Requirements

Ideally, an MOCVD precursor should have the following properties:
– Adequate volatility.

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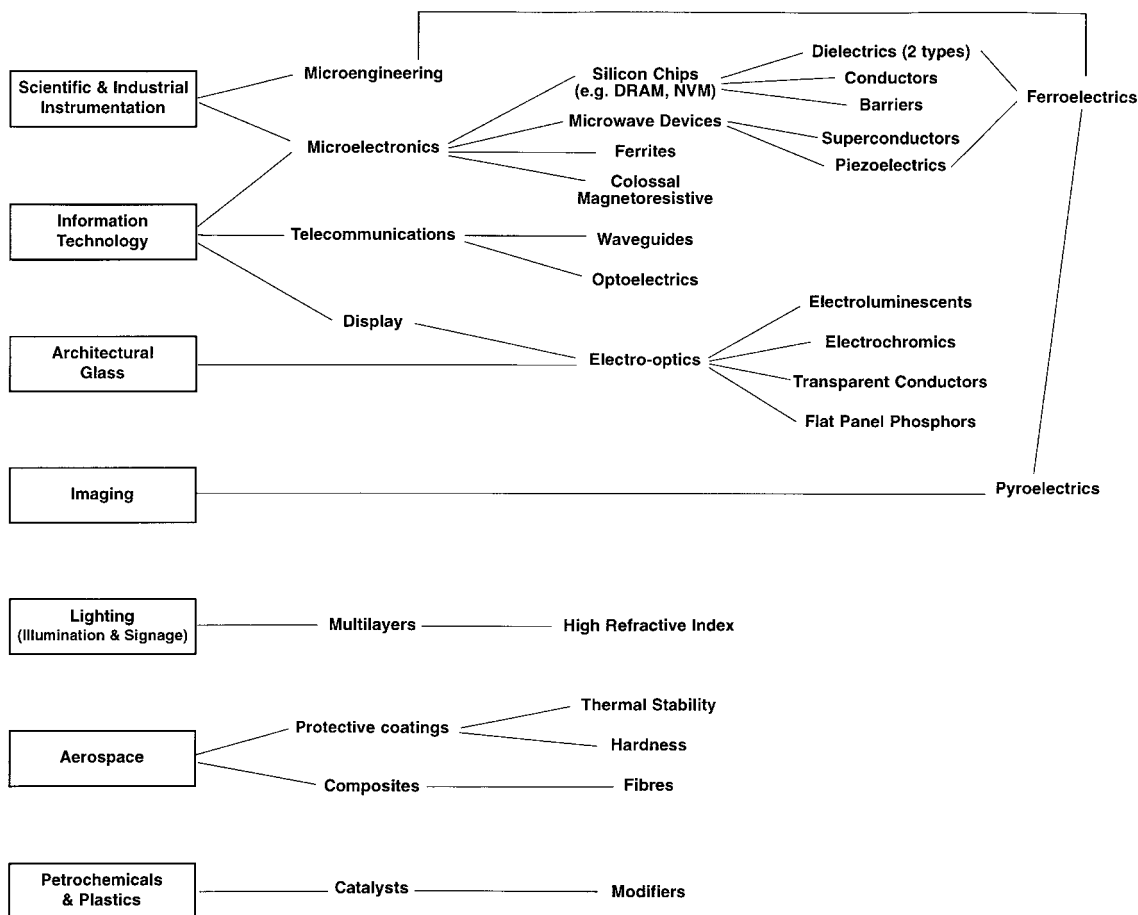25 James Carter Road, Mildenhall, Suffolk, IP28 7DE (UK)

Fig. 1. Application areas of metal oxides.

– A sufficiently large temperature window between evaporation and decomposition.

– A relatively low decomposition temperature (particularly important in microelectronics applications).

– Clean decomposition, without the incorporation of residual impurities.

– Compatibility with other precursors in the system.

– Good shelf-life, stable in solution in liquid injection MOCVD.

– "Manufacturability" (yield, purity, cost).

– Low toxicity.

It must be pointed out that all of these conditions are seldom met in a single organometallic precursor and there are very few , if any, "ideal" precursors. The precursor may often be toxic and its physical properties (vapor pressure, ambient stability, etc.) are often not ideal. Pre-reactions frequently occur between co-precursors, and different precursors often lead to metal oxide growth in different temperature regimes. Metal oxide precursors generally

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Table 1. Electroceramic metal oxides and their applications.

Oxide class	Material	Applications
Dielectric	TiO_2, Ta_2O_5, Nb_2O_5	Dielectric capacitor layers in computer memories
Ferroelectric	$(Ba,Sr)TiO_3$, $Pb(Zr,Ti)O_3$ $Pb(Mg,Nb)O_3$, $SrBi_2Ta_2O_9$	Computer memories (DRAMs, NVFERAMs), infrared detectors, thermal imaging, electrooptic storage
Ferrites	$(Ni,Zn)Fe_2O_4$, $(Mn,Zn)Fe_2O_4$	Recording media, high frequency read heads
Superconductors	$YBa_2Cu_3O_{7-x}$	Filters, bolometers, SQUIDS
Garnets	$Y_3Fe_5O_{12}$	Microwave elements, magnetooptic recording

have only very low vapor pressures ($\ll 1$ torr at room temperature) so that conventional MOCVD source containers (bubblers) may require heating at 150 °C or above to ensure adequate precursor transport. However, there is often an insufficient temperature window between precursor evaporation and decomposition, leading to precursor breakdown (or thermal aging) in the bubbler. The use of liquid injection MOCVD,[13] in which a solution of the precursor in an organic solvent (e.g., tetrahydrofuran) is fed into a heated evaporator alleviates this problem, but leads to the added requirements that the precursor must be stable for long periods in solution and must not pre-react with other precursors in solution.

2.2. General Classes of Oxide Precursors

The main classes of precursor used in the MOCVD of electroceramic oxides are metal β-diketonates, metal alkoxides, and metal alkyls.

Metal β-diketonates have been widely utilized in the MOCVD of electroceramic oxides,[14] and some of the most widely used precursors are shown in Table 2. They

Table 2. Typical precursors used in the MOCVD of electroceramic metal oxides.

Metal Oxides	Alkoxides	β-Diketonates [a]	Alkyls
TiO_2	$Ti(OR)_4$ ($R = {}^iPr$, ${}^tBu$)		
ZrO_2	$Zr(OR)_4$ ($R = {}^iPr$, ${}^tBu$)	$Zr(acac)_4$, $Zr(thd)_4$	
Ta_2O_5, Nb_2O_5	$Ta(OEt)_5$, $Nb(OEt)_5$		
$(Ba,Sr)TiO_3$	$Ti(OR)_4$, $Ti(O^iPr)_2(thd)_2$	$Ba(thd)_2$, $Ba(hfac)_2$, $Sr(thd)_2$	
$Pb(Zr,Ti)O_3$, $(Pb,La)(Zr,Ti)O_3$	$Zr(OR)_4$, $Ti(OR)_4$, $Ti(OR)_2(thd)_2$	$Pb(thd)_2$, $Pb(fod)_2$, $Zr(thd)_4$, $La(thd)_3$	$PbEt_4$, (neopentoxy)$PbEt_3$
$Pb(Mg,Nb)O_3$	$Nb(OEt)_5$	$Pb(thd)_2$, $Mg(thd)_2$, $Nb(thd)_4$	
$(Ni,Zn)Fe_2O_4$		$Ni(thd)_2$, $Ni(acac)_2$, $Zn(thd)_2$, $Zn(acac)_2$, $Fe(thd)_3$, $Fe(acac)_3$	
$YBa_2Cu_3O_{7-x}$		$Y(thd)_3$, $Ba(thd)_2$, $Ba(hfac)_2$, $Cu(thd)_2$, $Cu(hfac)_2$	

[a] Abbreviations for β-diketonate ligands. acac: 2,4-pentanedionate; thd: 2,2,6,6-tetramethyl-3,5-heptanedionate; hfac: 1,1,1,5,5,5-hexafluoropentane-2,4-dionate; fod: 1,1,1,2,2,3,3,-heptafluoro-7,7-dimethyloctane-4,6-dionate.

are generally stable up to ~200 °C and are relatively unreactive to air and moisture. In contrast to metal alkyls, they are of low toxicity and are non-pyrophoric so that they can be handled with relative ease. One of the advantages of metal β-diketonates is that their physical and chemical properties can be altered by "tailoring" the β-diketonate group. For example, precursor volatility can be increased by increasing the steric bulk of the R group as shown by the lead β-diketonates, in which volatility decreases in the order $Pb(thd)_2 > Pb(dhd)_2 > Pb(acac)_2$.[15] This arises from the increased shielding of the positively charged metal center by the bulky R group, which reduces intermolecular interactions that would otherwise lower precursor vapor pressure. The volatility of metal β-diketonates can also be increased by increasing fluorine substitution on the R group. For instance, volatility decreases in the order $Zr(hfac)_4 > Zr(tfac)_4 > Zr(acac)_4$,[8] due to an increased concentration of negative charge on the β-diketonate ligand, shielding the positively charged metal center and preventing it from increasing its coordination number by forming intermolecular bonds.

Some metal β-diketonates are, however, sensitive to air and moisture. Examples are $Ba(thd)_2$ and $Sr(thd)_2$, in which H_2O can coordinate to the highly positively charged metal center to form oligomeric oxygen/hydroxide bridged structures. The introduction of fluorine and/or bulky R groups into the β-diketonate ligand reduces the net positive charge on the metal center, rendering the compound less sensitive to O_2/H_2O. Alternatively, the metal center can be saturated with a polydentate coordinating ligand, such as polyethers $[CH_3O(CH_2CH_2O)_nCH_3]$. These form relatively stable complexes with fluorinated β-diketonates of the type $M(hfac)_2$(polyether), (M = Ba, Sr, Ca; polyether = tetraglyme, triglyme),[16] which have higher vapor pressures and higher ambient stability than $M(thd)_2$ complexes.

Because a metal–oxygen bond is already present in metal β-diketonates, the deposition of metal oxides can theoretically be achieved without an added oxidant. However, especially at low deposition temperatures, this can lead to heavy carbon contamination, so it is necessary to add oxygen to fully convert the β-diketonate to CO_2 and H_2O. The use of fluorinated β-diketonates often leads to fluorine contamination in the oxide films, which can only be reduced by the addition of H_2O during film growth.[14]

Metal alkoxides, $M^{n+}(OR)_n$ are also frequently used in dielectric metal oxide MOCVD (see Table 2). The volatility of metal alkoxides is strongly influenced by their tendency to form oligomers or $[M(OR)_n]_m$ clusters, and this is related to the positive charge on the metal center, which can coordinate to the negatively charged oxygen on neighboring $M(OR)_n$ molecules. Oligomerization is particularly likely to occur when the central positively charged metal atom has an incomplete coordination sphere. Mono- and divalent alkoxides that have a high tendency to expand their coordination sphere (e.g., $Ba(OR)_2$, $Sr(OR)_2$, $Ca(OR)_2$) generally form involatile high molecular weight

polymers, whereas pentavalent, trivalent, and tetravalent alkoxides (e.g., $Ta(OEt)_5$, $La(OR)_3$, $Ti(OR)_4$, and $Zr(OR)_4$) show a much lower degree of oligomerization with a corresponding increase in volatility.[17] Clustering of the alkoxides is suppressed by introducing bulky organic ligands such as *tert*-butoxide and *iso*-propoxide, as these shield the positive charge on the metal center from neighboring $M(OR)_n$ molecules; consequently volatility decreases in the order ${}^tBu > {}^iPr > Et$.[17] Advantages associated with metal alkoxide precursors are that metal oxides can frequently be deposited in the absence of an added oxidant, they are volatile and can be easily purified by fractional distillation. Disadvantages are that some are highly toxic (e.g., $Pb(OR)_2$), and they are often very sensitive to air and moisture, making them difficult to handle and store in large-scale MOCVD processes.

Metal alkyls, of general formula $M^{n+}R_n$ ($R = C_mH_{2m+1}$), are less frequently used to deposit dielectric and ferroelectric oxides than alkoxides or β-diketonates. Although generally more volatile, the metal alkyls are frequently toxic and highly reactive to air and moisture. For example, although high purity PbO can be grown from tetraethyl lead, $PbEt_4$,[11,18,19] and triethyl-neopentoxylead, Et_3Pb-$(OCCH_2C(CH_3)_3)$,[20] the very high toxicity of these precursors has limited their application in oxide MOCVD. Another common problem associated with metal alkyl precursors is the incorporation of carbon into the oxide film, illustrated by the heavy carbon contamination in ZrO_2 films deposited from $Zr(Cp)_2(OEt)_2$,[21] arising from incomplete decomposition of the cyclopentadienyl group.

Some of the important issues in the manufacture of metal β-diketonate and alkoxide precursors are discussed in the next section.

3. Manufacture of Metal Alkoxides and β-Diketonates

3.1. General Considerations

The reproducibility of MOCVD processes is critically dependent on precursor purity, both organic and metallic. It is therefore essential that the precursor can be manufactured in pure form by a reproducible process and is fully characterized for trace organic and metallic impurities. The synthesis process selected in the laboratory should thus be amenable to scale-up, and our experience at Inorgtech has shown that the synthesis criteria change markedly when scaling up by one, two, or three orders of magnitude,[22] as shown in Table 3.

Although the synthesis of many metal alkoxides or β-diketonates has been reported in the literature, in order to obtain economies of scale, the production batch often needs to be 100–1000 times larger than that described in the research paper.[22] This leads to a number of important pre-conditions, which are listed in Table 4. The final purity

Table 3. Criteria for scale-up from laboratory to plant.

Criterion	Laboratory scale	Production
Batch size	1 – 10 g	100 g – 5 kg
Yield	unimportant	80%
By-products	discard	address, reclaim, recycle
Quality	highest	consistent
Analysis methods	comprehensive	targeted
Time scale	less important	working day
Materials cost	secondary	minimize
Robustness of process	secondary	durable
Environmental impact	minor	major
Safety	important	overriding

Table 4. Pre-conditions for kilogram synthesis.

Raw Materials	Soluble or highly dispersed. Metal salts anhydrous, consistent quality; ammonia, alcohols and amines dry
Solvents	Dry (< 30 ppm H_2O). Oxygen free. Stable towards reactants and by-products. Free of contaminants and side reactants.
Equipment	Reliable and fail-safe. Easily dried and cleaned

of the precursor will be strongly dependent on the purity and integrity of the starting materials, as well as on the synthesis route itself. It is crucially important to determine the critical impurities that might ultimately cause problems in the MOCVD process (e.g., residual water, trace oxygen, organic impurities, particulate matter, etc.) and then to select the most appropriate synthesis route to minimize harmful impurities.

Production MOCVD processes require consistent and fully characterized precursors, and a range of analytical techniques must be employed by the precursor manufacturer, including:

- NMR spectroscopy to check for organic impurities and adducted solvent,

- infrared spectroscopy to analyze for associated water,

- thermogravimetric analysis (TGA) to assess precursor volatilization,

- atomic absorption spectroscopy or inductively coupled plasma mass spectrometry (ICP-MS) to analyze for trace metal impurities,

- visual inspection of stored precursor solutions used in liquid injection MOCVD to check for particulates.

The use of NMR and IR spectroscopy is intended to detect impurities that are likely to adversely affect precursor performance, together with TGA, which is used to ensure that the precursor evaporates cleanly without the build up of involatile residues in the evaporator or bubbler. In an area of developing technology, trace metal analysis is also crucially important to quantify contaminants, such as Li, Na, and Cu, which would be harmful in microelectronics applications. In addition to these routine analytical techniques, structural determination by X-ray crystallography can be useful, especially for new precursors or those which are difficult to characterize by conventional techniques.

Full precursor characterization allows the precursor manufacturer to judge the effectiveness of the synthesis

and purification routes used, and whether they are appropriate for MOCVD precursors. The specific synthesis routes will also be governed by the detailed chemistry of each individual precursor as discussed below.

3.2. Manufacture of Metal Alkoxides

Metal alkoxides of Ti, Zr, Ta, and Nb have been widely used in the deposition of dielectric and ferroelectric metal oxides. A large number of general synthesis routes are given in the literature,[17,23–39] however, only a few of these are suitable for the large-scale production of pure products, see Table 5. Involatile residues remaining after the evaporation of an alkoxide or β-diketonate precursor can often be traced to "water damage" arising from the presence of trace water during manufacture or storage. For the production of high purity precursors, solvents and starting materials should be dry and oxygen free (see Table 4) so that non-aqueous routes are generally preferred, provided the processes are cost effective.
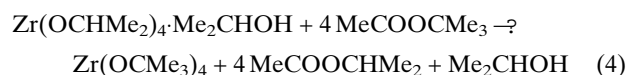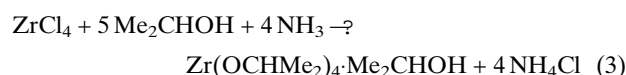
Table 5. General synthesis routes to metal alkoxides.

Route	Comments	Ref.
1. Direct reaction between metal and alcohol	Generally confined to highly electropositive metals (Li, Na, K, etc.).	[23]
2. Electrochemical synthesis — anodic dissolution of metal into alcohol	Can be used for less electropositive metals. Need supporting electrolyte (R_4NX). Difficult to control side-reactions.	[24,25]
3. Reaction between metal hydroxide or oxide and alcohol	Produces water, leading to cross-linking of alkoxides and low product yields.	[17,26]
4. Reaction between metal alkyl or hydride and alcohol	Requires prior synthesis of metal alkyl or hydride (often hazardous). Useful for Groups II, III (Zn, Mg, Al, Ga, In). Group IV alkyls (Ti, Zr, Hf) hard to make and react only slowly.	[27,28]
5. Direct reaction between metal halide and alcohol	Useful for less electropositive metals (B, Si, P). Fails to go to completion for lanthanides. Liberated HCl can attack alcohol (especially 3^y).	[17]
6. Reaction between metal chloride and alcohol with added base(e.g. NH_3)	Reaction forced to completion by addition of NH_3 and precipitation of NH_4Cl. Useful for wide range of transition metals (Si, Ge, Ti, Zr, Hf, V, Nb). Problem with O^{t}Bu due to side reactions with HCl.	[17,29–32]
7. Reaction between metal halide and Na or Li alkoxides	Non-aqueous route. Useful for lanthanides. Zr, Hf, Nb, Ta can form double alkoxides, which are difficult to remove. Only partial substitution for Ta, Zr alkoxides with bulky ligands.	[33,34]
8. Reaction between metal dialkylamides and alcohols	Useful for early transition metals. Need to synthesize intermediate alkylamide, which can be difficult. Best route to Zr(O^{t}Bu)$_4$, Mo^{III}, W^{III} alkoxides.	[35,36]
9. Transalcoholation	Interchange of alcohol follows order $3^y > 2^y > 1^y$. O^{t}Bu easily replaced by MeOH, EtOH.	[37,38]
10. Transesterification	Works well provided ester produced is volatile and can be removed by distillation. Useful for 3^y alkoxides of Ti, Zr, Hf.	[39]

The most appropriate routes for plant-scale operation are the alcoholysis of metal chlorides, transalcoholation, and transesterification. These are generally carried out in non-aqueous solvents and usually involve raw materials that are readily available. The preference is for direct synthesis routes in which the liberated HCl is removed by the addition of ammonia, sodium, or lithium (Eqs. 1 and 2).

$$MCl_x + x\,ROH \rightarrow M(OR)_x + x\,HCl \qquad (1)$$

$$HCl + NH_3 \rightarrow NH_4^+Cl^- \qquad (2)$$
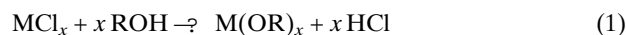
However, in some instances it is not possible to use the direct route, owing to side-reactions between the liberated HCl and the metal alkoxide. For instance, the reaction between $ZrCl_4$ and ^{t}BuOH gives low yields of $Zr(O^tBu)_4$ due to the reaction between the *tert*-butyl group and HCl. Ammonia is not a strong enough base to drive the reaction to completion, and the use of bases such as lithium or sodium leads to the formation of volatile double alkoxides, which carry unwanted alkali metal impurities into the final product. After investigating the transalcoholation of Zr alkoxides and alkylamides, we selected the transesterification reaction of Equations 3 and 4.

$$ZrCl_4 + 5\,Me_2CHOH + 4\,NH_3 \rightarrow$$
$$Zr(OCHMe_2)_4 \cdot Me_2CHOH + 4\,NH_4Cl \quad (3)$$

$$Zr(OCHMe_2)_4 \cdot Me_2CHOH + 4\,MeCOOCMe_3 \rightarrow$$
$$Zr(OCMe_3)_4 + 4\,MeCOOCHMe_2 + Me_2CHOH \quad (4)$$

The intermediate zirconium alkoxide has a convenient temperature coefficient of solubility and can be easily freed of impurities on the 5 kg scale to give an 80 % yield of pure material. Subsequent transesterification is followed by vacuum distillation to give an overall yield of $Zr(O^tBu)_4$ of approximately 50 % (based on $ZrCl_4$). NMR data[22] indicate that the $Zr(O^tBu)_4$ is free from significant organic impurities, and ICP-MS indicates that only trace levels of metallic impurities are present, see Table 6.

Table 6. Typical trace metallic impurities detected by ICP-MS in metal alkoxide precursors.

Metal alkoxide	Impurities [ppm]
Zr(O^{t}Bu)$_4$	Na 24.0; B 15.0; Cr 7.9; Ti 6.4; Mg 4.9; V 2.8; Ni 1.3; Cd 0.7; Cu 0.6; Co 0.25
Ti(O^{i}Pr)$_4$	Cr 7.6; Sn 5.9; B 5.5; Na 3.5; Mg 2.9; V 2.6; As 1.26; Ge 0.7
Ta(OEt)$_5$	Mg 4.8; Na 3.15; Ba 1.0; Cr 0.9; Nb 0.69; W 0.52; Sr 0.32
Nb(OEt)$_5$	As 1.9; Ag 1.7; Ti 1.33; W 0.46; Pt 0.3; Li 0.1

Direct routes (4–6, Table 5) can, however, be used for the manufacture of Ti, Ta, and Nb alkoxides. The alcohol reagents and solvents are generally relatively free from me-

tallic impurities, or can be readily purified by distillation, so that the trace metallic impurities present in certain of these alkoxides (see Table 6) derive largely from the metal salt starting material.

3.3. Manufacture of Metal β-Diketonates

For Groups IA, IIA, and IIIB, the β-diketonates are generally the only accessible volatile derivatives. Therefore, the synthesis and properties of these compounds have been the subject of recent comprehensive reviews,[12,40] and will be only briefly discussed here. Some general routes[41–47] are shown in Table 7. Since the precise nature of the β-di-

Table 7. General synthesis routes to metal β-diketonates.

Route	Comments	Ref
1. Addition of β-diketone to aqueous solution of metal chloride	Aqueous route, often leads to involatile polymers.	[41]
2. Addition of β-diketone to aqueous solution of metal hydroxide	Aqueous route. Leads to involatile hydrated molecular aggregates.	[42,43]
3. Reaction of metal with β-diketone (neat or in hydrocarbon solvent)	Avoids moisture damage of product. Need to remove excess ligand by washing. Not generally applicable.	[44]
4. Addition of Na(thd) to hydrated metal chloride	Presence of water leads to hydrated products.	[45]
5. Addition of Na(thd) to anhydrous metal chloride in alcohol	Reaction often incomplete. NaCl can be difficult to precipitate.	[46]
6. Addition of β-diketone to metal alkoxide in alcohol or hydrocarbon solvent ("labile ligand displacement")	Avoids moisture damage of product. Intermediate alkoxide can be purified, leading to high purity metal β-diketonate.	[22,47]

ketonates Ba(thd)$_2$ and Sr(thd)$_2$ is critically dependent on whether aqueous or non-aqueous synthesis routes are used, air and moisture must be rigorously excluded during precursor manufacture and storage. For example, the product from the reaction between Ba(OH)$_2$ and thdH is not Ba(thd$_2$)$_2$, but rather the hydrated species Ba$_5$(thd)$_5$(OH)(H$_2$O)$_3$.[48] Similarly, the presence of trace water and oxygen during storage or handling of Ba(thd)$_2$ can lead to β-diketonate peroxo compounds of the type shown in Figure 2, which contain an (O$_2$) moiety encapsulated in an octahedron of six Ba atoms.[49] Although such compounds are undoubtedly of academic interest, they are poor MOCVD precursors as they decompose during evaporation at elevated temperature to an involatile oxide residue, which leads to blocking of the evaporator and reactor inlet lines.

In contrast, when anhydrous preparative methods, such as the direct reaction between the metal and thdH, or the addition of β-diketone to metal alkoxide are employed, the tetrameric [Ba(thd)$_2$]$_4$ species is formed,[44,47] see Figure 3, and it has been found that Ba(thd)$_2$, synthesized under water-free conditions, vaporizes at a temperature 30 °C lower than material synthesized in aqueous solution.[12]

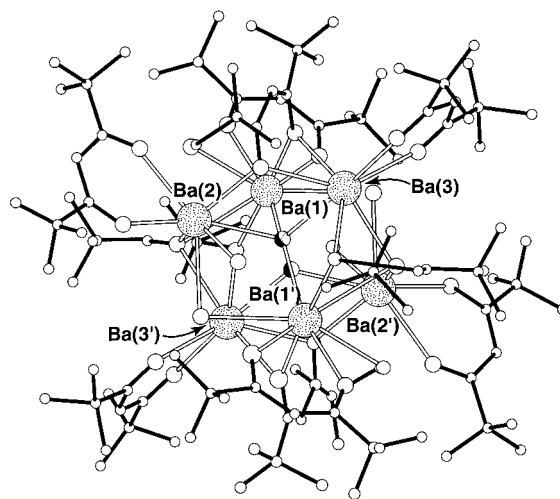Fig. 2. Ba$_6$(thd)$_{10}$(H$_2$O)$_4$(OH)$_2$(O$_2$) dianion (central O$_2$ atoms shaded), isolated after ingress of air to a solution of Ba(thd)$_2$ in NEt$_3$ during early liquid injection MOCVD studies [49].

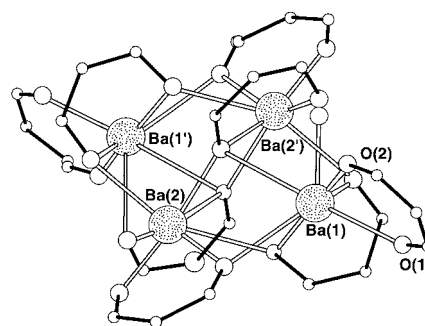Fig. 3. Molecular structure of tetrameric [Ba(thd)$_2$]$_4$ prepared under non-aqueous conditions (C(CH$_3$) groups omitted) [47].

Inorgtech has developed a general synthesis route to metal β-diketonates called "labile ligand displacement".[22] This involves the formation of an intermediate alkoxide complex that can be purified by distillation or recrystallization, followed by the displacement of the labile alkoxide with a β-diketonate group (see Eqs. 5 and 6 for an example).

$$M + n\,ROH \rightarrow M(OR)_n + H_2 \tag{5}$$

$$M(OR)_n + n\,thdH \rightarrow M(thd)_n + n\,ROH \tag{6}$$
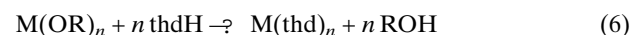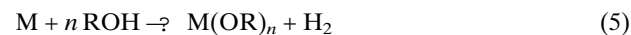
Significantly, the labile ligand displacement process is carried out in non-aqueous media, and is particularly useful for the large-scale manufacture of the moisture-sensitive metal β-diketonates Ba(thd)$_2$ and Sr(thd)$_2$. The Ba(thd)$_2$ produced by this route frequently contains traces of adducted organic impurities, giving rise to the TGA behavior shown in Figure 4, in which loss of organic impurities can be seen at temperatures of ~126 °C, and residues of ~3–5 % often remain after precursor evaporation.
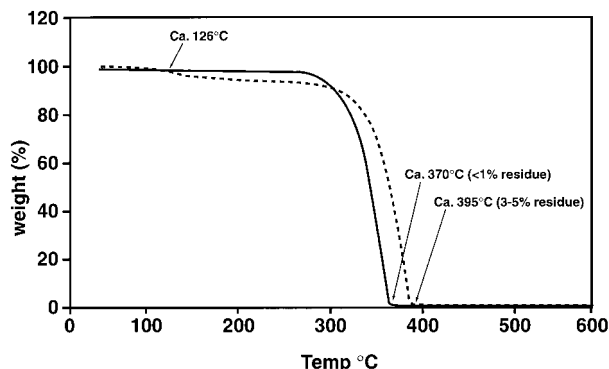
Fig. 4. TGA of standard grade Ba(thd)$_2$ (ca. 5 % residue) superimposed on TGA of "low-residue grade" Ba(thd)$_2$ (<1 % residue).

Purification of this material by proprietary techniques leads to a "low-residue" grade of product that is free from these organic impurities and that consistently leaves <1 % residue on evaporation (see TGA data, Fig. 4). This low-residue grade of Ba(thd)$_2$ also evaporates at lower temperatures than unpurified Ba(thd)$_2$, possibly due to reduced adduct formation or a lower degree of crosslinking between Ba(thd)$_2$ units in the absence of oxygen-containing organic impurities. This is a significant observation as there has been considerable debate about the most suitable Ba source for the MOCVD of (Ba,Sr)TiO$_3$ and YBa$_2$Cu$_3$O$_{7-x}$. A major problem has undoubtedly been the difficulty of reproducibly transporting Ba(thd)$_2$, and although numerous fluorinated alternatives and various adducts have been investigated,[14] none has proved entirely satisfactory. The availability of higher purity Ba(thd)$_2$, with improved evaporation characteristics, may now lead to a reassessment of this precursor for MOCVD applications.

The chemistry of Sr(thd)$_2$ differs significantly from that of Ba(thd)$_2$, with adduct formation being more prevalent.[12] For instance, synthesis of Sr(thd)$_2$ by labile ligand displacement produces the trimeric species [Sr$_3$(thd)$_6$(thdH)] containing adducted tetramethyl-heptanedione ligand.[47] Recrystallization of Sr(thd)$_2$ in ethanol gave a species that evaporated at a significantly lower temperature than Sr(thd)$_2$ synthesized in aqueous conditions, which was attributed to the formation of weak adducts between Sr(thd)$_2$, with the associated ethanol ligand inhibiting the formation of oligomeric [Sr(thd)$_2$]$_n$ species.[12]

The labile ligand displacement process can be extended to the large-scale manufacture of a range of metal β-diketonates, including Ca(thd)$_2$, Cu(thd)$_2$, Zr(thd)$_4$, Hf(thd)$_4$, Mg(thd)$_2$, and Ti(O^{i}Pr)$_2$(thd)$_2$, giving products which are low in organic and metallic impurities. The identification of labile ligand displacement as a general manufacturing route to metal β-diketonates has greatly simplified large-scale production processes. Plant design can be standardized and costed more precisely, and process parameters can be defined more clearly. Most importantly, the factors governing *safe* plant operation can be defined and transferred from plant to plant without an extensive rethink.

Due to the toxicity of Pb alkoxides, the labile ligand displacement process is not used for the manufacture of Pb(thd)$_2$. This is best manufactured using an aqueous route involving a lead salt and Na(thd), as the presence of an aqueous phase allows the extraction and removal of by-products. The Pb(thd)$_2$ product is carefully recrystallized from hydrocarbon, and infrared spectroscopy is then used to ensure that the product is free from trace water. The Pb(thd)$_2$ has been further characterized structurally by X-ray diffraction, in joint research between Inorgtech and Imperial College.[50] The structure, shown in Figure 5, comprises Pb(thd)$_2$ units in which four oxygen atoms are distorted away from a lone pair of electrons on the Pb^{II} center.
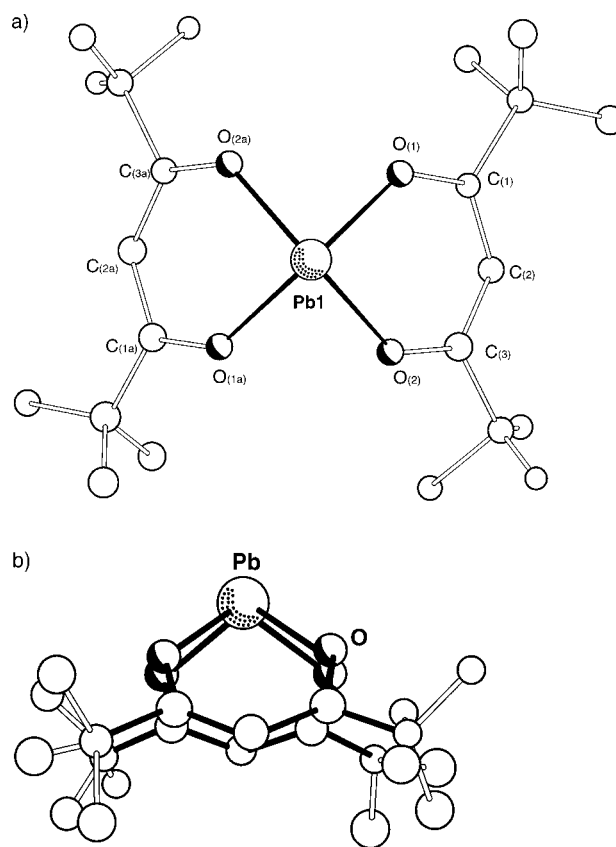

Fig. 5. a,b) Molecular structure of Pb(thd)$_2$ [50].

Ni(thd)$_2$, Zn(thd)$_2$, and Fe(thd)$_3$ are synthesized from the metal salt (halide or acetate) by addition of Na(thd) or thdH, in a non-aqueous solvent such as an alcohol or hydrocarbon. Metallic contaminants in the metal salt raw material carry through to the final product, although these can be reduced to ppm levels by careful recrystallization, see Table 6. Characterization of Ni(thd)$_2$, Zn(thd)$_2$, and Fe(thd)$_3$ by TGA (Fig. 6), indicates that they evaporate in a similar temperature regime (190–230 °C) and they have recently been used to deposit (Ni,Zn)Fe$_2$O$_4$ thin films by liquid injection MOCVD.[51]
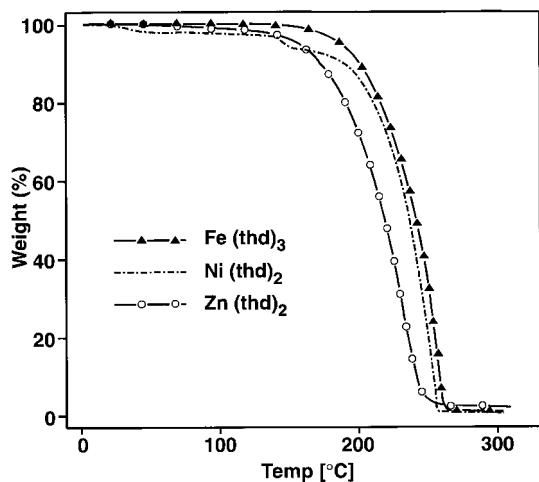
Fig. 6. TGA data for the thd derivatives of Ni, Zn, and Fe.

4. Development of New Precursors

In some MOCVD processes the use of existing precursors can be problematic, and it is necessary to consider modifying the precursor to improve its physical properties and/or its decomposition behavior. Many problems encountered with Zr, Ti, Ta, and Nb alkoxide precursors arise from their tendency to expand their coordination sphere by addition of water or solvent, or by dimerization or oligomerization. This can lead to poor solution stabilities and to low vapor pressure species. A general method of preventing this is to replace simple alkoxide groups with bidentate β-diketonates, or donor-functionalized groups that contain two or more donor groups in the same alkoxide ligand (such as dimethyl aminoethoxide and dimethyl aminopropoxide). This leads to a more fully saturated metal center, stabilizing the precursor to O_2/H_2O, and increases the precursor vapor pressure by preventing oligomerization. The application of this approach at Inorgtech to give improved Ta, Nb, Zr and Ti oxide precursors is described below.

4.1. Modification of Physical Properties of Precursors

Tantalum and niobium alkoxides such as $Ta(OEt)_5$[52,53] and $Nb(OEt)_5$[54] have frequently been used for the MOCVD of Ta_2O_5 and Nb_2O_5 dielectric films. Although pure films can be grown, both $Ta(OEt)_5$ and $Nb(OEt)_5$ are dimeric molecules with only very low vapor pressures (e.g., 0.075 torr at 108 °C for $Ta(OEt)_5$), which makes it necessary to use high evaporation temperatures and heated reactor inlet lines. Dimerization of $Ta(OEt)_5$ and $Nb(OEt)_5$ occurs because the positively charged Ta^V and Nb^V centers prefer six coordination for saturation, and achieve this by alkoxide bridging to an adjacent $Ta(OEt)_5$ or $Nb(OEt)_5$ unit. An approach favored by Inorgtech to satisfy the coordination requirements of electropositive metal centers is to

insert donor-functionalized alkoxide groups[55] containing more than one donor function, such as dimethyl aminoethoxide, $OCH_2CH_2NMe_2$ (DMAE). In the case of $Ta(OEt)_5$ and $Nb(OEt)_5$, this allows the metal center to achieve six coordination within a monomeric unit, $M(OR)_4(OCH_2CH_2NMe_2)$, which, in turn, leads to a significant increase in precursor vapor pressure (e.g., 0.75 torr at 108 °C for $Ta(OEt)_4(DMAE)$).

Both $Ta(OEt)_4(DMAE)$ and $Nb(OEt)_4(DMAE)$ are liquids and cannot be characterized by X-ray crystallography, however, their structure and stoichiometry can be readily confirmed by ^1H NMR, as illustrated by the data for $Ta(OEt)_5$ and $Ta(OEt)_4(DMAE)$ shown in Figures 7 and 8, respectively. The NMR spectrum of $[Ta(OEt)_5]_2$ displays two triplets (d = 1.3, 1.5) arising from terminal and bridging OCH_2CH_3 protons, and two quartets (d = 4.5, 4.7) associated with bridging and terminal OCH_2CH_3 protons. In the NMR spectrum of $Ta(OEt)_4(DMAE)$ (see Fig. 8), as well as the expected resonances for the DMAE protons, there is only one set of triplets and quartets visible, as bridging ethoxide groups are no longer present. This confirms the monomeric nature of the compound, and integration of these peaks also confirms the precursor stoichiometry. Similarly, NMR studies confirm the monomeric nature of $Nb(OEt)_4(DMAE)$, and both $Ta(OEt)_4(DMAE)$ and $Nb(OEt)_4(DMAE)$ have been used very successfully to deposit Ta_2O_5 and Nb_2O_5 by MOCVD at relatively low growth temperatures (350–400 °C).[56]

Ti alkoxides can also be modified by the presence of DMAE groups. For instance, one or two *iso*-propoxide groups in $Ti(O^iPr)_4$, a four-coordinate monomer,[57] can be replaced with DMAE to give more fully saturated $Ti(O^iPr)_3(DMAE)$ and $Ti(O^iPr)_2(DMAE)_2$ precursors.[58] These compounds are significantly less moisture sensitive than the parent alkoxide, which is likely to be of significance in liquid injection MOCVD, where trace water in the solvent may lead to decomposition of the precursor on extended storage. Both $Ti(O^iPr)_3(DMAE)$ and $Ti(O^iPr)_2(DMAE)_2$ have been used to deposit good quality TiO_2 films by liquid injection MOCVD.[58]

Variable temperature NMR studies[58] indicate that $Ti(O^iPr)_3(DMAE)$ exists as a mixture of monomers and dimers in solution, whereas $Ti(O^iPr)_2(DMAE)_2$ is a single compound, probably a six-coordinate monomer (see Fig. 9). Thus compounds of the type $Ti(OR)_2(DMAE)_2$ are good alternatives to $Ti(OR)_4$ precursors, especially where air sensitivity and ambient stability are major considerations.

It has recently been shown[59] that the dielectric constant of bulk Ta_2O_5 can be significantly increased by the addition of a small percentage of TiO_2. This offers the potential for improved performance Ta_2O_5-based dynamic random access memories (DRAMs), and studies into the deposition of Ta_2O_5 thin films for this application have now begun.[60] The new Ti precursors $Ta(OR)_2(DMAE)_2$ (R = Et, ^iPr) are likely to be fully compatible with $Ta(OEt)_4(DMAE)$ and
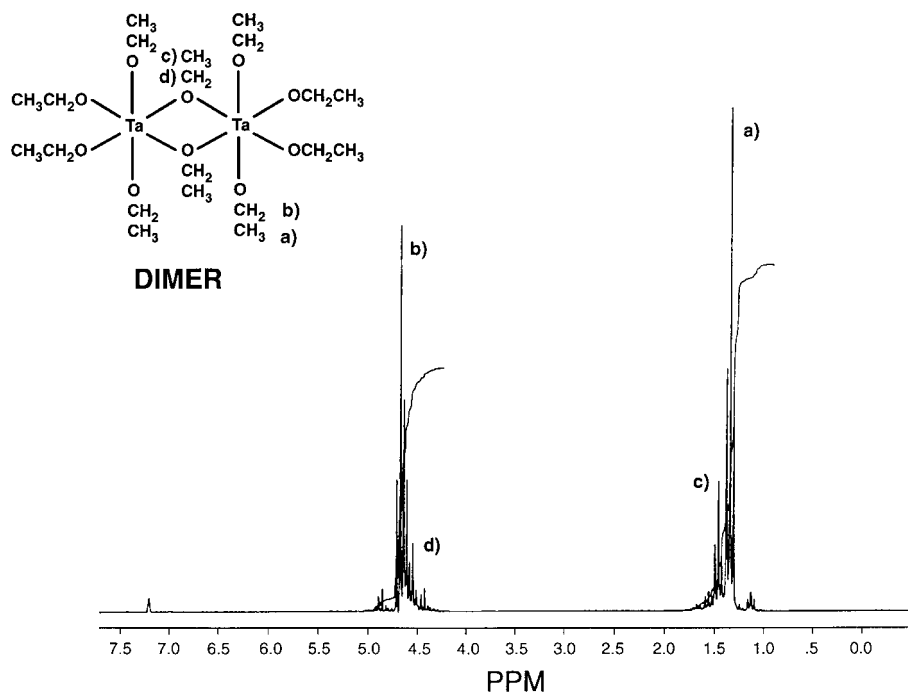
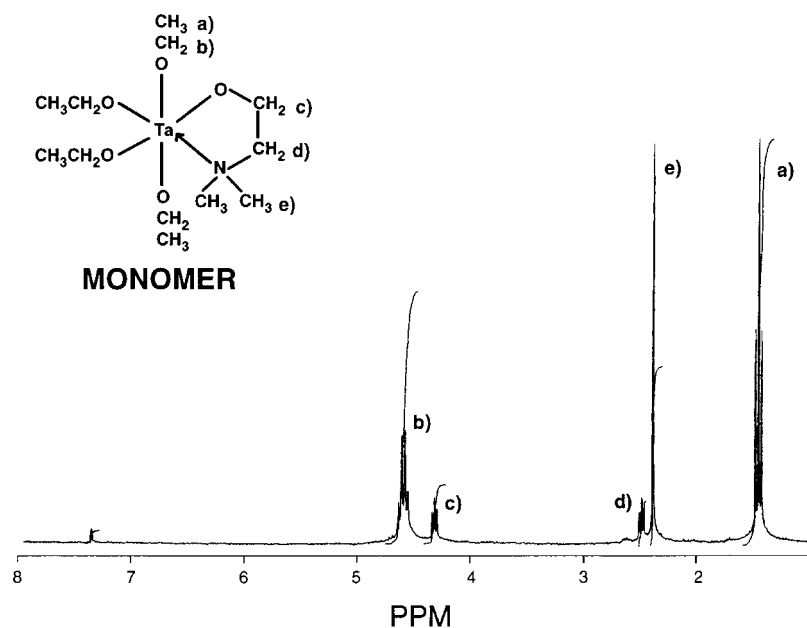Fig. 7. NMR data for dimeric [Ta(OEt)$_5$]$_2$ with probable structure superimposed.

Fig. 8. NMR data for monomeric Ta(OEt)$_4$(DMAE) with probable structure of molecule shown.

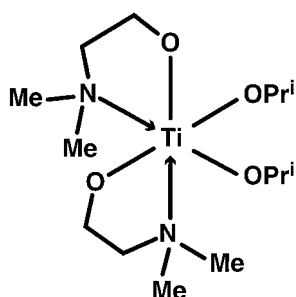Fig. 9. Probable structure of Ti(O^{i}Pr)$_2$(DMAE)$_2$.

may find a future application in the MOCVD of the Ta$_2$O$_5$/TiO$_2$ mixed oxide.

4.2. Modification of Precursor Decomposition Kinetics

The use of the conventional zirconium β-diketonate precursors Zr(acetylacetonate)$_4$ and Zr(trifluoroacetylacetonate)$_4$ for the MOCVD of ZrO$_2$ and Pb(Zr,Ti)O$_3$ can lead to serious problems of carbon and fluorine contamination, respectively.[61] Although higher purity films can be deposited using Zr(thd)$_4$,[8] this precursor has a rather high ther-

mal stability, which only allows optimized growth of ZrO_2 at substrate temperatures greater than 600 °C. Although suitable for the deposition of ZrO_2 and yttria-stabilized ZrO_2 protective coatings, these high growth temperatures are incompatible with the low growth temperatures (<550 °C) required for deposition onto pre-processed circuits in microelectronics.

In the growth of $Pb(Zr,Ti)O_3$ by liquid injection MOCVD using $Pb(thd)_2$, $Zr(thd)_4$, and $Ti(O^iPr)_2(thd)_2$, the high thermal stability of $Zr(thd)_4$ relative to $Pb(thd)_2$ leads to loss of Pb by desorption at the high substrate temperatures necessary to optimize ZrO_2 deposition.[62] The use of higher Zr precursor flow rates, or increased evaporator temperatures, leads either to the blocking of reactor lines by unreacted $Zr(thd)_4$ or the decomposition of $Pb(thd)_2$ in the evaporator. Although Zr alkoxides, $Zr(OR)_4$ (R = ^iPr, ^tBu), have a lower thermal stability than $Pb(thd)_2$, they contain a highly positively charged Zr^{IV} center with an incomplete coordination sphere. The compounds are consequently highly sensitive to oxygen and moisture, and susceptible to pre-reaction in the MOCVD reactor. Their reactivity may also lead to a reduced shelf life in solution-based liquid injection MOCVD. Therefore, in collaboration with DERA (Malvern) and Imperial College, we have investigated the mixed alkoxide/β-diketonate complexes $Zr(OR)_2(thd)_2$ (R = ^iPr, ^tBu).[62] The addition of the chelating β-diketonate group to zirconium alkoxides increases the coordinative saturation around the Zr^{IV} center and may be expected to render the compound less moisture sensitive. This approach aims to combine the advantages of high ambient stability associated with metal β-diketonates with the lower thermal stability and increased volatility of alkoxides.

The most successful alternative to $Zr(thd)_4$ was found to be a compound with the stoichiometry $Zr(O^iPr)_2(thd)_2$, which allowed ZrO_2 deposition in the same temperature regime as $Pb(thd)_2$ (ca. 470 °C), and was also much less likely than $Zr(thd)_4$ to block the reactor inlet line.[62] ^1H and $^{13}C\{^1H\}$NMR studies indicated that $Zr(O^iPr)_2(thd)_2$ exists as a mixture of monomers and dimers in solution,[63] and the alkoxide-bridged dimer $Zr_2(O^iPr)_6(thd)_2$ has recently been isolated from solution and characterized by X-ray crystallography,[63,64] see Figure 10. $Zr_2(O^iPr)_6(thd)_2$ has proved to be an extremely effective precursor for the deposition of ZrO_2 thin films by liquid injection MOCVD,[65] allowing oxide growth over a much wider temperature range (from 250 °C to at least 600 °C) than conventional precursors such as $Zr(OR)_4$ and $Zr(thd)_4$. The novel $Zr_2(O^iPr)_6(thd)_2$ source genuinely combines the advantages associated with the individual classes of $Zr(OR)_4$ and $Zr(thd)_4$ precursor, and has great potential for the MOCVD of $Pb(Zr,Ti)O_3$ at low to moderate growth temperatures, as well as for the growth of yttria-stabilized zirconia at more elevated temperatures.
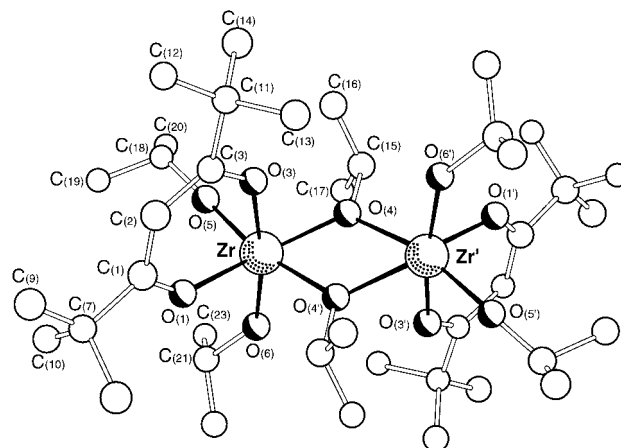

Fig. 10. Molecular structure of $Zr_2(O^iPr)_6(thd)_2$ [63].

5. Conclusions

In order to offer a consistent supply of high purity precursors for oxide MOCVD, the manufacturer must combine continuous precursor development and careful selection of manufacturing routes with full precursor characterization, using a range of analytical techniques. There is an important role for a specialist manufacturer dedicated to supplying specific high-technology markets.

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