

Molecular design of improved precursors for the MOCVD of electroceramic oxides

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Metalorganic chemical vapour deposition (MOCVD) is a highly promising technique for the deposition of dielectric and ferroelectric oxide thin films such as TiO_2 , ZrO_2 , HfO_2 , $\text{Pb}(\text{Zr,Ti})\text{O}_3$, $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ which have a variety of applications in electronic devices. A key requirement in this technology is the availability of precursors with appropriate physical properties and decomposition characteristics, but there are problems associated with many of the existing precursors. Therefore, in order to exploit the full potential of MOCVD it is sometimes necessary to “tailor” the properties of the precursor in order to optimise process parameters such as evaporation temperature, deposition temperature, layer purity and uniformity. In this paper the molecular design of a number of new oxide precursors is described, illustrating how the replacement of simple alkoxide groups by other groups, such as donor-functionalised alkoxide or β -diketonate ligands, can result in precursors with improved physical properties and enhanced MOCVD performance.

1. Introduction

Metal oxides exist in a variety of compositions and crystal structures and their physical and electrical properties vary widely, leading to a vast range of potential applications.¹ Thin films of metal oxides are finding an ever increasing application in advanced materials technology and there are a wide variety of “electroceramic” oxides which have important applications in the fields of microelectronics and telecommunications, such as next-generation computer memories, gate dielectric layers, infrared detectors, optical wave-guides and electro-optic storage, see Table 1.

A number of techniques have been used for the deposition of electroceramic oxide films, and these can be divided into three general categories:

(1) Physical vapour deposition (radio-frequency and magnetron sputtering, ion beam sputtering, molecular beam epitaxy, laser ablation).^{2–5}

(2) Solution deposition (sol–gel, metal-organic decomposition).^{6,7}

(3) Chemical vapour deposition (metalorganic chemical vapour deposition, MOCVD),^{8–13} atomic layer deposition, ALD.¹⁴

Of these techniques, MOCVD, which generally uses vapour-phase mixtures of metal alkoxides or β -diketonates, is the most versatile and promising deposition technique, offering the potential for large area growth, and having the advantages of good composition control, high film uniformity, good doping control and excellent conformal step coverage on non-planar device geometries. However, an essential requirement of the MOCVD process is the availability of suitable precursors which ideally possess a number of properties:

(1) Adequate volatility to achieve acceptable oxide growth rates at moderate evaporation temperatures.

(2) A sufficiently large temperature “window” between evaporation and thermal decomposition.

(3) Clean decomposition without the incorporation of residual impurities.

(4) Good compatibility with co-precursors during the growth of complex oxides.

(5) Long shelf-life, stable in solution for liquid injection MOCVD applications.

(6) Readily manufactured in high yield at low cost.

(7) Low hazard.

It is, of course, highly unlikely that all these criteria will be met in a single precursor, and precursor selection and design is almost always a compromise, and over the past few years there have been a number of developments in MOCVD reactor design to circumvent problems arising from the limitations of the available precursors. In conventional MOCVD techniques, of the type used very successfully for the MOCVD of III–V compound semiconductors, the precursor is contained in a

Table 1 Some electroceramic oxides and their applications

Oxide class	Material	Applications
Dielectric	TiO_2 , ZrO_2 , ZrSi_xO_y , HfO_2 , HfSi_xO_y , La_2O_3 , LaSi_xO_y , Ta_2O_5 , Nb_2O_5	High- <i>k</i> gate dielectric layers in CMOS technology, dielectric capacitor layers in DRAMs
Ferroelectric	SrTiO_3 , $(\text{Ba,Sr})\text{TiO}_3$, $\text{Pb}(\text{Zr,Ti})\text{O}_3$, $\text{SrBi}_2(\text{Ta}_x\text{Nb}_{1-x})_2\text{O}_9$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Pb}(\text{Sc,Ta})\text{O}_3$, $\text{Pb}(\text{Mg,Nb})\text{O}_3$	DRAMs, NVFERAM computer memories, infrared detectors, microelectromechanical devices, transducers, ceramic capacitors
Ferrites	$(\text{Ni,Zn})\text{Fe}_2\text{O}_4$, $(\text{Mn,Zn})\text{Fe}_2\text{O}_4$	Recording media, high frequency read heads
Superconductors	$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, Bi-Sr-Ca-Cu-O	Josephson junctions, bolometers, SQUIDS
Conducting	$(\text{La,Sr})\text{CoO}_3$, LaNiO_3 , RuO_2 , SrRuO_3	Ferroelectric capacitor electrodes
Garnets	$\text{Y}_3\text{Fe}_5\text{O}_{12}$	Microwave elements, magneto-optic recording

stainless steel container (bubbler) held at moderate temperatures (usually $< 50\text{ }^{\circ}\text{C}$) and transported into the gas phase using a carrier gas delivered through a dip-pipe. However, in marked contrast to III–V precursors, the available metal oxide precursors generally have only very low vapour pressures ($\ll 1$ Torr at RT), and thus require high evaporation temperatures for efficient oxide deposition. Early studies into oxide MOCVD using conventional methods therefore utilised extensively modified reactors in which the precursor container and inlet pipe-work was heated at high temperature (*e.g.* $150\text{--}250\text{ }^{\circ}\text{C}$) throughout the MOCVD process. Although this approach has been successfully used for the growth of a number of complex ferroelectric oxides such as PbTiO_3 , $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ¹¹ and high T_c superconducting oxides,¹³ the majority of metal alkoxide or β -diketonate precursors have insufficient thermal stability to withstand heating for long periods and decompose in the bubbler or in the inlet pipe-work leading to poor oxide layer uniformity and reactor blockages.

However, the problems of premature thermal decomposition associated with low volatility precursors can be largely overcome by the use of liquid injection MOCVD,^{15–17} in which the precursor is dissolved in an inert solvent, usually an ether (*e.g.* tetrahydrofuran) or a hydrocarbon (*e.g.* heptane or nonane). The precursor solution is held at room temperature until required in the MOCVD process, and this prevents the thermal decomposition of the precursor prior to use. The precursor solution is then delivered at a precisely controlled rate and quantity into a heated evaporator and transported by a carrier gas into the reactor zone. Separate precursor solutions can be used for the growth of multi-component oxides, but more usually a number of precursors are dissolved in an appropriate molar ratio in a single solution. A schematic diagram of a liquid injection MOCVD reactor is shown in Fig. 1.

Liquid injection MOCVD is now widely used for the deposition of electroceramic oxides. However, it leads to the added requirements that precursors must be soluble and stable for long periods in the chosen solvent, and must not react with other precursors in the same solution. In addition, the presence of a single heated evaporator at a fixed temperature makes it important that co-precursors evaporate at similar temperatures, otherwise it will be difficult to control the composition of complex oxides. To optimise uniformity in complex oxide films it is also important that the various precursors deposit oxide in a similar temperature regime, and for many applications in microelectronics it is desirable to limit the deposition temperature to $\sim 500\text{ }^{\circ}\text{C}$ to avoid damaging the underlying circuitry in Si-based devices. Although some existing precursors satisfy the majority of requirements for liquid injection MOCVD, the rapid growth in the number and complexity of metal oxides deposited by MOCVD is making it increasingly necessary to “tailor” the physical properties of a precursor to optimise its physical properties and MOCVD performance, as well as

making it more compatible with other precursors used for the MOCVD of complex oxides.

In this paper some recent advances in the molecular design of selected precursors used for the MOCVD of a variety of dielectric and ferroelectric oxides are described. The influence of molecular structure on the physical properties of a precursor and on the growth dynamics of the MOCVD process is outlined, with emphasis throughout on precursors used in liquid injection MOCVD applications where precursor compatibility and stability in solution are key requirements.

2. General classes of oxide precursors

Before the selection and molecular design of liquid injection MOCVD precursors are dealt with in detail, it may be useful to outline some general trends and properties associated with the main types of precursor used for the MOCVD of electroceramic oxides. These fall into four general classes, namely metal β -diketonates, metal alkoxides, metal alkylamides and metal alkyls, although a number of heteroleptic precursors containing more than one type of ligand (*e.g.* metal alkoxy/ β -diketonates) have also been used in oxide MOCVD.

Metal β -diketonate complexes have been used extensively in oxide MOCVD.^{13,18,19} Their physical and chemical properties can be “tailored” by altering the structure of the β -diketonate ligands^{18,20} and some examples of ligands used in these precursors are shown in Fig. 2. For instance, the volatility of β -diketonate complexes can be increased by increasing the steric bulk of the R group, as shown by lead β -diketonates in which volatility increases in the order $[\text{Pb}(\text{acac})_2] < [\text{Pb}(\text{dhd})_2] < [\text{Pb}(\text{thd})_2]$,²¹ due to the increased shielding of the highly positively charged metal centre and reduction of intermolecular oxygen–metal interactions in the solid state.

The volatility of metal β -diketonates can also be increased by increasing fluorine substitution on the R group, for instance volatility increases in the order $[\text{Zr}(\text{acac})_4] < [\text{Zr}(\text{tfac})_4] < [\text{Zr}(\text{hfac})_4]$, due to a reduction in the positive charge density of the central atom which in turn lowers intermolecular interactions. Metal β -diketonates of larger positively charged metal ions (*e.g.* Sr, atomic radius $\sim 1.91\text{ \AA}$ and Ba, atomic radius $\sim 1.96\text{ \AA}$) tend to form low volatility oxygen-bridged polynuclear clusters in order to fulfil the saturation requirement of the central metal atom, for example $[\text{Sr}(\text{thd})_2]$ is trimeric (see Fig. 3)²² and $[\text{Ba}(\text{thd})_2]$ is tetrameric.²³ There has thus been a large research effort aimed at increasing the vapour pressure of these complexes for MOCVD applications, especially in the field of high T_c superconducting oxides.^{13,18,19} Addition of polyethers or polyamines leads to a range of monomeric complexes, including $[\text{M}(\text{thd})_2(\text{polyether})]$,²⁴ see Fig. 4, $[\text{M}(\text{hfac})_2(\text{polyether})]$ ($\text{M} = \text{Sr, Ba}$; polyether = triglyme, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ or tetraglyme, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$)²⁵ and $[\text{M}(\text{thd})_2(\text{pmdeta})]$ ($\text{M} = \text{Sr, Ba}$; pmdeta = pentamethyl-diethylenetriamine, $\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}\{\text{Me}\}\text{CH}_2\text{CH}_2\text{NMe}_2$).²⁶

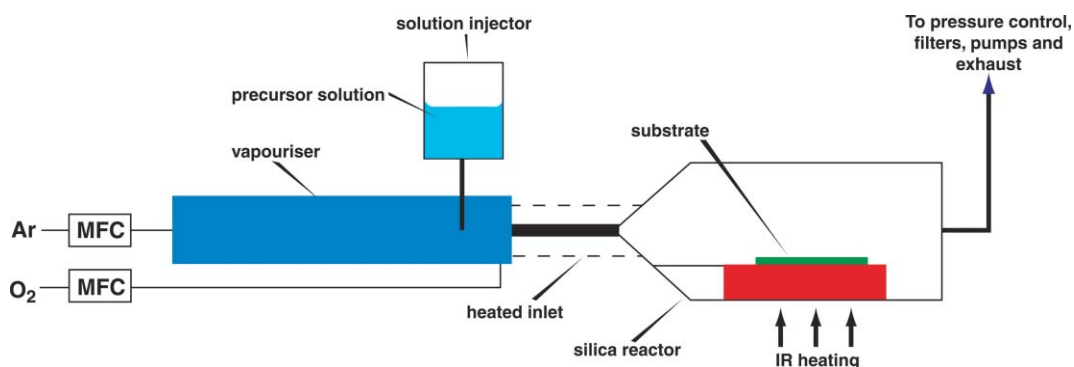
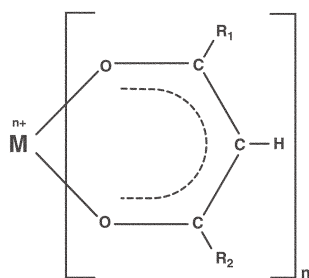


Fig. 1 Schematic diagram of a liquid injection MOCVD reactor (after ref. 17).



R ₁	R ₂	Name	Abbreviation
CH ₃	CH ₃	Pentane-2,4-dionate (acetylacetonate)	acac
CH ₃	CF ₃	1,1,1-trifluoropentane-2,4-dionate (trifluoroacetylacetonate)	tfac
CF ₃	CF ₃	1,1,1,5,5,5-hexafluoropentane-2,4-dionate (hexafluoroacetylacetonate)	hfac
CH ₃	C(CH ₃) ₃	1,1-dimethylhexane-3,5-dionate	dhd
C(CH ₃) ₃	C(CH ₃) ₃	2,2,6,6-tetramethylheptane-3,5-dionate	thd
CH ₃	CH ₂ CH(CH ₃) ₂	6-methylheptane-2,4-dionate	mhd
C(CH ₃) ₃	CH ₂ CH(CH ₃) ₂	2,2,7-trimethyloctane-3,5-dionate	tmod
C ₆ H ₅	C ₆ H ₅	1,3-diphenylpropane-1,3-dionate (dibenzoylimethanate)	dbm

Fig. 2 Some β-diketonate ligands used in metal oxide MOCVD precursor complexes.

The presence of the adducting ligands is undoubtedly useful in protecting the [Ba(thd)₂] and [Sr(thd)₂] complexes from hydrolysis and stabilising the complex in solution during liquid injection MOCVD,²⁶ but in the gas phase the non-fluorinated-thd complexes dissociate, whilst the fluorinated complexes lead to fluorine contamination in MOCVD-grown oxide films.

The bidentate and chelating β-diketonate ligands help saturate highly positively charged metal centres and impart

good ambient stability to the metal complexes, making them robust MOCVD precursors which are relatively un-reactive to air and moisture. Although a metal–oxygen bond is present in the molecule, metal β-diketonates cannot generally be used as “single-source” precursors. Oxide films deposited in the absence of oxygen, especially at low substrate temperature, are often heavily contaminated with carbon, and so a large excess of oxygen is usually added to oxidise the organic fragments and form simple volatile products such as CO₂, which are readily

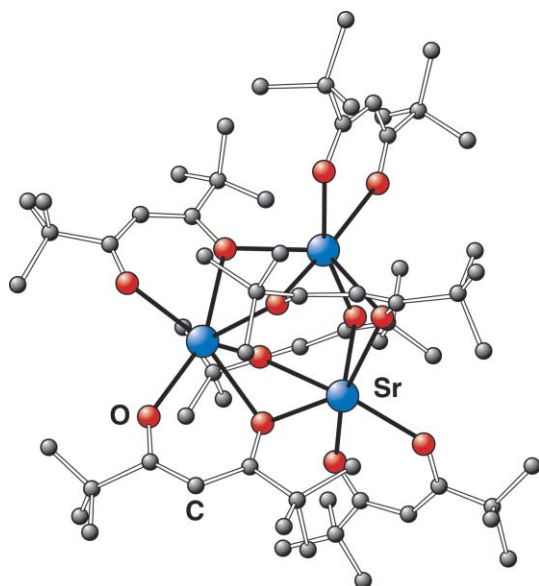


Fig. 3 Crystal structure of [Sr(thd)₂]₃ (after ref. 22).

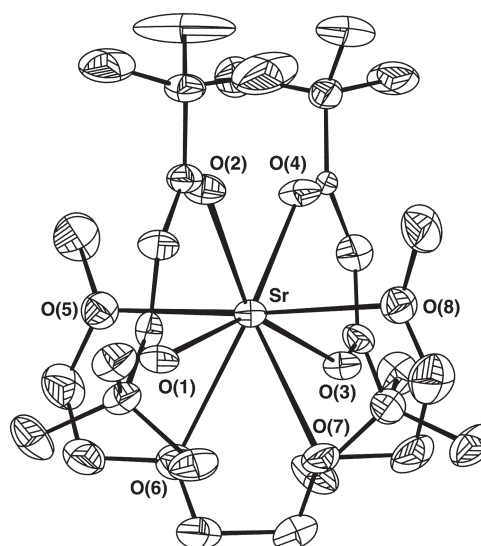


Fig. 4 Crystal structure of [Sr(thd)₂](triglyme) (after ref. 24).

removed from the reaction zone, thereby minimising carbon contamination. The presence of oxygen in the growth system also lowers the onset temperature of oxide growth.²⁷

The use of fluorinated β -diketonates often leads to fluorine contamination in the resulting oxide films, which can only be reduced by the addition of H₂O during film growth.¹³ The presence of fluorine in the growth system can also lead to degradation of the Si substrate, which is highly undesirable in Si-based microelectronics applications. It is likely that the thermal decomposition of metal β -diketonate complexes proceeds by complex ring opening reactions,²⁷ and relatively high temperatures are generally required to cleave the chelating β -diketonate ring which is further stabilised by resonance stabilisation.¹⁸ Therefore metal β -diketonates are in general more thermally stable than metal alkoxides and metal alkyls, and deposit oxide films at higher substrate temperatures.

Metal alkoxides have also been widely used in the MOCVD of oxide thin films.²⁸ The volatility of metal alkoxides is strongly influenced by their tendency to form oligomeric $[M(OR)_x]_n$ clusters, which in turn is related to the positive charge density on the metal centre. Oligomerisation is particularly likely to occur when the central atom has an incomplete coordination sphere. Oligomerisation can be suppressed by introducing bulky alkoxide ligands such as *tert*-butoxide and isopropoxide, which shield the metal centres from metal–oxygen intermolecular interactions; for example Zr alkoxide volatility increases in the order $[Zr(OEt)_4] \ll [Zr(OPr^i)_4] < [Zr(OBu^t)_4]$.²⁹ Another approach to inhibiting oligomerisation and increasing the volatility of metal alkoxide complexes is to insert donor functionalised alkoxide ligands, such as dimethylaminoethoxide, $[OCH_2CH_2NMe_2]$ (dmae) and bis(dimethylamino)isopropoxide $[OCH(CH_2NMe_2)_2]$ (bis-dmap) (see Table 2),³⁰ which can chelate *via* an extra donor group, leading to a more fully saturated metal centre, inhibiting dimerisation and polymerisation and rendering the complex less susceptible to hydrolysis. The ability of bulky alkoxide ligands or donor functionalised alkoxide ligands to suppress oligomerisation is critically dependent on the radius of the central metal atom. For example, $[Zr(OBu^t)_4]$ (Zr atomic radius ~ 1.45 Å) and $[Hf(OBu^t)_4]$ (Hf atomic radius ~ 1.44 Å) are monomeric, whilst the larger Th atom (radius ~ 1.65 Å) forms an oligomeric *tert*-butoxide complex.²⁹

Metal oxide films can often be deposited at relatively low temperature from metal alkoxides, and high purity films containing little or no carbon can be obtained in the absence of added oxygen, although an oxidant is generally used to minimise the possibility of carbon contamination. However, some metal alkoxides (*e.g.* $Pb(OR)_2$) are toxic, and many are highly moisture sensitive (*e.g.* $[Zr(OBu^t)_4]$, $[Hf(OBu^t)_4]$),²⁸ making them difficult to store and handle in large-scale MOCVD processes.

Metal alkylamides, $[M(NR_2)_x]$, widely used for the MOCVD of metal nitrides (*e.g.* TiN),³¹ are now being investigated as precursors to oxide films, and ZrO₂ has been deposited from $[Zr(NEt_2)_4]$.³² Although a metal–oxygen bond is not present in the precursor, the alkylamide ligand is readily displaced in the presence of excess oxygen, which allows the growth of high purity oxide films at relatively low substrate temperatures.

Table 2 Some donor functionalised alkoxide ligands

Formula	Name	Abbreviation
$[OCH_2CH_2NMe_2]$	2-dimethylaminoethanolate	[dmae]
$[OCHMeCH_2NMe_2]$	1-dimethylaminopropan-2-olate	[dmap]
$[OCH(CH_2NMe_2)_2]$	1,3-bis(dimethylamino)propan-2-olate	[bis-dmap]
$[OCH_2CH_2OMe]$	2-methoxyethanolate	[mee]
$[OCMe_2CH_2OMe]$	1-methoxy-2-methyl-2-propanolate	[mmp]

Metal alkyls are seldom used as precursors in the MOCVD of electroceramic oxides, as very few stable or volatile alkyl complexes are known in Groups IIA, IIIB, IVB and VB. The lead alkyls $[PbEt_4]$ ^{10,11} and $[Et_3Pb(OCH_2C(CH_3)_3)]$ ³³ have been used for the MOCVD of PbO and Pb(Zr,Ti)O₃, but their use has been restricted by their very high toxicity. Another common problem associated with metal alkyl precursors is carbon incorporation, illustrated by the heavy carbon contamination in ZrO₂ films deposited from $[Zr(Cp)_2(OEt)_2]$.³⁴

3. Developments in Group IVB oxide precursors

3.1. Ti-oxide precursors

Thin films of titanium oxide (TiO₂) have several potential applications in microelectronics, such as an alternative to SiO₂ as the gate dielectric material in metal oxide semiconductor field effect transistors (MOSFETS),^{35,36} and titanium oxide is a component of a number of ferroelectric oxides such as SrTiO₃, (Ba,Sr)TiO₃ and Pb(Zr,Ti)O₃ used in infrared detectors and non-volatile computer memories.^{1,37}

Titanium tetrachloride, $[TiCl_4]$, has been widely used as a precursor to TiO₂,^{38–40} however $[TiCl_4]$ is toxic and requires special equipment and safety installations. Its use can lead to severe chloride contamination in CVD films,³⁸ and the presence of chloride is likely to lead to unwanted side-reactions with co-precursors in solution or in the gas phase in liquid injection MOCVD of complex oxides. Titanium isopropoxide, $[Ti(OPr^i)_4]$ is the most volatile titanium alkoxide,²⁹ and has frequently been used for the MOCVD of high purity TiO₂ at relatively low substrate temperatures (< 500 °C).^{41–45} However, $[Ti(OPr^i)_4]$ contains an unsaturated four-coordinate Ti(IV) centre, which is highly reactive to air and moisture and can lead to problems in storage and handling, especially in solution-based liquid injection MOCVD applications.

In order to reduce the moisture sensitivity of the Ti precursor, chelating β -diketonate groups have been inserted to increase the coordinative saturation of the Ti(IV) centre. $[Ti(OPr^i)_2(acac)_2]$ has been used for the MOCVD of TiO₂,⁴⁶ and the related complex $[Ti(OPr^i)_2(thd)_2]$ was used in preference to $[Ti(OPr^i)_4]$ for the liquid injection MOCVD of Pb(Zr,Ti)O₃, in order to minimise the possibility of pre-reactions in solution with co-precursors $[Pb(thd)_2]$ and $[Zr(thd)_4]$.⁴⁷ The structure of $[Ti(OPr^i)_2(thd)_2]$ has not been determined, but NMR studies on similar Ti alkoxy- β -diketonates⁴⁸ indicate that it is likely to be a six-coordinate monomer in solution (see Fig. 5(a)). $[Ti(OPr^i)_2(thd)_2]$ is

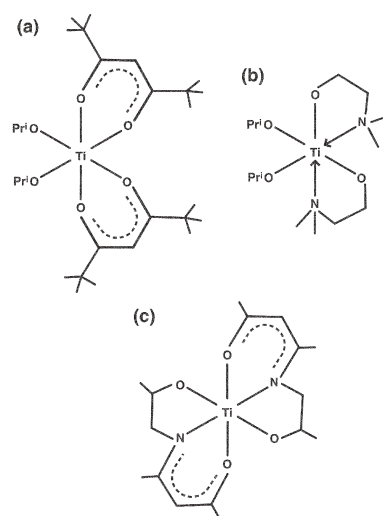


Fig. 5 Probable structures of some Ti complexes used as alternatives to $[Ti(OPr^i)_4]$: (a) $[Ti(OPr^i)_2(thd)_2]$, (b) $[Ti(OPr^i)_2(dmae)_2]$, (c) $[Ti(2meip)_2]$ (after ref. 60).

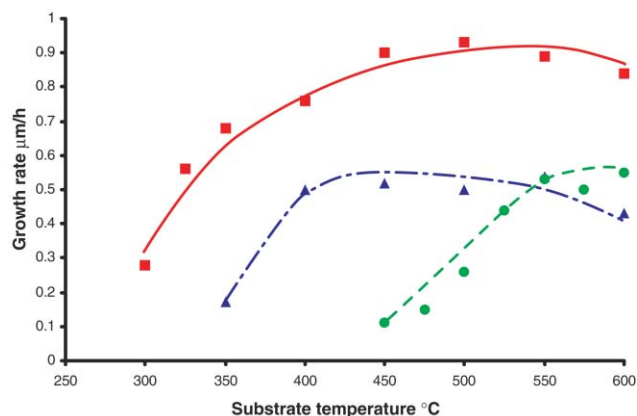


Fig. 6 Variation in oxide growth rate with substrate temperature for $[\text{Ti}(\text{OPr}^i)_4]$ (■), $[\text{Ti}(\text{mmp})_4]$ (▲) and $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$ (●). Low pressure liquid injection MOCVD (20 mbar).

significantly more stable in solution than $[\text{Ti}(\text{OPr}^i)_4]$, and the presence of the β -diketonate group gives $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$ a significantly higher thermal stability than $[\text{Ti}(\text{OPr}^i)_4]$, with the onset temperature of oxide growth from $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$ occurring some 150 °C higher than from $[\text{Ti}(\text{OPr}^i)_4]$, see Fig. 6. The high thermal stability of $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$ is a good match to the thermal stabilities of Ba, Sr and Zr β -diketonate co-precursors commonly used in multi-component oxide growth, and therefore $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$ is now widely employed for the liquid injection MOCVD of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$,^{26,49,50} $\text{Pb}(\text{La},\text{Ti})\text{O}_3$,⁵¹ SrTiO_3 ,⁴⁹ and $(\text{Ba},\text{Sr})\text{TiO}_3$.²⁶

Another approach to increasing the coordinative saturation of the metal centre is to introduce bidentate donor functionalised alkoxide ligands, such as [dmae] (see Table 2), and the complexes $[\text{Ti}(\text{OPr}^i)_3(\text{dmae})]$ and $[\text{Ti}(\text{OPr}^i)_2(\text{dmae})_2]$ have been used to deposit TiO_2 at 300–450 °C by liquid injection MOCVD.⁵² The complexes were found to be significantly less air sensitive than $[\text{Ti}(\text{OPr}^i)_4]$ and on the basis of ¹H NMR studies it was proposed that $[\text{Ti}(\text{OPr}^i)_2(\text{dmae})_2]$ is monomeric in solution with a six-coordinate pseudo-octahedral configuration, shown in Fig. 5(b). In this case, the thermal stability of the complexes is not appreciably different to the thermal stability of the parent $[\text{Ti}(\text{OR})_4]$ complexes. Titanium alkoxide complexes of the type $[\text{Ti}(\text{OR})_2(\text{dmae})_2]$ have also proved to be a good match with the analogous Ta complexes, and a liquid mixture of $[\text{Ta}(\text{OEt})_4(\text{dmae})]$ (90%)/ $[\text{Ti}(\text{OEt})_2(\text{dmae})_2]$ (10%), which evaporates as a single component,⁵³ was used to deposit a $\text{Ta}_2\text{O}_5/\text{TiO}_2$ mixed oxide,⁵⁴ which has potential applications as a high-*k* gate dielectric material. The related complex $[\text{Ti}(\text{dmae})_4]$ has been used in combination with $[\text{Ba}(\text{thd})_2(\text{pmdeta})]$ and $[\text{Sr}(\text{thd})_2(\text{pmdeta})]$ to deposit $(\text{Ba},\text{Sr})\text{TiO}_3$ by liquid injection MOCVD.⁵⁵ It was proposed that the complex is monomeric in the liquid state, and significantly, it was found that $[\text{Ti}(\text{dmae})_4]$ was a more efficient low temperature source of Ti over the temperature range 420–480 °C than $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$, leading to $(\text{Ba},\text{Sr})\text{TiO}_3$ with improved uniformity,⁵⁵ and this was attributed to the reduced thermal stability of $[\text{Ti}(\text{dmae})_4]$ fragments relative to $[\text{Ti}(\text{thd})_4]$.

The sterically hindered [mmp] ligand has been shown to be more effective at shielding electropositive centres than [dmae],³⁰ and the ligand has been used to form the Ti alkoxide complex $[\text{Ti}(\text{mmp})_4]$, which has recently been investigated as a TiO_2 precursor.⁵⁶ The complex is less air sensitive than $[\text{Ti}(\text{OPr}^i)_4]$ and allows the growth of TiO_2 at significantly lower substrate temperatures than $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$, as shown by the growth rate data in Fig. 6.⁵⁶ This indicates that $[\text{Ti}(\text{mmp})_4]$, like $[\text{Ti}(\text{dmae})_4]$, is likely to be an excellent source for the growth of high uniformity $(\text{Ba},\text{Sr})\text{TiO}_3$ at relatively low substrate temperatures, as well as being useful for

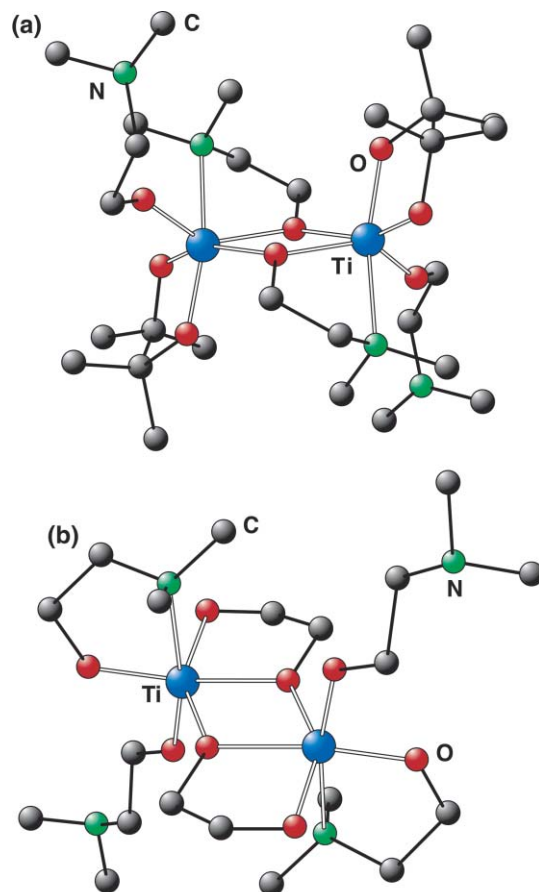


Fig. 7 Crystal structures of (a) $[\text{Ti}(\text{OCMe}_2\text{CMe}_2\text{O})(\text{dmae})_2]_2$ and (b) $[\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})(\text{dmae})_2]_2$ (after ref. 58).

the MOCVD of other titanium-containing oxides such as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

Diolate alkoxide ligands have also been used to increase the saturation on the Ti(IV) centre in Ti-oxide MOCVD precursors, and $[\text{Ti}(\text{mpd})(\text{thd})_2]$ (mpd = 2-methylpentane-2,4-diolate) has been used for the liquid injection MOCVD of $(\text{Ba},\text{Sr})\text{TiO}_3$.⁵⁷ However, the precursor showed no clear advantages over $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$ in terms of Ti incorporation. The dimeric alkoxy diolate $[\text{Ti}(\text{OCMe}_2\text{CMe}_2\text{O})(\text{dmae})_2]_2$, see Fig. 7(a), was used for the liquid injection MOCVD of TiO_2 over the temperature range 325–450 °C,⁵⁸ but again, there seem to be no particular advantages associated with its use compared with $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$. A similar complex, $[\text{Ti}(\text{mpd})(\text{dmae})_2]$ has also been used for the liquid injection MOCVD of TiO_2 .⁵⁹ The complex is likely to be dimeric in the solid state with a similar structure to $[\text{Ti}(\text{OCMe}_2\text{CMe}_2\text{O})(\text{dmae})_2]_2$ and was found to extend the available temperature window for oxide growth compared with the conventional source $[\text{Ti}(\text{OPr}^i)_4]$.⁵⁹ Interestingly, a similar complex $[\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})(\text{dmae})_2]_2$, see Fig. 7(b), failed to deposit TiO_2 in a reproducible fashion, and this was attributed to an intramolecular disproportionation reaction leading to pre-deposition of involatile polymeric $[\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2]_n$ species.⁵⁸

A few complexes other than alkoxides or β -diketonates have been used for the MOCVD of TiO_2 and related oxides. For example, it has been claimed that the monomeric β -ketoiminate complex $[\text{Ti}(\text{2meip})_2]$ [2meip = 4-(2-methylethoxy)imino-2-pentanoate], see Fig. 5(c), incorporates Ti more efficiently than $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$ at < 500 °C, and is therefore a superior precursor for the MOCVD of $(\text{Ba},\text{Sr})\text{TiO}_3$.⁶⁰ The anhydrous metal nitrate precursor $[\text{Ti}(\text{NO}_3)_4]$ (see Fig. 8) is also an efficient source for the deposition of TiO_2 at low substrate temperatures (230 °C).⁶¹ The absence of carbon in the molecule was seen as an advantage for optimising layer purity, but

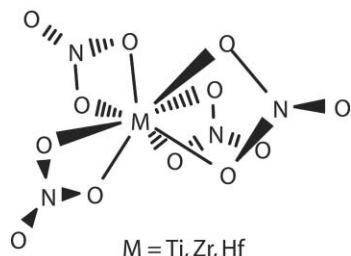


Fig. 8 Structure of $[M(NO_3)_4]$ ($M = Ti, Zr, Hf$) (after ref. 61).

doubts must remain about the thermal stability of metal nitrate MOCVD precursors, and the associated safety implications.

3.2. Zr-oxide and Hf-oxide precursors for gate dielectric films

Thin films of zirconium dioxide (ZrO_2) and hafnium dioxide (HfO_2) and the related silicates $ZrSi_xO_y$ and $HfSi_xO_y$ have high permittivities and are stable in contact with silicon, making them promising candidates to replace SiO_2 as the gate dielectric material for sub-0.1 μm complementary metal-oxide-semiconductor (CMOS) technology.³⁶

There are a number of problems associated with existing Zr and Hf oxide precursors. For instance, $ZrCl_4$ ⁶² and $HfCl_4$ ⁶³ are low volatility solids, which need substrate temperatures of 800 °C and above for oxide deposition, and the possibility exists of chloride contamination in the resulting films. The β -diketonates $[Zr(acac)_4]$ and $[Hf(acac)_4]$ contain a fully saturated eight-coordinate metal centre in a square antiprismatic configuration⁶⁴ (Fig. 9), which makes them relatively stable towards air and moisture, and both decompose to give ZrO_2 and HfO_2 . However, they require high evaporation temperatures (~ 200 °C) for sufficient vaporisation,⁶¹ and the oxide films are generally heavily contaminated with carbon.⁶⁵ $[Zr(thd)_4]$ is likely to have a similar eight-coordinate structure to $[Zr(acac)_4]$ and is especially stable towards air and moisture. $[Zr(thd)_4]$ has been successfully used for the MOCVD of high purity ZrO_2 ,^{65,66} although it is relatively involatile and requires high substrate temperatures (> 600 °C) for oxide growth. The fluorinated complexes $[Zr(tfac)_4]$ and $[Hf(tfac)_4]$ are more volatile,⁴⁶ but the presence of fluorine, which can degrade the Si substrate, is highly undesirable in microelectronics applications.

The metal nitrate complexes $[Zr(NO_3)_4]$ and $[Hf(NO_3)_4]$ ^{61,67} (see Fig. 8) have been used for the MOCVD of high purity

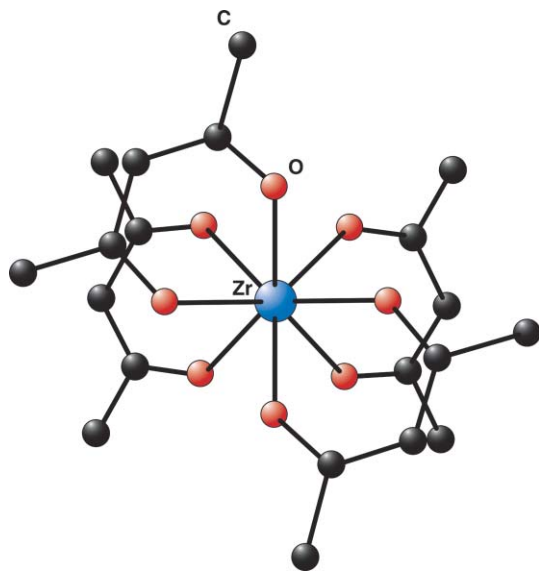
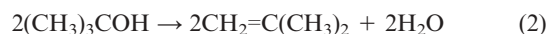
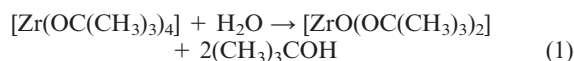


Fig. 9 Crystal structure of $[Zr(acac)_4]$ (reproduced with permission from ref. 64: <http://journals.iucr.org/>).

ZrO_2 and HfO_2 films at growth temperatures as low as 300 °C, but there are serious safety concerns about the widespread use of anhydrous nitrate complexes in MOCVD processes. The metal alkylamide complex $[Zr(NEt_2)_4]$ has shown considerable promise, and was used for the MOCVD of high quality ZrO_2 films in the temperature range 500–580 °C.⁶⁸

Metal alkoxides are attractive MOCVD precursors as they allow low deposition temperatures, and under optimum growth conditions allow the deposition of carbon-free films.⁶⁹ However, the majority of $[Zr(OR)_4]$ and $[Hf(OR)_4]$ complexes are dimeric or polymeric with limited volatility, due to the pronounced tendency of the Zr(IV) and Hf(IV) atoms to expand their coordination sphere to six, seven or eight.²⁹ For instance, even when the alkoxide groups are relatively bulky, such as in zirconium neo-pentoxide, $[Zr(OCH_2C(CH_3)_3)_4]$, the complex is a low volatility dimeric solid.⁶⁹

However, by increasing the steric hindrance of the alkoxide group by the insertion of [Me] groups on the α -carbon close to the metal centre it is possible to prevent dimerisation, and $[Zr(OBu^t)_4]$ and $[Hf(OBu^t)_4]$ are volatile monomeric complexes which have been successfully used for the MOCVD of ZrO_2 ^{70–72} and HfO_2 .^{63,73} However, these precursors contain unsaturated four-coordinate metal centres and the *tert*-butoxide ligand undergoes a catalytic “hydrolytic thermal decomposition” reaction in the presence of trace water which is generated during the decomposition process (see eqn. (1) and (2)).²⁸



Zr- and Hf-*tert*-butoxide complexes are therefore highly air- and moisture-sensitive and are susceptible to pre-reaction in the MOCVD reactor. Their reactivity also leads to a greatly reduced shelf life, especially in solution-based liquid injection MOCVD applications. There is thus an urgent requirement for stable and volatile Zr and Hf alkoxide MOCVD precursors.

Our favoured strategy for inhibiting oligomerisation in metal alkoxides, as well as increasing the coordination number of the highly positively charged central metal atoms, has been to incorporate bidentate donor functionalised ligands (see Table 2) into the complex. For example, the insertion of [dmae] into $[Ta(OEt)_5]_2$ and $[Nb(OEt)_5]_2$ leads to the monomeric complexes $[Ta(OEt)_4(dmae)]$ and $[Nb(OEt)_4(dmae)]$,^{12,66} which have significantly higher vapour pressures than the parent dimeric alkoxides. However, the insertion of [dmae], [dmap] or [bis-dmap] ligands into $[Zr(OR)_4]$ ($R = Pr^i, Bu^t$) failed to produce mononuclear species, resulting instead in the asymmetric bi-nuclear complexes $[Zr(OPr^i)_3(dmap)]_2$,⁷⁴ $[Zr(OPr^i)_3(bis-dmap)]_2$,⁷⁴ and $[Zr(OBu^t)_2(dmae)_2]_2$,⁷⁵ (see Fig. 10), which have relatively low volatilities, and which may also disproportionate into their asymmetric components (e.g. $Zr(OBu^t)_3(dmae)$ and $Zr(OBu^t)(dmae)_3$) on evaporation during the MOCVD process.⁶⁶ It has been suggested that the related complex $[Zr(dmae)_4]$ is monomeric,⁷⁶ but ¹H NMR data, see Fig. 11(a), indicate that the molecule is highly fluxional. As well as chelating to one Zr centre, the [dmae] ligand can also bridge two Zr centres (see Fig. 10), so it is likely that dimeric species $[Zr(dmae)_4]_2$ are formed, which may exist in dynamic equilibrium with monomeric $[Zr(dmae)_4]$ species.

The sterically hindered ligand [mmp], which contains two [Me] groups on the α -carbon atoms close to the metal centre, inhibits nucleophilic attack at the metal centre and is thus more effective than the [dmae] or [bis-dmap] ligands in preventing dimerisation or polymerisation of metal alkoxides. This facilitates the formation of mononuclear metal alkoxide complexes,³⁰ and we have therefore used the [mmp] ligand to prepare a series of complexes, $[Zr(OBu^t)_2(mmp)_2]$, $[Hf(OBu^t)_2(mmp)_2]$, $[Zr(mmp)_4]$ and $[Hf(mmp)_4]$, which are

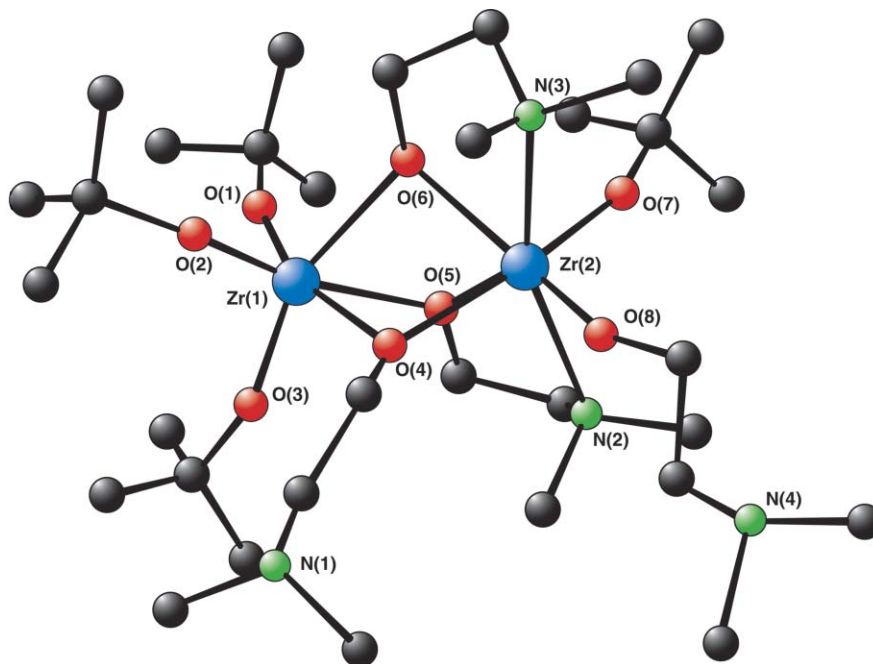


Fig. 10 Crystal structure of $[\text{Zr}(\text{OBU}^t)_2(\text{dmae})_2]$ (after ref. 75).

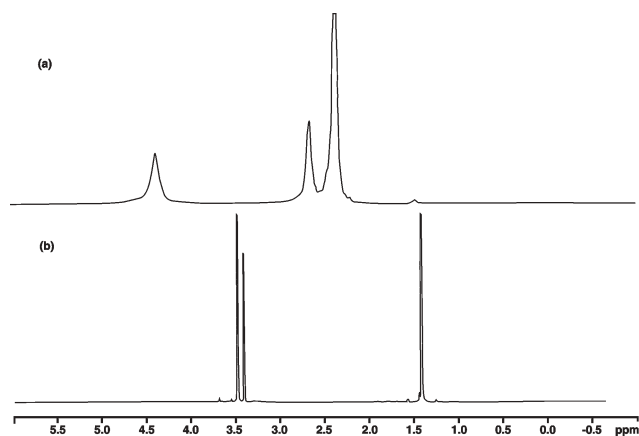


Fig. 11 ^1H NMR data (d_8 -toluene, 25 °C) for (a) $[\text{Zr}(\text{dmae})_4]$ and (b) $[\text{Zr}(\text{mmp})_4]$ (after ref. 78).

six-coordinate octahedral monomers in the solid state (see Figs. 12 and 13).^{77,78} The increased ligand saturation around the metal centres makes the complexes significantly less reactive to air and moisture than the four coordinate $[\text{M}(\text{OBU}^t)_4]$ complexes.

^1H NMR analysis of $[\text{Zr}(\text{mmp})_4]$, Fig. 11(b), and $[\text{Hf}(\text{mmp})_4]$ shows that in solution all four [mmp] groups are equivalent, indicating that the long $[\text{Zr}-\text{O}(\text{Me})]$ and $[\text{Hf}-\text{O}(\text{Me})]$ dative bonds cleave to give four-coordinate species containing monodentate [mmp] groups (see Fig. 14). The sharp resonance peaks in the NMR spectra of $[\text{Zr}(\text{mmp})_4]$ and $[\text{Hf}(\text{mmp})_4]$ indicate that the molecules are not fluxional and remain mononuclear in solution, with oligomerisation being inhibited by the steric hindrance of the two $[-\text{OCMe}_2\text{CH}_2\text{OMe}]$ methyl groups close to the central Zr and Hf atoms. The lack of ligand fluxionality in $[\text{Zr}(\text{mmp})_4]$ and $[\text{Hf}(\text{mmp})_4]$ is in marked contrast to analogous complexes such as $[\text{Zr}(\text{dmae})_4]$, and other Zr and Hf alkoxides, such as $[\text{Zr}(\text{OPr}^i)_3(\text{dmap})]_2$ and $[\text{Zr}(\text{OPr}^i)_3(\text{bis-dmap})]_2$,⁷⁴ for which broad resonance peaks in their ^1H NMR spectra provide clear evidence of ligand exchange, see Fig. 11(a). Although $[\text{Zr}(\text{mmp})_4]$ and $[\text{Hf}(\text{mmp})_4]$ are less coordinatively saturated in solution than in the solid state, the presence of [Me] groups close to the metal centre shields them from nucleophilic attack by water, in contrast to

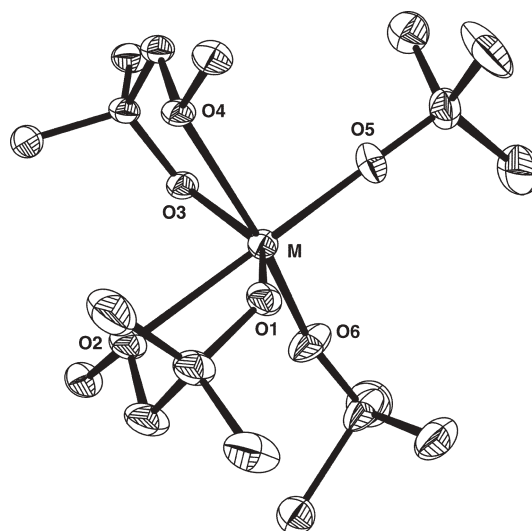


Fig. 12 Crystal structure of $[\text{M}(\text{OBU}^t)_2(\text{mmp})_2]$ (M = Zr, Hf) complexes (after ref. 77).

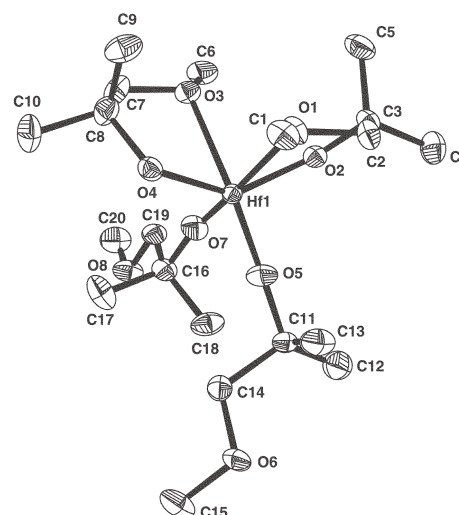


Fig. 13 Crystal structure of $[\text{Hf}(\text{mmp})_4]$ (after ref. 78).

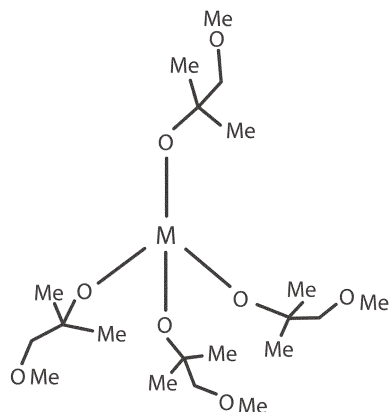


Fig. 14 Schematic representation of $[M(mmp)_4]$ ($M = \text{Zr}, \text{Hf}$) in solution.

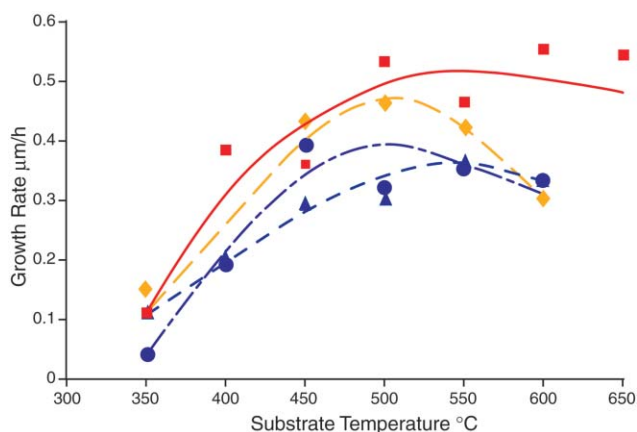


Fig. 15 Variation in oxide growth rate with substrate temperature: (■) $[\text{Zr}(\text{OBu}^1)_2(\text{mmp})_2]$, (◆) $[\text{Hf}(\text{OBu}^1)_2(\text{mmp})_2]$, (▲) $[\text{Zr}(\text{mmp})_4]$ and (●) $[\text{Hf}(\text{mmp})_4]$. Low pressure liquid injection MOCVD (20 mbar).

$[\text{M}(\text{OBu}^1)_4]$ complexes which are susceptible to catalytic decomposition in the presence of trace water, and this significantly increases their shelf-life and solution stability relative to $[\text{Zr}(\text{OBu}^1)_4]$ and $[\text{Hf}(\text{OBu}^1)_4]$.

The $[\text{M}(\text{OBu}^1)_2(\text{mmp})_2]$ and $[\text{M}(\text{mmp})_4]$ ($M = \text{Zr}, \text{Hf}$) complexes are excellent precursors for both conventional and liquid injection MOCVD applications, and have been used successfully for the liquid injection MOCVD of ZrO_2 and HfO_2 thin films over the temperature range 350–650 °C (see Fig. 15).⁷⁸ The related complex $[\text{Zr}(\text{dmae})_4]$ has also been used for the liquid injection MOCVD of ZrO_2 films.⁷⁹ However, the growth rate of films grown from $[\text{Zr}(\text{dmae})_4]$ was found to be strongly dependent on the substrate temperature. In the presence of oxygen, growth commenced at temperatures as low as 300 °C, but decreased very rapidly at temperatures above 360 °C. This contrasts with the growth data from $[\text{Zr}(\text{mmp})_4]$ (see Fig. 15), in which oxide growth commences at higher temperature (~ 350 °C) with the highest growth rates occurring at 550 °C. The oxide growth rate from $[\text{Zr}(\text{mmp})_4]$ shows little decrease at temperatures as high as 600 °C. This strongly suggests that $[\text{Zr}(\text{dmae})_4]$ has a significantly lower thermal stability than $[\text{Zr}(\text{mmp})_4]$, which is likely to give $[\text{Zr}(\text{dmae})_4]$ a rather narrow range of low-temperature MOCVD applications.

3.4. Precursors for $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$

The lead-based perovskite $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ has an exceptionally high remanent polarisation, and has thus been extensively investigated for non-volatile ferroelectric random access

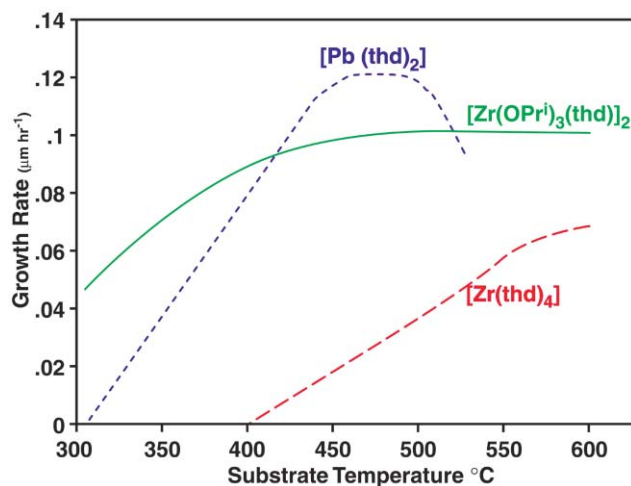


Fig. 16 Variation in oxide growth rate with substrate temperature for $[\text{Zr}(\text{OPr}^i)_3(\text{thd})_2]$, $[\text{Pb}(\text{thd})_2]$ and $[\text{Zr}(\text{thd})_4]$. Atmospheric pressure liquid injection MOCVD.

memory (NV-FERAM) applications.^{80,81} Monomeric $[\text{Pb}(\text{thd})_2]$ is the preferred lead precursor for the MOCVD of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$, due to its reduced toxic risk compared to the more volatile alkyls, $[\text{PbEt}_4]$ or $[\text{Et}_3\text{Pb}(\text{OCH}_2\text{C}(\text{CH}_3)_3)]$, and the most widely used precursor combination has been $[\text{Pb}(\text{thd})_2]$, $[\text{Zr}(\text{thd})_4]$ and $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$.^{47,49} However, the transport and MOCVD process characteristics of these precursors are not well matched.^{17,26} $[\text{Zr}(\text{thd})_4]$ is much less volatile than $[\text{Pb}(\text{thd})_2]$ and has a significantly higher thermal stability, depositing oxide at higher substrate temperatures,⁶⁶ see Fig. 16. This leads to uniformity problems in the resulting $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ film, and to blockages in the injector and inlet pipe-work of the MOCVD reactor. It is thus necessary to “tailor” the Zr precursor to improve its volatility and make its thermal decomposition behaviour more compatible with $[\text{Pb}(\text{thd})_2]$.

The heteroleptic Zr complex $[\text{Zr}(\text{OPr}^i)_2(\text{thd})_2]$ has been investigated as a precursor to ZrO_2 ¹⁷ and $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$,²⁶ with the aim of combining the high ambient stability of Zr β -diketonates with the lower thermal stability and higher volatility of Zr alkoxides. This mixed alkoxy/ β -diketonate complex contains a similar combination of ligands to $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$, and has a thermal stability which is compatible with both $[\text{Pb}(\text{thd})_2]$ and $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$.¹⁷ This has given rise to improved run to run reproducibility in the liquid injection MOCVD of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ and to higher uniformity films.²⁶ Variable temperature ¹H NMR studies indicated that in toluene solution $[\text{Zr}(\text{OPr}^i)_2(\text{thd})_2]$ exists as a dynamic mixture of three species, $[\text{Zr}(\text{OPr}^i)_4]$, $[\text{Zr}(\text{thd})_4]$ and $[\text{Zr}(\text{OPr}^i)_3(\text{thd})_2]$.⁸² Recrystallisation of the solid products from this solution yielded the symmetric dimer $[\text{Zr}(\text{OPr}^i)_3(\text{thd})_2]_2$ (see Fig. 17) as the most stable complex, and it has been shown that this precursor has significant advantages over $[\text{Zr}(\text{thd})_4]$. For instance, it is more volatile (see TGA data, Fig. 18) and deposits oxide films over a wider temperature range. The physical properties of $[\text{Zr}(\text{OPr}^i)_3(\text{thd})_2]$ are well-matched to those of $[\text{Pb}(\text{thd})_2]$ and, significantly, the optimum temperature range for oxide deposition from $[\text{Zr}(\text{OPr}^i)_3(\text{thd})_2]$ overlaps with that from $[\text{Pb}(\text{thd})_2]$, see Fig. 16. $[\text{Zr}(\text{OPr}^i)_3(\text{thd})_2]$ has proved to be a good precursor to ZrO_2 ⁸³ and superior to $[\text{Zr}(\text{thd})_4]$ for the liquid injection MOCVD of high uniformity $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$.^{26,84} A fluorinated mixed alkoxy/ β -diketonate, $[\text{Zr}(\text{OPr}^i)_2(\text{hfip})_2]$ (hfip = hexafluoroisopropoxide), which is probably a monomeric six-coordinate complex, has also been proposed as a possible precursor for ZrO_2 and $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$,⁸⁵ but trace fluorine contamination was observed under certain growth conditions in ZrO_2 films deposited by conventional MOCVD, which is a serious concern in microelectronics applications.

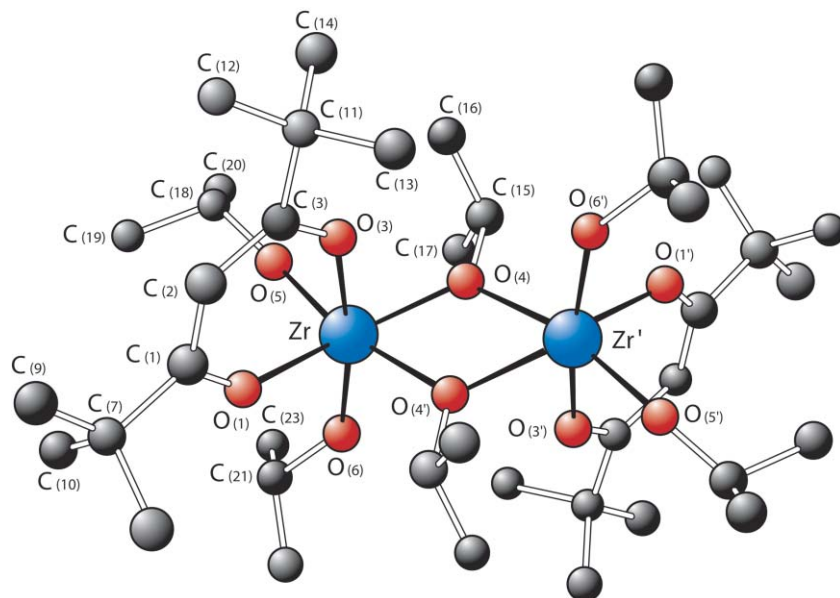


Fig. 17 Crystal structure of $[\text{Zr}(\text{OPr}^i)_3(\text{thd})]_2$ (after refs. 82, 83).

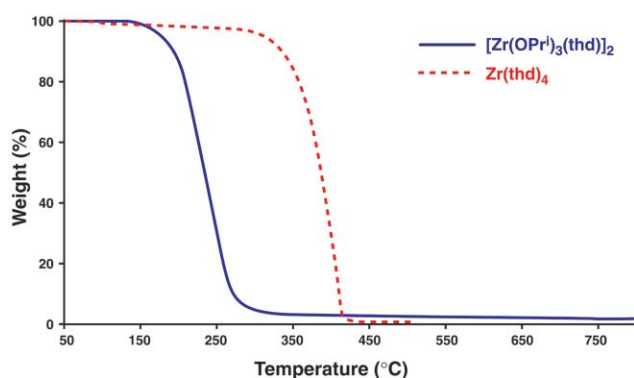


Fig. 18 TGA data for $[\text{Zr}(\text{OPr}^i)_3(\text{thd})]_2$ and $[\text{Zr}(\text{thd})_4]$.

4. Precursors for $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$

Lead scandium tantalate, $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$, has a high pyroelectric figure of merit relative to other lead-based perovskites such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ and thus has potential applications in un-cooled thermal imaging such as night sight technologies and fire detection.⁸⁶ To realise the full potential of $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ it is necessary to deposit thin films in the perovskite phase at temperatures compatible with any underlying circuitry in the substrate. Conventional precursors for the MOCVD of $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ include $[\text{Pb}(\text{thd})_2]$, $[\text{Sc}(\text{thd})_3]$ and $[\text{Ta}(\text{OEt})_5]$.⁸⁷ However, these are generally incompatible for liquid injection MOCVD applications. For instance, $[\text{Sc}(\text{thd})_3]$ deposits oxide in the region 550–600 °C compared to 400–450 °C for the less thermally stable $[\text{Ta}(\text{OEt})_5]$ precursor, leading to $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ with poor layer uniformity. $[\text{Sc}(\text{thd})_3]$ is also much less volatile than $[\text{Ta}(\text{OEt})_5]$ and requires an evaporator temperature >250 °C to give acceptable oxide growth rates which can lead to the decomposition of $[\text{Ta}(\text{OEt})_5]$. Consequently a more thermally stable Ta source and a more volatile Sc source are required.

4.1. Ta oxide precursors

The design of a suitable alternative to $[\text{Ta}(\text{OEt})_5]$ presents a considerable challenge to the precursor chemist. There are no β -diketonates available, and therefore $[\text{Ta}(\text{OME})_5]$ was investigated initially in the hope that substitution of $[\text{OEt}]$ groups by $[\text{OMe}]$ groups would impart increased thermal stability to the

molecule.⁸⁸ However, the optimum region of oxide deposition from $[\text{Ta}(\text{OME})_5]$ actually occurs at lower temperature than from $[\text{Ta}(\text{OEt})_5]$, and at much lower temperature than $[\text{Sc}(\text{thd})_3]$ (see Fig. 19). However, as shown in section 3.1, the thermal stability of an alkoxide complex can be increased by insertion of a β -diketonate group and the addition of $[\text{acac}]$ or $[\text{thd}]$ to $[\text{Ta}(\text{OR})_5]$ results in more thermally stable complexes of the type $[\text{Ta}(\text{OR})_4(\text{acac})]$ and $[\text{Ta}(\text{OR})_4(\text{thd})]$.^{89,90} Accordingly, the optimum oxide deposition temperature from $[\text{Ta}(\text{OME})_4(\text{acac})]$ and $[\text{Ta}(\text{OEt})_4(\text{thd})]$ is higher than from the parent $[\text{Ta}(\text{OR})_5]$ complexes, and increases in the order $[\text{Ta}(\text{OME})_4(\text{acac})] < [\text{Ta}(\text{OPr}^i)_4(\text{thd})] < [\text{Ta}(\text{OEt})_4(\text{thd})] < [\text{Ta}(\text{OME})_4(\text{thd})]$, as shown by the growth rate data in Fig. 20. These $[\text{Ta}(\text{OR})_4(\beta\text{-diketonate})]$ precursors are monomeric six-coordinate octahedral complexes (Fig. 21), and are generally more volatile and less air-sensitive than the parent alkoxides.⁹⁰ Significantly, $[\text{Ta}(\text{OR})_4(\beta\text{-diketonate})]$ precursors undergo much less decomposition in the evaporator during liquid injection MOCVD than $[\text{Ta}(\text{OEt})_5]$.⁸⁹ This leads to major process advantages and $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ in the required perovskite phase has been deposited at 600 °C using the optimum precursor combination $[\text{Pb}(\text{thd})_2]$, $[\text{Sc}(\text{thd})_3]$ and $[\text{Ta}(\text{OME})_4(\text{thd})]$ in a single THF solution.^{88,91}

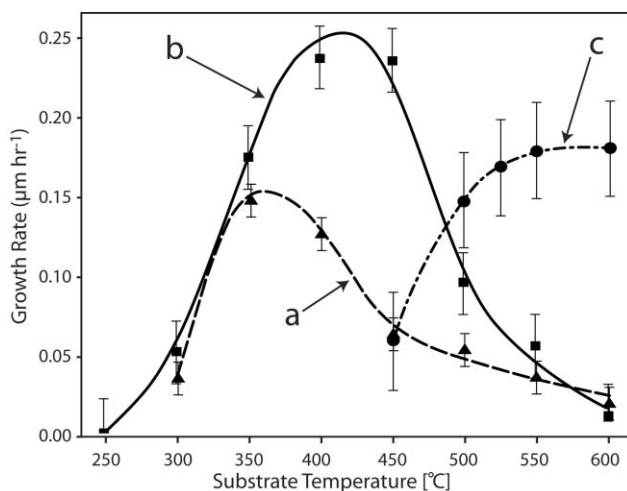


Fig. 19 Variation in oxide growth rate with substrate temperature for (a) $[\text{Ta}(\text{OME})_5]$, (b) $[\text{Ta}(\text{OEt})_5]$ and (c) $[\text{Sc}(\text{thd})_3]$. Atmospheric pressure liquid injection MOCVD (after ref. 88).

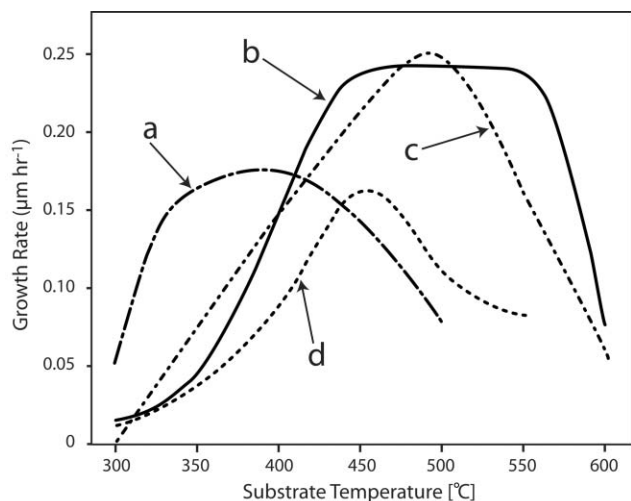


Fig. 20 Variation in oxide growth rate with substrate temperature for (a) $[\text{Ta}(\text{OMe})_4(\text{acac})]$, (b) $[\text{Ta}(\text{OMe})_4(\text{thd})]$, (c) $[\text{Ta}(\text{OEt})_4(\text{thd})]$ and (d) $[\text{Ta}(\text{OPr})_4(\text{thd})]$. Atmospheric pressure liquid injection MOCVD (after ref. 88).

Recently, it has been found that the phenyl-substituted β -diketonate complex, $[\text{Ta}(\text{OEt})_4(\text{dbm})]$ (see Fig. 21(c)), has a significantly enhanced thermal stability relative to $[\text{Ta}(\text{OEt})_4(\text{thd})]$ and other $[\text{Ta}(\text{OR})_4(\beta\text{-diketonate})]$ precursors,⁹² depositing oxide in a similar temperature region to $[\text{Sc}(\text{thd})_3]$, illustrated by the growth rate data in Fig. 22. The remarkable thermal stability of the $[\text{Ta}(\text{OEt})_4(\text{dbm})]$ complex has been attributed to the resonance stabilisation of the $[\text{C}-\text{O}]$ bonds in the β -diketonate group by delocalisation of negative charge into an extended conjugated electron system involving the π -orbitals of the phenyl groups in the dibenzoylmethanate ligand.⁹² This promises a further improvement in the uniformity of $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ grown by liquid injection MOCVD. The analogous Nb complex $[\text{Nb}(\text{OEt})_4(\text{dbm})]$ showed a similar increase in thermal stability relative to $[\text{Nb}(\text{OEt})_3]$.⁹²

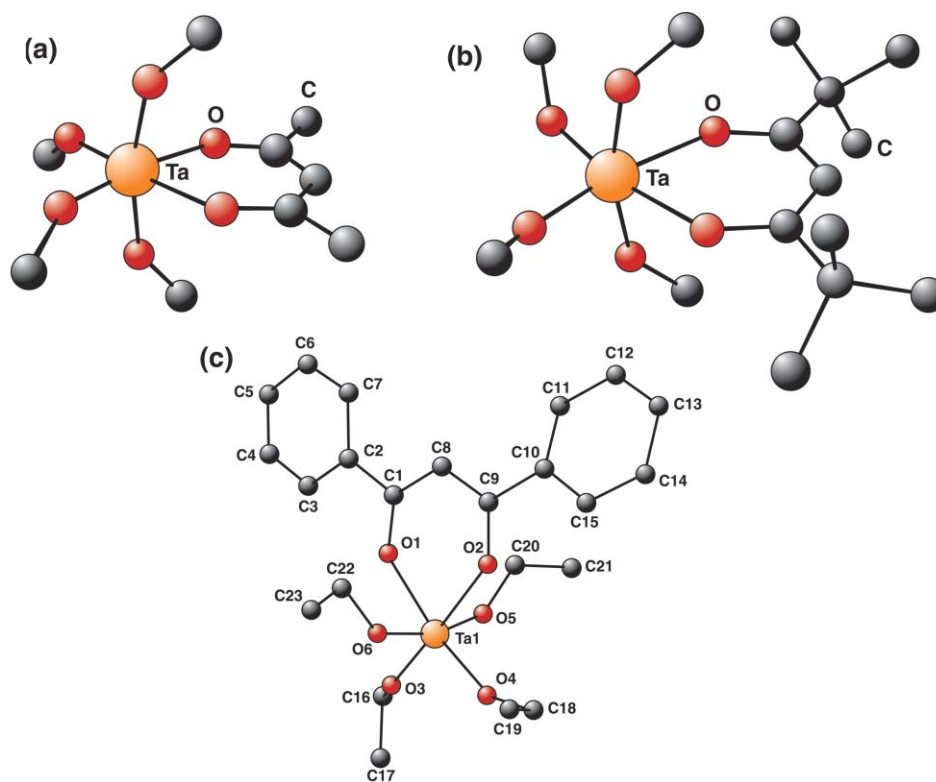


Fig. 21 Crystal structures of various $[\text{Ta}(\text{OR})_4(\text{L})]$ precursors: (a) $[\text{Ta}(\text{OMe})_4(\text{acac})]$, (b) $[\text{Ta}(\text{OMe})_4(\text{thd})]$ and (c) $[\text{Ta}(\text{OEt})_4(\text{dbm})]$ (after refs. 88, 92).

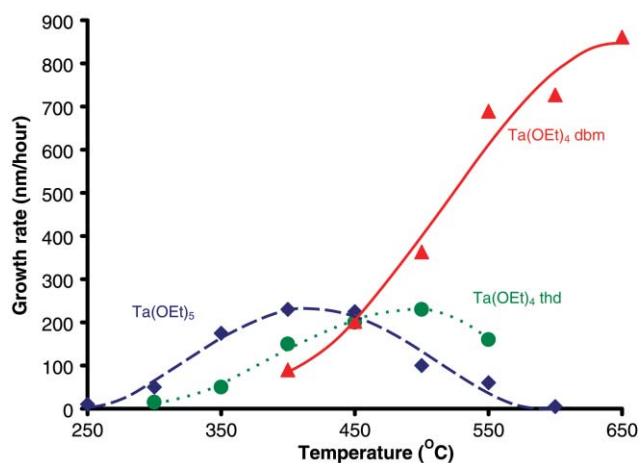


Fig. 22 Variation in oxide growth rate with substrate temperature for $[\text{Ta}(\text{OEt})_5]$, $[\text{Ta}(\text{OEt})_4(\text{thd})]$ and $[\text{Ta}(\text{OEt})_4(\text{dbm})]$. Low pressure liquid injection MOCVD (20 mbar) (after ref. 92).

This “resonance stabilisation” effect is well known in organic chemistry,⁹³ and may have important implications for the future design of MOCVD precursors, as the addition of electron withdrawing (*e.g.* NO_2 , halide) or donating (*e.g.* OR, NR_3 , PR_3) groups may alter the degree of stabilisation of the β -diketonate group, and thus alter the thermal stability of the complex, allowing precursors to be more closely “tailored” for a particular application.

4.2. Sc-oxide precursors

Despite the improvements in Ta precursor chemistry, there remains a need for a more volatile Sc oxide source than $[\text{Sc}(\text{thd})_3]$. Mixed alkoxide/ β -diketonates of scandium do not exist, and so we have used a different approach to increasing precursor volatility. Asymmetric β -diketonate ligands [tmod] and [mhd] (see Fig. 2) have been shown to influence the volatility of yttrium β -diketonates,⁹⁴ and we have found that

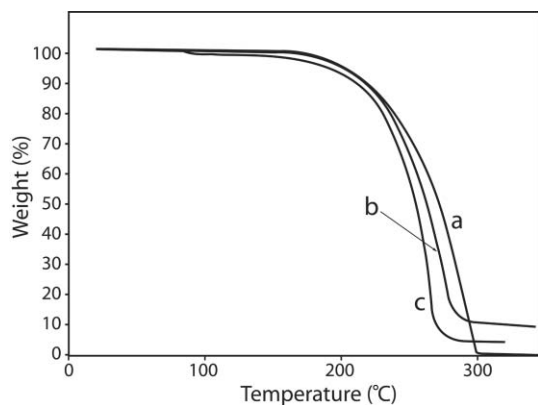


Fig. 23 TGA data for (a) [Sc(thd)₃], (b) [Sc(mhd)₃] and (c) [Sc(tmod)₃] (after ref. 95).

[Sc(tmod)₃] and [Sc(mhd)₃] are both more volatile than [Sc(thd)₃], as shown by the TGA data in Fig. 23. All three complexes are monomeric in the solid state (the crystal structures of [Sc(thd)₃] and [Sc(tmod)₃] are shown in Fig. 24) and so the increased volatility must arise from a disruption in the molecular packing of the scandium β-diketonate complexes in the solid state.⁹⁵ [Sc(tmod)₃] is a particularly promising precursor for Pb(Sc_{0.5}Ta_{0.5})O₃, as it allows the use of significantly lower evaporator temperatures than [Sc(thd)₃], and deposits oxide films in a similar temperature regime to [Pb(thd)₂] and [Ta(OMe)₄(thd)].⁹⁵

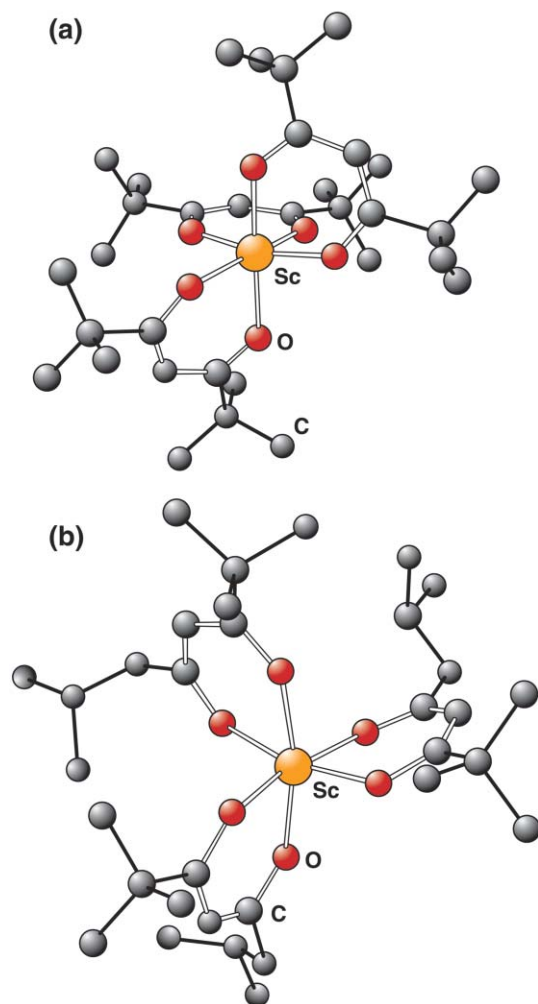


Fig. 24 Crystal structures of (a) [Sc(thd)₃] and (b) [Sc(tmod)₃] (after ref. 95).

5. Precursors for SrBi₂(Ta_xNb_{1-x})₂O₉

Thin films of the layered perovskites strontium bismuth tantalate, SrBi₂Ta₂O₉, strontium bismuth niobate, SrBi₂Nb₂O₉, and strontium bismuth tantalate niobate, SrBi₂(Ta_xNb_{1-x})₂O₉, have important potential applications in non-volatile ferroelectric (FERAM) computer memories.^{96,97} The application of liquid injection MOCVD techniques to the deposition of SrBi₂Ta₂O₉ and SrBi₂(Ta_xNb_{1-x})₂O₉ has been seriously restricted by a lack of stable and compatible precursors. Conventional precursors include [Sr(thd)₂], [Bi(C₆H₅)₃], [BiMe₃], [Bi(OC₅H₁₁)₃] and [Ta(OEt)₅] or [Ta(OPrⁱ)₄(thd)].^{98,99} but these are generally incompatible, having very different physical properties and decomposition characteristics which can lead to poor layer uniformity. A potential solution to this problem is the use of “single-source” precursors which contain elements required in the oxide film in a single molecule, an approach which has been successfully used for the MOCVD of LiNbO₃ and LiTaO₃ using the heterometal alkoxides LiNb(OEt)₆,¹⁰⁰ LiNb(OEt)₅(thd),¹⁰¹ and LiTa(OEt)₅(thd).¹⁰² More recently, a number of Sr–Ta and Sr–Nb heterometal alkoxides have been used for the liquid injection MOCVD of SrBi₂Ta₂O₉ and SrBi₂(Ta_xNb_{1-x})₂O₉, as described below.

5.1. Sr–Ta and Sr–Nb heterometal single source precursors

The Sr–Ta and Sr–Nb heterometal alkoxides, [Sr{Ta(OEt)₆}₂],^{97,99} [Sr{Ta(OPrⁱ)₆}₂]¹⁰³ and [Sr{Nb(OEt)₆}₂]⁹⁷ have been used for the MOCVD of SrBi₂Ta₂O₉ and SrBi₂(Ta_xNb_{1-x})₂O₉. The major advantage of this approach is that the metal/metal ratio in the precursor matches that in the deposited oxide film, but a potential disadvantage of precursors such as [Sr{Ta(OEt)₆}₂] is that the vastly different volatilities of the [Sr(OR)₂] and [Ta(OR)₅] fragments lead to a partitioning of the Sr and Ta components in the gas phase and to an excess of the more volatile Ta component in the gas phase. Another disadvantage is that [Sr{Ta(OR)₆}₂] precursors contain an unsaturated Sr centre, which makes them susceptible to attack by moisture and reduces their shelf-life, especially in solution-based liquid injection MOCVD. We have therefore inserted donor-functionalised alkoxide ligands, such as [dmae] and [bis-dmap] (see Table 2), into the heterometal alkoxide to increase the ligand coordination around the central Sr atom, and render the complexes less susceptible to decomposition in solution and in the gas phase.

Replacement of two of the [EtO] ligands in [Sr{Ta(OEt)₆}₂] with [dmae] or [bis-dmap] leads to the complexes [Sr{Ta(OEt)₅(dmae)}₂] and [Sr{Ta(OEt)₅(bis-dmap)}₂]. The crystal structure of [Sr{Ta(OEt)₅(bis-dmap)}₂] (Fig. 25)¹⁰⁴ shows that the [bis-dmap] ligand acts in a bidentate fashion, leading

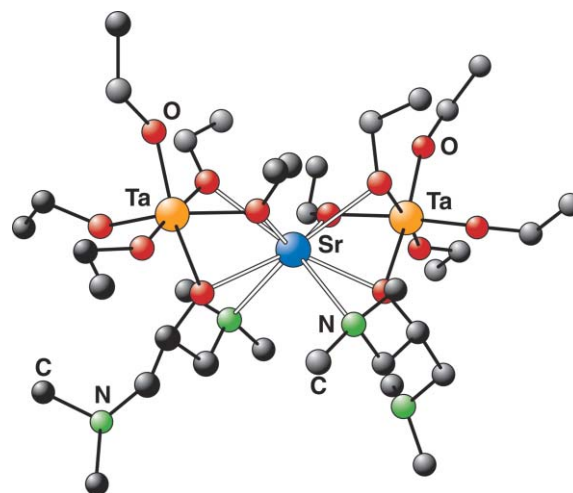


Fig. 25 Crystal structure of [Sr{Ta(OEt)₅(bis-dmap)}₂] (after ref. 104).

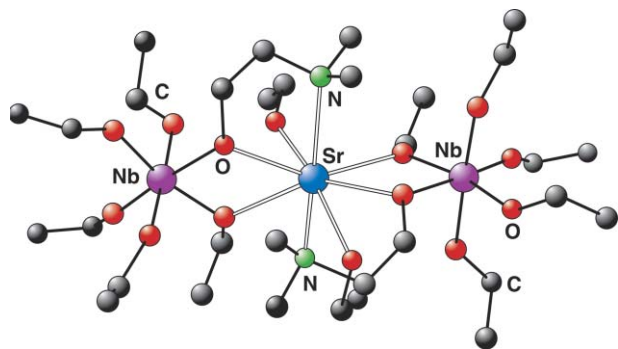


Fig. 26 Crystal structure of $[\text{Sr}\{\text{Nb}(\text{OEt})_5(\text{dmae})\}_2](\text{EtOH})_2$.

to a fully saturated eight-coordinate Sr atom. Both precursors have been used in liquid injection MOCVD to deposit strontium tantalate,¹⁰⁵ but $[\text{Sr}\{\text{Ta}(\text{OEt})_5(\text{dmae})\}_2]$ was found to be the most useful MOCVD precursor in terms of volatility and deposition behaviour. The Sr:Ta ratio was found to be a strong function of substrate temperature and O_2 flow, and under optimum growth conditions the Ta/Sr ratio in strontium tantalate was found to be close to 2, corresponding to the Sr/Ta ratio in $\text{SrBi}_2\text{Ta}_2\text{O}_9$. Liquid injection MOCVD studies at other laboratories have confirmed that $[\text{Sr}\{\text{Ta}(\text{OEt})_5(\text{dmae})\}_2]$ leads to improved stoichiometry control in $\text{SrBi}_2\text{Ta}_2\text{O}_9$.¹⁰⁶

Other donor functionalised alcohols such as [mee] are also effective in stabilising Sr–Ta and Sr–Nb heterometal alkoxides, and studies in other laboratories confirm that, in contrast to $[\text{Sr}\{\text{Ta}(\text{OPr}^i)_6\}_2]$, the Sr/Ta mole ratio remains constant during the distillation of $[\text{Sr}\{\text{Ta}(\text{OEt})_5(\text{mee})\}_2]$.¹⁰⁷

The analogous Sr–Nb complexes, $[\text{Sr}\{\text{Nb}(\text{OEt})_5(\text{dmae})\}_2]$ and $[\text{Sr}\{\text{Nb}(\text{OEt})_5(\text{bis-dmap})\}_2]$, have been synthesised by the insertion of the dmae ligand or bis-dmap ligand into the parent alkoxide $[\text{Sr}\{\text{Nb}(\text{OEt})_6\}_2]$.¹⁰⁸ $[\text{Sr}\{\text{Nb}(\text{OEt})_5(\text{dmae})\}_2]$ is an oil, but in the presence of a slight excess of ethanol it crystallises as the bis-ethanol adduct $[\text{Sr}\{\text{Nb}(\text{OEt})_5(\text{dmae})\}_2(\text{EtOH})_2]$, shown in Fig. 26. The liquid complex $[\text{Sr}\{\text{Nb}(\text{OEt})_5(\text{dmae})\}_2]$ is particularly suited to MOCVD applications, evaporating in $[\text{Sr}\{\text{Ta}(\text{OEt})_5(\text{dmae})\}_2]$ (150–320 °C determined by TGA). We have found that 1:1 mixtures of $[\text{Sr}\{\text{Nb}(\text{OEt})_5(\text{dmae})\}_2]$ and $[\text{Sr}\{\text{Ta}(\text{OEt})_5(\text{dmae})\}_2]$ form a free flowing volatile liquid which distils as a *single* fraction at 140 °C (0.1 mmHg) without any change in composition, and thus $[\text{Sr}\{\text{Ta}(\text{OEt})_5(\text{dmae})\}_2]/[\text{Sr}\{\text{Nb}(\text{OEt})_5(\text{dmae})\}_2]$ mixtures are promising multi-component precursors for the liquid injection MOCVD of $\text{SrBi}_2(\text{Ta}_x\text{Nb}_{1-x})_2\text{O}_9$.

5.2. Bi oxide precursors

The progress in heterometal alkoxide chemistry described above leads to the requirement for a compatible Bi source. The conventional sources $[\text{Bi}(\text{C}_6\text{H}_5)_3]$ and $[\text{Bi}(\text{thd})_3]$ are not particularly compatible with Sr–Ta and Sr–Nb alkoxides, having significantly higher thermal stabilities and different evaporation characteristics.⁹⁷ BiMe_3 is a better match, and has been used with $[\text{Sr}\{\text{Ta}(\text{OEt})_6\}_2]$ and $[\text{Sr}\{\text{Nb}(\text{OEt})_6\}_2]$ to deposit $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{SrBi}_2(\text{Ta}_x\text{Nb}_{1-x})_2\text{O}_9$,⁹⁷ but it is highly reactive and potentially explosive which seriously restricts its practical use. Bi-alkoxides are more suitable co-precursors, as they are likely to have similar volatility and decomposition characteristics to Sr–Ta and Sr–Nb heterometal alkoxides. However, simple bismuth alkoxides, $[\text{Bi}(\text{OR})_3]$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^i$) are poorly characterised and have limited stability and volatility, subliming in only very low yields under high vacuum.¹⁰⁹ This is due to the high tendency of the Bi(III) centre to expand its coordination sphere to six, which favours the formation of polymeric $[\text{Bi}(\text{OR})_3]_n$ aggregates.

In order to inhibit oligomerisation, sterically demanding alkoxide ligands have again been employed and $[\text{Bi}(\text{O}i\text{Bu})_3]$ has

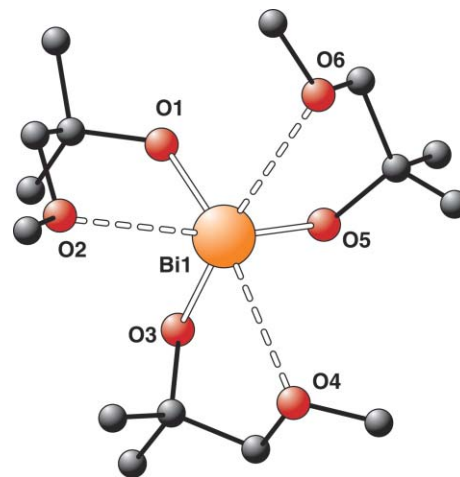


Fig. 27 Crystal structure of $[\text{Bi}(\text{mmp})_3]$ (after ref. 114).

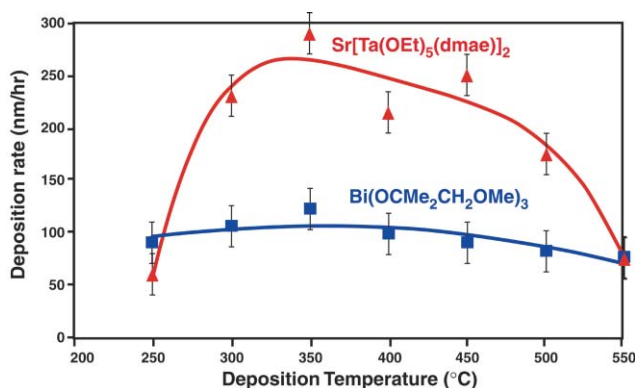


Fig. 28 Variation of growth rate with substrate temperature for (\blacktriangle) strontium tantalate grown from $[\text{Sr}\{\text{Ta}(\text{OEt})_5(\text{dmae})\}_2]$ (0.1 M THF solution) and (\blacksquare) Bi_2O_3 grown from $\text{Bi}(\text{mmp})_3$ (0.06 M heptane solution). Low pressure liquid injection MOCVD (20 mbar) (after ref. 114).

been shown to be a volatile monomeric species;¹¹⁰ but is highly air sensitive and has only a limited stability in solution. $[\text{Bi}(\text{OC}_5\text{H}_{11})_3]$ is also volatile,¹¹¹ and has been used with $[\text{Sr}\{\text{Ta}(\text{OPr}^i)_6\}_2]$ for the liquid injection MOCVD of $\text{SrBi}_2\text{Ta}_2\text{O}_9$,¹¹² although there are doubts about the evaporation characteristics of this source. The sterically hindered ligand [mmp] has been shown to be highly effective in reducing polymerisation in metal alkoxides,³⁰ and the monomeric complex $[\text{Bi}(\text{mmp})_3]$ has recently been synthesised^{113,114} and characterised by single crystal X-ray diffraction (Fig. 27).¹¹⁴ $[\text{Bi}(\text{mmp})_3]$ evaporates in a similar temperature range to $[\text{Sr}\{\text{Ta}(\text{OEt})_5(\text{dmae})\}_2]$ and $[\text{Sr}\{\text{Nb}(\text{OEt})_5(\text{dmae})\}_2]$, and deposits oxide at similar substrate temperatures, as shown in Fig. 28. Therefore $[\text{Bi}(\text{mmp})_3]$ has a number of advantages over existing Bi sources for the liquid injection MOCVD of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{SrBi}_2(\text{Ta}_x\text{Nb}_{1-x})_2\text{O}_9$ and is currently under intensive investigation.

6. Precursors for $\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.66})\text{O}_3$

The perovskite phase of lead magnesium niobate, $\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.66})\text{O}_3$, is an important relaxor ferroelectric material. It has several unique properties, including a high dielectric constant, low thermal expansion, broadened dielectric maxima, and a high electrostrictive strain coefficient.¹¹⁵ This makes $\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.66})\text{O}_3$ attractive for a variety of microelectromechanical (MEM) and electronic applications, such as in transducers and ceramic capacitors.

The MOCVD of $\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.66})\text{O}_3$ has previously been

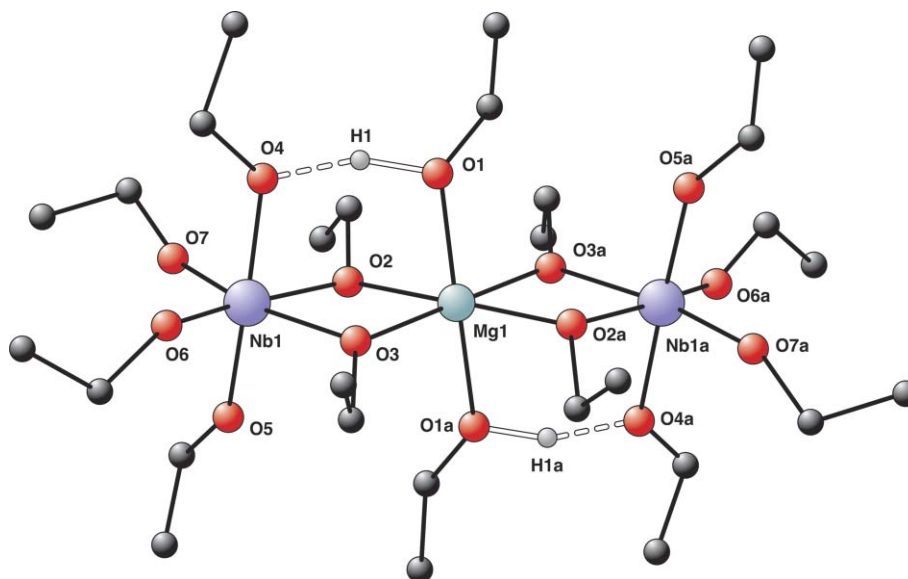


Fig. 29 Crystal structure of $[\text{Mg}\{\text{Nb}(\text{OEt})_6\}_2(\text{EtOH})_2]$ (after ref. 118).

carried out using conventional bubbler-based techniques with precursors such as $[\text{PbEt}_4]$, $[\text{Pb}(\text{acac})_2]$, $[\text{Mg}(\text{acac})_2]$, $[\text{Mg}(\text{thd})_2]$ and $[\text{Nb}(\text{OEt})_5]$.^{116,117} These precursors are not particularly compatible, and are therefore not well suited to liquid injection MOCVD. For instance, alkoxides such as $[\text{Nb}(\text{OEt})_5]$ decompose at lower temperatures than Pb and Mg β -diketonates, and are also significantly more volatile. One potential solution to this problem is the use of “single source” precursors, and the bimetallic alkoxide precursor $[\text{Mg}\{\text{Nb}(\text{OEt})_6\}_2(\text{EtOH})_2]$ (see Fig. 29)¹¹⁸ has recently been investigated in combination with $[\text{Pb}(\text{thd})_2]$.¹¹⁹ In the absence of $[\text{Pb}(\text{thd})_2]$, $[\text{Mg}\{\text{Nb}(\text{OEt})_6\}_2(\text{EtOH})_2]$ gave magnesium niobium oxide films with a Mg : Nb ratio of 1 : 2 at lower substrate temperatures, but was shown to partially decompose in the gas phase at higher substrate temperatures to give Nb-rich oxide films. The addition of $[\text{Pb}(\text{thd})_2]$ to the system was found to significantly alter the deposition chemistry of $[\text{Mg}\{\text{Nb}(\text{OEt})_6\}_2(\text{EtOH})_2]$. In marked contrast to growth using $[\text{Mg}\{\text{Nb}(\text{OEt})_6\}_2(\text{EtOH})_2]$ alone, there was no incorporation of Mg at low substrate temperatures (425–500 °C), but at higher substrate temperatures (550–600 °C) the Mg : Nb ratio of 1 : 2 required in $\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.66})\text{O}_3$ was obtained.¹¹⁹

The mechanism by which $[\text{Pb}(\text{thd})_2]$ influences the decomposition behaviour of $[\text{Mg}\{\text{Nb}(\text{OEt})_6\}_2(\text{EtOH})_2]$ has not been established. However, it is possible that decomposition of $[\text{Pb}(\text{thd})_2]$ leads to the liberation of $[\text{thd}]$ ligands in the gas phase which then interact with the oxygen-deficient Mg centre in $[\text{Mg}\{\text{Nb}(\text{OEt})_6\}_2(\text{EtOH})_2]$ to give $[\text{Mg}\text{-thd}]$ species which have a relatively high thermal stability, thus leading to a deficiency of Mg in the oxide films at low substrate temperatures and more efficient incorporation of Mg at higher temperatures.

In view of the process complexities arising from the use of $[\text{Mg}\{\text{Nb}(\text{OEt})_6\}_2(\text{EtOH})_2]$, it may be more appropriate to investigate more thermally stable Nb alkoxide precursors for the MOCVD of $\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.66})\text{O}_3$. For example, the new monomeric complex, $[\text{Nb}(\text{OEt})_4(\text{dbm})]$, which has an almost identical structure to $[\text{Ta}(\text{OEt})_4(\text{dbm})]$, see Fig. 15(c), has been shown to have a considerably higher thermal stability than other Nb alkoxides,⁹² and is likely to be a close thermal match to $[\text{Mg}(\text{thd})_2]$.

7. Conclusions and future prospects

The use of new precursors specifically designed for MOCVD process has resulted in significant process improvements and higher quality electroceramic oxides. Precursor properties

and decomposition characteristics have been modified and improved by the addition of chelating β -diketonate ligands or donor-functionalised alkoxide groups. Up to now, readily available ligands, such as commercially available alkoxides and β -diketonates, have been used in the tailoring of precursors. In the future, it is likely that we will see the growing use of “designed” ligands, which will lead to even more scope for precursor tailoring. For instance, it may be possible to fine-tune the thermal stability of precursors by substituting electron withdrawing or donating groups on to phenyl-substituted β -diketonate ligands such as $[\text{dbm}]$. In this area, the organic chemist can undoubtedly contribute, and there will thus be an increasing overlap between disciplines, including inorganic and organometallic chemists, organic chemists, materials scientists and device physicists. To date, advances in MOCVD have often been largely empirical, however in future we are likely to see the increasing use of *in-situ* monitoring techniques, such as quadrupole mass spectroscopy and reflectance difference spectroscopy which are already being used in the related technique of atomic layer deposition (ALD).¹⁴ Feedback from these techniques should contribute to the design and development of new precursors specifically designed for the MOCVD of a variety of oxides. Progress in advanced technologies, such as microelectronics, will be heavily dependent on further advances in MOCVD technology, in which precursor design and synthesis will play an essential role. The precursor chemist is likely to be gainfully employed for a very long time.

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