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Novel mononuclear zirconium and hafnium alkoxides; improved precursors for the MOCVD of ZrO_2 and HfO_2

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The novel complexes $[Zr(OBu^t)_2(OCMe_2CH_2OMe)_2]$ (1) and $[Hf(OBu^t)_2(OCMe_2CH_2OMe)_2]$ (2) are mononuclear and volatile, and are highly promising precursors for the deposition of zirconium dioxide and hafnium dioxide thin films by metalorganic chemical vapour deposition (MOCVD).

Thin films of zirconium dioxide (ZrO_2) and hafnium dioxide (HfO_2) have a wide variety of important technological applications. In particular, they 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.[1] Metalorganic chemical vapour deposition (MOCVD) is an attractive technique for the deposition of these materials,[2] offering the potential for large area growth, good composition control and film uniformity, and excellent conformal step coverage at device dimensions less than 2 μm, which is particularly important in microelectronics applications.

An essential requirement for a successful MOCVD process is the availability of precursors with the appropriate physical properties (*e.g.* volatility) for vapour phase transport and a suitable reactivity for deposition. There must be an adequate temperature window between evaporation and decomposition, and for most electronics applications oxide deposition is restricted to temperatures in the region of 500 °C, to prevent degradation of the underlying silicon circuitry and metal interconnects.

Unfortunately, there are a number of problems associated with existing Zr and Hf oxide precursors. For instance, $ZrCl_4$[3] and $HfCl_4$[4] are low volatility solids which need substrate temperatures of 800 °C and above for oxide deposition. Metal β-diketonates, such as $[Zr(acac)_4]$[5] and $[Zr(thd)_4]$[5,6] (thd = 2,2,6,6-tetramethylheptane-3,5-dionate) also require high substrate temperatures (>600 °C) for oxide growth, and the films are generally contaminated with carbon. Metal alkoxides are more attractive MOCVD precursors as they allow lower deposition temperatures, and under optimum growth conditions allow the deposition of carbon-free films.[7] 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.[8] In order to inhibit oligomerisation, bulky sterically demanding ligands such as *tert*-butoxide have been employed, and $[Zr(OBu^t)_4]$ and $[Hf(OBu^t)_4]$ have been successfully used for the MOCVD of ZrO_2 and HfO_2.[9] However, these precursors contain unsaturated four-coordinate metal centres, making them highly air and moisture sensitive and 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 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 into the complex. For example, the insertion of dimethylaminoethoxide ($OCH_2CH_2NMe_2$, dmae) into $[Ta(OEt)_5]_2$ and $[Nb(OEt)_5]_2$ leads to the monomeric complexes $[Ta(OEt)_4(dmae)]$ and $[Nb(OEt)_4(dmae)]$,[6] which have significantly higher vapour pressures than the parent dimeric alkoxides. However, the insertion of dmae, dmap ($OCH(Me)CH_2NMe_2$) or bis-dmap ($OCH(CH_2NMe_2)CH_2NMe_2$) into $[Zr(OR)_4]$ (R = Pr^i, Bu^t) failed to produce mononuclear species, resulting instead in the asymmetric bi-nuclear complexes $[Zr(OPr^i)_3(dmap)]_2$,[10] $[Zr(OPr^i)_3(bis\text{-}dmap)]_2$,[10] and $[Zr(OBu^t)_2(dmae)_2]_2$,[11] 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.[6]

The sterically hindered ligand 1-methoxy-2-methyl-2-propanolate ($OCMe_2CH_2OMe$) has been shown to be highly effective in minimising the molecularity of metal alkoxides,[12] facilitating the formation of mononuclear metal alkoxide complexes such as $[Bi(OCMe_2CH_2OMe)_3]$.[12,13] We have now found that the $[OCMe_2CH_2OMe]$ ligand can be used to inhibit the oligomerisation of Zr and Hf alkoxides, and in this communication we report the synthesis and structural characterisation of the novel mononuclear complexes $[Zr(OBu^t)_2(OCMe_2CH_2OMe)_2]$ (**1**) and $[Hf(OBu^t)_2(OCMe_2CH_2OMe)_2]$

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(**2**),† and highly promising preliminary MOCVD results are reported.

These are the first mononuclear Zr and Hf alkoxide complexes to be structurally characterised, although the structures of some fluoroalkoxide and siloxide complexes have been reported, *i.e.* $[Zr(OCCH_3(CF_3)_2)_4]$,[14] $[Zr(OSi(OBu^t)_3)_4]$,[15] and $[Hf(OSi(OBu^t)_3)_4]$.[15]

The molecular structure of **1** was determined by single crystal X-ray diffraction‡ and is shown in Fig. 1, together with selected bond lengths and angles. The complex is mononuclear containing two *tert*-butoxide groups and two chelating $[OCMe_2CH_2OMe]$ groups, which form a distorted octahedron of oxygen atoms around the central Zr(IV) atom. The Zr–O bonds fall into three groups. The $Zr–O(Bu^t)$ are the shortest (1.938(2), 1.945(2) Å), the $Zr–O(CMe_2)$ bonds are intermediate in length (2.018(2) Å), whilst, unsurprisingly, the dative Zr–O(OMe) bonds are longest (2.403(2), 2.411(2) Å). The $Zr–O(Bu^t)$ bond lengths in **1** are similar to those in $[Zr(OBu^t)_2(dmae)_2]_2$ (1.883(13)–1.959(13) Å)[11] and $[Zr_2(OBu^t)_3(bis\text{-}dmap)_4(OH)]$ (1.939(4)–1.968(3) Å),[10] and are close to the terminal $Zr–O(Bu^t)$ bond lengths in the oxoalkoxide cluster, $[Zr_3O(OBu^t)_{10}]$ (1.886(12)–1.940(9)).[16] The bite angles of the chelating $[OCMe_2CH_2OMe]$ groups are the smallest in the molecule (70.50(9), 70.63(8)°) and deviate significantly from the ideal octahedral angle of 90°. Comparison with other mononuclear alkoxides, $[Bi(OCMe_2CH_2OMe)_3]$[13] and $[Cr(OCMe_2CH_2OMe)_3]$[12] shows that the bite angle of the $[OCMe_2CH_2OMe]$ group tends to decrease with increasing atomic radius, varying from 78.63(8)–84.10(8)° in the Cr complex (Cr atomic radius: 1.30 Å), through 70.50(9)–70.63(8)° in **1** (Zr atomic radius: 1.60 Å) to 67.0(3)–69.5(2)° in the Bi alkoxide (Bi atomic radius: 1.70 Å). The other *cis* O–Zr–O bond angles in **1** vary widely in the range 82.13(9)–104.35(10)°. The *trans* O–Zr–O bond angles also deviate significantly from the ideal 180° angle, with O(3)–Zr(1)–O(1) showing the largest deviation (141.54(10)°).

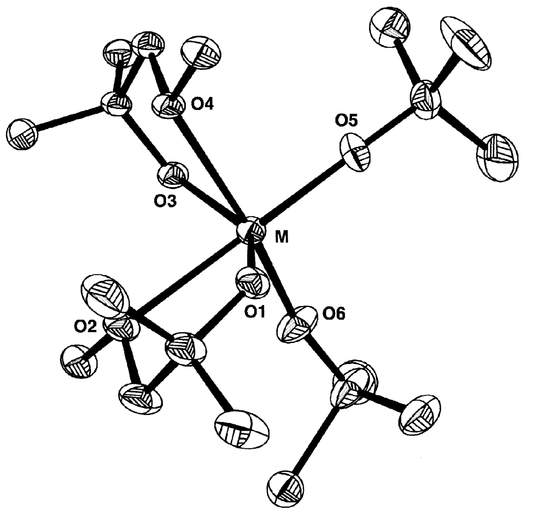

Fig. 1 The molecular structure of $[M(OBu^t)_2(OCMe_2CH_2OMe)_2]$ complexes (M = Zr, Hf). Selected bond lengths (Å) and angles (°): M = Zr (**1**): Zr(1)–O(1) 2.018(2), Zr(1)–O(2) 2.411(2), Zr(1)–O(3) 2.018(2), Zr(1)–O(4) 2.403(2), Zr(1)–O(5) 1.945(2), Zr(1)–O(6) 1.938(2); O(6)–Zr(1)–O(5) 100.95(12), O(5)–Zr(1)–O(3) 104.35(10), O(6)–Zr(1)–O(1) 104.12(11), O(5)–Zr(1)–O(1) 99.64(10), O(3)–Zr(1)–O(1) 141.54(10), O(6)–Zr(1)–O(4) 170.30(9), O(5)–Zr(1)–O(4) 85.06(10), O(3)–Zr(1)–O(4) 70.63(8), O(1)–Zr(1)–O(4) 82.13(9), O(6)–Zr(1)–O(2) 85.45(12), O(5)–Zr(1)–O(2) 169.47(10), O(3)–Zr(1)–O(2) 82.46(9), O(1)–Zr(1)–O(2) 70.50(9), O(4)–Zr(1)–O(2) 89.79(8). M = Hf (**2**): Hf(1)–O(1) 2.006(3), Hf(1)–O(2) 2.382(3), Hf(1)–O(3) 2.009(3), Hf(1)–O(4) 2.377(3), Hf(1)–O(5) 1.932(3), Hf(1)–O(6) 1.932(3), O(6)–Hf(1)–O(5) 100.75(15), O(6)–Hf(1)–O(1) 104.59(15), O(5)–Hf(1)–O(1) 98.63(13), O(6)–Hf(1)–O(3) 99.21(14), O(5)–Hf(1)–O(3) 105.22(13), O(1)–Hf(1)–O(3) 142.29(13), O(6)–Hf(1)–O(4) 170.21(12), O(5)–Hf(1)–O(4) 84.80(12), O(1)–Hf(1)–O(4) 82.33(12), O(3)–Hf(1)–O(4) 71.41(11), O(6)–Hf(1)–O(2) 85.77(15), O(5)–Hf(1)–O(2) 168.90(13), O(1)–Hf(1)–O(2) 70.87(12), O(3)–Hf(1)–O(2) 82.34(12), O(4)–Hf(1)–O(2) 90.09(11).

Complex **2**‡ is isomorphous with **1** (see Fig. 1) and as expected, the Hf–O bond lengths show precisely the same trends as the Zr–O bond lengths in **1**, although in general the Hf–O bonds are slightly shorter than the analogous Zr–O bonds. The $Hf–O(Bu^t)$ bonds are shortest (1.932(3) Å), the $Hf–O(CMe_2)$ bonds are intermediate (2.006(3), 2.009(3) Å), and the dative Hf–O(OMe) bonds are the longest (2.377(3), 2.382(3) Å). There are few relevant Hf alkoxide structures to make a meaningful comparison, but the $Hf–O(Bu^t)$ bond lengths in **2** are similar in length to the terminal Hf–O(Et) bonds in $[Hf_6O_2(OEt)_{20}(EtOH)_2]$ (1.90(2)–2.06(2) Å).[16] The bite angles of the $[OCMe_2CH_2OMe]$ groups in **2** are 70.87(12) and 71.41(11)°, very slightly larger than the equivalent angles in **1**. The other *cis* O–Hf–O bonds in **2** vary in the range 82.33(12)–106.6(3)°, similar to the spread in values observed in **1**. Of the *trans* O–Hf–O angles, O(1)–Hf(1)–O(3) at 142.29(13)° shows the largest deviation from the ideal 180° angle.

Significantly, **1** and **2** were found to be much less moisture sensitive than their respective parent alkoxides, $[Zr(OBu^t)_4]$ and $[Hf(OBu^t)_4]$. This greatly increased ambient stability makes **1** and **2** particularly suitable for liquid injection MOCVD applications, and both complexes were successfully used for the deposition of ZrO_2 and HfO_2 films over a wide range of substrate temperatures (350–650 °C).§

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†Synthesis of **1**: 1-methoxy-2-methyl-2-propanol ($HOCMe_2CH_2OMe$) (1.44 g, 13.9 mmol) was added dropwise to a stirred solution of $[Zr(OBu^t)_4]$ (2.69 g, 7 mmol)) in hexane (40 ml). The mixture was boiled under reflux for two hours and then allowed to cool. Volatiles were removed *in vacuo* to give a white crystalline solid, which was recrystallised from hexane to give crystals suitable for X-ray diffraction. Yield: 2.98 g (96% based on $[Zr(OBu^t)_4)]$. Mp 96–101 °C (uncorrected). Anal: Calcd. for $C_{18}H_{40}O_6Zr$: C, 48.71; H: 9.10; Found: C, 46.32; H: 8.77%. ^1H NMR: (400 MHz, d_8-tol) 1.19 (s, 12H, $OC(CH_3)_2CH_2OCH_3$), 1.37 (s, 18H, $OC(CH_3)_3$), 3.23 (s, 4H, $OC(CH_3)_2CH_2OCH_3$), 3.40 (s, 6H, $OC(CH_3)_2CH_2OCH_3$). ^{13}C NMR: 34.1 ($OC(CH_3)_2CH_2OCH_3$), 38.5 ($OC(CH_3)_3$), 65.4 ($OC(CH_3)_2CH_2OCH_3$), 78.6 ($OC(CH_3)_2CH_2OCH_3$ and $OC(CH_3)_3$), 90.5 ($OC(CH_3)_2CH_2OCH_3$). IR: (ν/cm^{-1}, Nujol, NaCl) 3588(w), 3442(w), 2725(m), 2360(w), 1356(s), 1277(m), 1227(m), 1206(s), 1177(s), 1115(s), 1080(s), 1012(s), 974(s), 936(s), 801(s), 782(s), 595(s). Complex **2** was synthesised by a precisely similar procedure to that described for **1**, using $[Hf(OBu^t)_4]$ instead of $[Zr(OBu^t)_4]$. X-Ray quality crystals of **2** were obtained by recrystallisation of the white crystalline product from hexane. Yield: 4.4 g (97% based on $[Hf(OBu^t)_4]$). Mp 100–104 °C (uncorrected). Anal. Calcd. for $C_{18}H_{40}O_6Hf$: C, 40.71; H: 7.61; Found: C, 38.93; H: 7.30%. ^1H NMR: (400 MHz, d_8-tol) 1.18 (s, 12H, $OC(CH_3)_2CH_2OCH_3$), 1.38 (s, 18H, $OC(CH_3)_3$), 3.21 (s, 12H, $OC(CH_3)_2CH_2OCH_3$), 3.42 (s, 12H, $OC(CH_3)_2CH_2OCH_3$). ^{13}C NMR: (100 MHz d_8-tol) 34.4 ($OC(CH_3)_2CH_2OCH_3$), 38.6 ($OC(CH_3)_3$), 65.7, ($OC(CH_3)_2CH_2OCH_3$), 78.0, 79.1 ($OC(CH_3)_2CH_2OCH_3$ and $OC(CH_3)_3$), 90.9 ($OC(CH_3)_2CH_2OCH_3$). IR: (ν/cm^{-1}, Nujol, NaCl) 3441(w), 2726(m), 2256(w), 1272(s), 1177(s), 1074(s), 1016(s), 976(s), 802(s), 782(s), 593(s).

‡Crystal data for **1**: $C_{18}H_{40}O_6Zr$, $M = 443.73$, orthorhombic, space group $P21\,21\,21$, $a = 10.2970(12)$, $b = 10.7861(12)$, $c = 21.258(2)$ Å, $\beta = 90°$, $V = 2361.1(5)$ Å^3, $Z = 4$, $\rho = 1.248$ g cm^{-3}, $\mu = 0.491$ mm^{-1}, Refl. collected = 14636, Refl. unique = 5439, $R_1[I > 2\sigma(I)] = 0.0389$, wR_2 (all data) = 0.1030. Crystal data for **2**: $C_{18}H_{40}O_6Hf$, $M = 530.99$, orthorhombic, space group $P21\,21\,21$, $a = 10.1972(8)$, $b = 10.7413(8)$, $c = 21.3221(17)$ Å, $\beta = 90°$, $V = 2335.4(3)$ Å, $Z = 4$, $\rho = 1.510$ g cm^{-3}, $\mu = 4.492$ mm^{-1}, Refl. collected = 13992, Refl. unique = 5260, $R_1[I > 2\sigma(I)] = 0.0247$, wR_2 (all data) = 0.0609. Crystallographic data were recorded on a Bruker Smart APEX ccd diffractometer using graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $T = 150$ K). The structure was solved by Direct Methods and refined by full-matrix least squares against F^2 using all data. Except for disordered Bu^t carbon atoms, non-hydrogen atoms were refined anisotropically and H-atoms were fixed in geometrically ideal positions. CCDC reference numbers 171865 and 171866. See http://www.rsc.org/suppdata/jm/b1/b109994a/ for crystallographic data in CIF or other electronic format.

§Thin films of ZrO_2 or HfO_2 were deposited by liquid injection MOCVD (20–30 mbar) using 0.1 M solutions of **1** or **2** in toluene. Evaporator temperatures of 130–150 °C were used, and the precursor solutions were injected at a rate of 4–8 cm^3 h^{-1} (Ar carrier gas flow: 400–600 cm^3 min^{-1}; O_2 flow: 100–150 cm^3 min^{-1}). The films were deposited over the temperature range 350–650 °C on Si(100) substrates. Growth rates were in the range 0.35–0.50 μm h^{-1}.

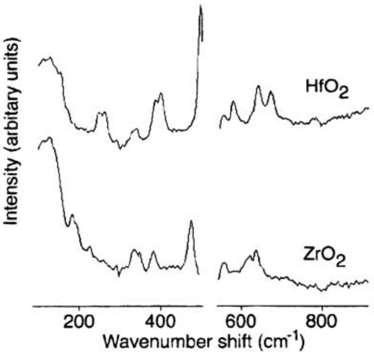

Fig. 2 Raman spectroscopy data for ZrO_2 and HfO_2 films deposited at 650 °C by liquid injection MOCVD using 0.1 M solutions of **1** or **2** in toluene.

During the MOCVD studies there was no evidence of pre-reaction, or of precursor decomposition upstream of the substrate. The films were shown to be ZrO_2 and HfO_2 by laser Raman spectroscopy and Auger electron spectroscopy (AES). The Raman spectra of films deposited at substrate temperatures of 650 °C are shown in Fig. 2 and comparison with bulk crystalline data[17,18] showed that both films are in the α- or monoclinic phase, a phase which often predominates in MOCVD-grown ZrO_2 and HfO_2 films.[19,20] The films were shown by AES to be high purity, with carbon levels close to, or below, the AES detection limit (approx. 1 at.%).

In conclusion, the novel mononuclear Zr and Hf alkoxides, **1** and **2** have been synthesised and structurally characterised. Both complexes have a number of advantages over existing MOCVD precursors to ZrO_2 and HfO_2 and have shown great promise in preliminary MOCVD studies.

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