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# Homoleptic zirconium amidates: single source precursors for the aerosol-assisted chemical vapour deposition of ZrO<sub>2</sub>†

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We report the development of a true single source precursor (i.e. without any need for an exogenous source of oxygen) for the growth of zirconia thin films by aerosol-assisted chemical vapour deposition (AACVD) using an original family of zirconium(v) amidate derivatives, which are easily prepared by protonolysis of [Zr(NMe<sub>2</sub>)<sub>4</sub>] with the free amide pro-ligands. In all but one case the reactions resulted in the isolation of the corresponding homoleptic eight-coordinate zirconium(w)tetrakis(amidato) derivatives. Three of these species along with a tris(amidato)dimethylamido zirconium(iv) derivative have been characterised by single crystal X-ray diffraction analysis. The materials potential of the homoleptic compounds was identified through the application of design criteria derived from consideration of the existing knowledge base relating to the pyrolysis of wholly organic amides. In this manner the thermal decomposition of the homoleptic derivatives benefits from facile, molecularly imposed pyrolysis pathways, which provide for the privileged generation of volatile small molecule by-products and the production of contaminant-free solid oxide material. Thermogravimetric analysis, in conjunction with NMR spectroscopic analysis of the volatile products resulting from their thermal decomposition, indicated the potential of the homoleptic species as exquisite single source precursors to ZrO<sub>2</sub> at moderate temperatures. The compound bearing both N- and C-iso-propyl substituents was, thus, applied as a true single source precursor under ambient pressure AACVD conditions. The resultant films, deposited on either SiO<sub>2</sub>-coated glass or quartz substrates, are smooth and comprise small and densely packed crystalline particulates that are shown by XRD to be primarily cubic ZrO<sub>2</sub>. Compositional analysis by X-ray photoelectron spectroscopy (XPS) revealed that the oxygen delivered, and the decomposition pathway provided, by the amidate ligand structure yields  $ZrO_2$  films which, though slightly sub-stoichiometric ( $ZrO_{1,8-1,9}$ ), contain undetectable levels of carbon incorporation.

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## Introduction

The successful deployment of true single-source precursor reagents for the metal organic chemical vapour deposition (MOCVD) of metal oxide thin films often necessitates a compromise. For many systems the realisation of the volatility necessary for vapour phase mass transport requires the introduction of peripheral organic substituents that reduce intermolecular association but which can act as sources of detrimental carbon contamination in the deposited films. A case in point is provided by many of the reported precursors to zirconium dioxide, which has attracted significant attention as a high permittivity ( $\kappa \sim 25$ ) dielectric thin film material with low leakage currents.<sup>1,2</sup> Although the initial evolution of the simple  $\beta$ -diketonate species, [Zr(acac)<sub>4</sub>] (acac = pentane-2,4-dionate),<sup>3</sup> to more volatile 2,2,6,6-tetramethylheptane-3,5-dionato and the fluorinated 1,1,1-trifluoropentane-2,4-dionato analogues facilitated enhanced oxide growth rates,<sup>4,5</sup> these modifications came at the expense of even greater levels of carbon and fluorine incorporation respectively. While a variety of alkoxide-,<sup>6</sup> organometallic-7 and, more recently, amidinate-based<sup>8</sup> zirconium systems have also been described, all such precursors require the use of oxygen as co-reagent and typically high temperatures  $(>600 \ ^{\circ}C)$  to achieve successful growth. These latter features are particularly unattractive if deposition onto oxidatively- or thermally-sensitive substrates is to be achieved. Although use of the carbon-free complex  $[Zr(NO_3)_4]$  has allowed single-source

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<sup>†</sup> Electronic supplementary information (ESI) available: Experimental procedures, instrumentation details and characterisation data for compounds **1–6**, NMR spectra relating to the thermal decomposition of compounds **2** and **5**, UV-vis, XPS and micro-XRD characterisation of the zirconia films. CCDC 1498668–1498671. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6tc03631g

#### Paper

and carbon-free growth at temperatures as low as 300  $^{\circ}$ C, the films were found to contain 10–20% excess oxygen while the potentially explosive nature of the precursor probably limits its more widespread application.<sup>9</sup> More general success has been achieved by a liquid injection CVD (LICVD) technique utilising a variety of heteroleptic alkoxides.<sup>10</sup> In these cases, however, O<sub>2</sub> is again required as a co-reagent resulting in oxygen-rich thin film stoichiometries.<sup>10</sup> Although a variety of volatile amidebased systems for the atomic layer deposition (ALD) of zirconia have also been described,<sup>11</sup> this approach to thin film growth necessarily requires a secondary oxygen source (typically water or ozone) and is potentially limited by its requirements for highly specialised equipment and high vacuum conditions.

Aerosol-assisted CVD (AACVD) is a modification of the atmospheric pressure CVD technique that is gradually finding more widespread application.<sup>12</sup> In this case the requirement for precursor volatility is circumvented through transport of the chemical precursor to the reaction chamber as a solution in the form of aerosol droplets using an inert carrier gas. Although the only limitation on precursor implementation is, thus, its solubility in an appropriate solvent, for a single source precursor system the requirement of a well-defined decomposition pathway with limited competing deleterious processes becomes even more rigorous. For the specific case of metal oxide AACVD, the development of true single source precursors is an even greater priority in order to obviate the hazards inherent in the use of oxidising co-reagents in the presence of volatilised flammable solvents. Kin et al. have described the sole use of the AACVD technique for the deposition of zirconia films using ultrasonic nebulisation of [Zr(OBu)<sub>4</sub>], [Zr(OBu)<sub>3</sub>(acac)], [Zr(OBu)<sub>2</sub>(acac)<sub>2</sub>], and [Zr(OBu)(acac)<sub>3</sub>] as 0.1 M 1-butanol solutions.<sup>13</sup> Although polycrystalline thin films were deposited at temperatures between 300 and 550 °C, no compositional data for the films were provided and, taking account of the behaviour of zirconium alkoxide and acetylacetonate derivatives under conventional MOCVD conditions,<sup>3-6</sup> it appears likely that these films also suffered from significant levels of carbon contamination.

With these specific considerations in mind we have implemented a general programme of research to identify and synthesise single-source precursors for the AACVD of metal oxides that will completely fulfil the requirements of not only ultimate materials integrity but also scalability and cost effectiveness. From this perspective, metal amidates provide an as yet unexploited opportunity for precursor design. Whereas it has been understood for a century that wholly organic acid amides decompose thermally by a selective process of nitrile and water elimination,<sup>14</sup> no information is available for the products resulting from the pyrolysis of metal amidate derivatives. We speculated, therefore, that an archetypical multivalent metal amidate would thermally decompose under AACVD conditions by the route shown in Scheme 1. The initial proposed alkene elimination step is reminiscent of the Chugaev elimination established for isolobal and isoelectronic metal xanthate-based sulphide precursor chemistry.<sup>15</sup> Although there are no directly relevant literature species to provide comparison, we postulate that the acidity of the resultant metal hemiamilate will be sufficient to effect the



Scheme 1 Proposed decomposition pathway for a metal amidate single source oxide precursor under AACVD conditions.

protonolysis of other amidate ligands whereupon the established nitrile elimination step will result in clean formation of the metal oxide.<sup>14</sup> It is notable that the only source of oxygen in any resultant oxide material arises from the amidate ligands and that this process should occur with the maintenance of the metal's initial oxidation state. Although the materials potential of several metal amidate derivatives was highlighted some years ago in the patent literature,<sup>16</sup> the embodiments highlighted in these claims were specifically derived from the volatility of the metal amidate species and their consequent utility in conventional direct delivery CVD or atomic layer deposition (ALD) processes. Most notably, no claims were made for the utility of these species as single source oxide precursors or as suitable reagents for any type of solution-based materials deposition processs.

In this study we target a series of zirconium amidate derivatives as single source AACVD precursors to zirconium oxide. Although our general interest in this material is derived from its technological importance, more specifically, the diamagnetic nature and stability of the Zr(w) oxidation state lends itself ideally to structural and mechanistic analysis. From this perspective the  $ZrO_2$  deposition study described herein provides a suitably challenging exemplar with which to begin to address the broader potential of metal amidates as single source precursors to metal oxides under mild AACVD conditions.

## Results and discussion

The zirconium amidate derivatives, compounds **1–6**, were synthesised in a manner similar to that employed by Schafer and co-workers in their studies of the use of heteroleptic zirconium amidates as pre-catalytic reagents for a variety of catalytic transformations.<sup>17</sup> Addition of 4 molar equivalents of the relevant amide pro-ligand at 0 °C to a solution of tetra-kis(dimethylamido)zirconium afforded the homoleptic amidate complexes, **2–6**, in excellent yields (>80%) after heating at 60 °C for 18 hours (Scheme 2). In contrast, and presumably for steric reasons, the corresponding reaction of  $[Zr(NMe_2)_4]$  with the *N-tert*-butyl-2,2-dimethylpropanamide pro-ligand bearing both *N-t*-Bu (R<sup>1</sup>) and *C-t*-Bu (R<sup>2</sup>) substitution was observed to be

Paper



Scheme 2 Synthesis of the homoleptic zirconium derivatives, compounds 2-6.

limited to protonolysis of only three dimethylamide residues to provide the heteroleptic species, tris(*N-tert*-butyl-2,2-dimethylpropanamidato)dimethylamido-zirconium, compound **1**. All six compounds were readily isolated as colourless crystalline solids after removal of the reaction solvent.

Compounds **1–6** were characterised in d<sub>s</sub>-toluene solution by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy and by elemental analysis. The <sup>1</sup>H NMR spectra of compounds **2–6** confirmed the absence of the dimethylamido singlet resonance at *ca.*  $\delta$  3.10 ppm and clearly evidenced their constitution as homoleptic tetrakis(amidato) species with, in each case, all four amidate ligands in equivalent environments. In contrast the <sup>1</sup>H NMR spectrum of compound **1** displayed a resonance at  $\delta$  3.06 ppm characteristic of the retention of a single dimethylamide ligand along with two sets of *tert*butyl methyl signals for each of the *C*- and *N*-bonded organic residues, which were observed in a 2:1 ratio by integration. Although a <sup>1</sup>H EXSY NMR experiment demonstrated that these latter signals were not exchanging on the NMR timescale, compound **1** displayed only a single signal associated with its sp<sup>2</sup> amidato carbon centres in its <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. This signal was observed to resonate at  $\delta$  165.3 ppm, significantly less deshielded than the comparable signals of the homoleptic compounds (**2–6**, *ca.*  $\delta$  186–189 ppm).

The likely origin of these solution-based observations was resolved by X-ray diffraction analysis performed on single crystals of compounds **1**, **2**, **5** and **6** after crystallisation from toluene at room temperature. The results of these experiments are illustrated in Fig. 1 while details of the analyses and selected bond length and angle data are presented in Tables 1 and 2 respectively.

Fig. 1(a) illustrates that compound **1** is a distorted octahedral tris-amidato dimethylamido zirconium species. Two of the amidate ligands are bound in a chelating  $\kappa^2$  fashion while the third coordinates to the zirconium centre *via* a  $\kappa^1$ -binding mode through its basic oxygen centre, presumably to alleviate unfavourable steric congestion as a result of the multiplicity of bulky tertiary-butyl substituents. Although the Zr–O bond length



Fig. 1 ORTEP representations (25% probability ellipsoids) of (a) compound 1; (b) compound 2; (c) compound 5; (d) the Zr(1) containing molecule of compound 6. Hydrogen atoms are removed for clarity.

1	2	E	6
1	Z	5	0
$C_{29}H_{60}N_4O_3Zr$	$C_{32}H_{64}N_4O_4Zr$	$C_{32}H_{64}N_4O_4Zr$	$C_{28}H_{56}N_4O_4Zr$
604.03	660.09	660.09	603.98
150.00(10)	150(2)	150(2)	150.0(3)
Monoclinic	Monoclinic	Monoclinic	Triclinic
$P2_1/n$	C2	Cc	$P\bar{1}$
10.8077(5)	18.3482(7)	20.1357(5)	11.7212(6)
17.3778(8)	11.9920(5)	15.0949(4)	16.1788(9)
18.1390(9)	8.9002(4)	12.2443(3)	19.0915(10)
90	90	90	68.599(5)
90.090(4)	112.527(2)	98.836(2)	79.594(4)
90	90	90	81.912(5)
3406.7(3)	1808.90(13)	3677.44(16)	3304.3(3)
4	2	4	4
1.178	1.212	1.192	1.214
0.354	0.341	0.336	0.367
1304.0	712	1424	1296.0
0.214 imes 0.197 imes 0.132	0.250 imes 0.200 imes 0.150	$0.256 \times 0.222 \times 0.046$	0.25 imes 0.171 imes 0.1
6.738 to 52.136	3.398 to 27.090	3.36 to 27.48	6.602 to 52.744
$-13 \le h \le 13,$	$-23 \le h \le 23,$	$-26 \le h \le 26;$	$-12 \leq h \leq 14$ ,
$-21 \leq k \leq 20,$	$-15 \leq k \leq 15,$	$-19 \leq k \leq 19;$	$-18 \leq k \leq 20,$
$-22 \leq l \leq 22$	$-11 \leq l \leq 11$	$-15 \leq l \leq 10$	$-23 \leq l \leq 22$
25 934	13 994	6983	28 277
6663, 0.0506	3951, 0.0518	6983, 0.0000 – <i>hkl</i> f5 data	13 381, 0.0587
6663/195/385	3951/80/342	6983/2/391	13 381/0/699
1.026	1.061	1.024	0.810
0.0521, 0.1245	0.0318, 0.0631	0.0517, 0.1460	0.0464, 0.0701
0.0710, 0.1360	0.0342, 0.0643	0.0649, 0.1553	0.0924, 0.0756
1.41 / -0.45	0.248 / -0.701	1.570/-1.785	0.56/-0.51
	$\begin{array}{c} 1 \\ & \mathbf{C}_{29}\mathbf{H}_{60}\mathbf{N}_{4}\mathbf{O}_{3}\mathbf{Zr} \\ & 604.03 \\ & 150.00(10) \\ & \mathbf{Monoclinic} \\ & P2_{1}/n \\ & 10.8077(5) \\ & 17.3778(8) \\ & 18.1390(9) \\ & 90 \\ & 90.090(4) \\ & 90 \\ & 90.090(4) \\ & 90 \\ & 3406.7(3) \\ & 4 \\ & 1.178 \\ & 0.354 \\ & 1304.0 \\ & 0.214 \times 0.197 \times 0.132 \\ & 6.738 \text{ to } 52.136 \\ & -13 \leq h \leq 13, \\ & -21 \leq k \leq 20, \\ & -22 \leq l \leq 22 \\ & 25934 \\ & 6663, 0.0506 \\ & 6663/195/385 \\ & 1.026 \\ & 0.0521, 0.1245 \\ & 0.0710, 0.1360 \\ & 1.41/-0.45 \\ \end{array}$	$\begin{array}{cccccccc} 1 & 2 \\ \hline C_{29}H_{60}N_4O_3Zr & C_{32}H_{64}N_4O_4Zr \\ 604.03 & 660.09 \\ 150.00(10) & 150(2) \\ \hline \text{Monoclinic} & \text{Monoclinic} \\ P_{2_4}/n & C^2 \\ 10.8077(5) & 18.3482(7) \\ 17.3778(8) & 11.9920(5) \\ 18.1390(9) & 8.9002(4) \\ 90 & 90 \\ 90.090(4) & 112.527(2) \\ 90 & 90 \\ 3406.7(3) & 1808.90(13) \\ 4 & 2 \\ 1.178 & 1.212 \\ 0.354 & 0.341 \\ 1304.0 & 712 \\ 0.214 \times 0.197 \times 0.132 & 0.250 \times 0.200 \times 0.150 \\ 6.738 \ to 52.136 & 3.398 \ to 27.090 \\ -13 \leq h \leq 13, & -23 \leq h \leq 23, \\ -21 \leq k \leq 20, & -15 \leq k \leq 15, \\ -22 \leq l \leq 22 & -11 \leq l \leq 11 \\ 25934 & 13994 \\ 6663,0.0506 & 3951,0.0518 \\ 6663/195/385 & 3951/80/342 \\ 1.026 & 1.061 \\ 0.0521, 0.1245 & 0.0318, 0.0631 \\ 0.0710, 0.1360 & 0.0342, 0.0643 \\ 1.41/-0.45 & 0.248/-0.701 \\ \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 2 Selected bond lengths and angles for compounds 1, 2, 5 and 6

	1	2	5	<b>6</b> <sup><i>a</i></sup>
Zr(1)-N(1)	2.368(4)	2.307(11)	2.315(5)	2.280(3)
Zr(1) - N(2)	2.296(3)	2.334(11)	2.289(5)	2.272(2)
Zr(1) - N(3)	2.027(4)	2.298(8)	2.301(5)	2.302(3)
Zr(1)-N(4)	_	2.378(9)	2.313(5)	2.295(2)
Zr(1) - O(1)	2.125(3)	2.221(12)	2.194(4)	2.207(2)
Zr(1) - O(2)	2.164(3)	2.280(12)	2.202(4)	2.197(2)
Zr(1) - O(3)	1.978(3)	2.089(3)	2.200(3)	2.194(2)
Zr(1) - O(4)	_	2.154(3)	2.198(4)	2.1893(19)
O(1)-Zr(1)-O(2)	156.97(13)	77.87(13)	128.91(16)	125.92(8)
N(1)-Zr(1)-N(2)	92.36(15)	167.03(16)	89.68(19)	91.31(9)
O(1)-Zr(1)-N(1)	57.16(13)	55.3(5)	57.69(15)	58.42(8)
O(2)-Zr(1)-N(2)	57.92(10)	58.9(4)	58.05(16)	58.67(8)
O(1)-Zr(1)-N(3)	107.62(15)	84.1(6)	134.34(16)	134.79(9)
O(2)-Zr(1)-N(3)	83.43(12)	82.8(6)	85.42(17)	83.32(9)
N(1)-Zr(1)-O(3)	146.47(13)	89.4(7)	133.86(17)	135.89(9)
N(2)-Zr(1)-O(3)	94.15(13)	84.4(6)	84.63(16)	88.67(8)
O(1)-Zr(1)-O(3)	89.59(13)	128.0(6)	76.24(15)	77.78(8)
O(2)-Zr(1)-O(3)	108.31(13)	126.5(5)	127.91(16)	131.96(7)
N(1)-Zr(1)-N(4)		86.5(8)	91.28(17)	87.40(9)
N(2)-Zr(1)-N(4)	—	90.8(8)	166.96(18)	164.64(9)

 $^{a}$  Zr(1)-containing molecule only. The corresponding measurements for the Zr(2)-containing molecule are closely comparable.

to the unique amidate [Zr(1)-O(3) 1.978(3) Å] is unsurprisingly shorter than either of the Zr–O contacts of the bidentate ligands [Zr(1)-O(1) 2.125(3); Zr(1)-O(2) 2.164(3) Å], it is notable that the C–N bonds lengths across all three amidate moieties are closely comparable [C(1)-N(1) 1.271(6); C(10)-N(2) 1.297(5); C(20)-N(4) 1.280(7) Å]. On this basis, we suggest that, despite this significant adjustment in binding mode, the unidentate ligand is also best represented as a delocalised amidate anion, rather than as an alternative localised alkoxo-imino tautomer. Furthermore, we suggest that the close correspondence of these measurements is, thus, reflective of the facility for rapid exchange between  $\kappa^{1-}$  and  $\kappa^{2-}$ -binding modes highlighted in the solution NMR spectra of this compound (*vide supra*).

In contrast to the heteroleptic constitution of compound 1 the tetrakis(amidato) derivatives, compounds 2, 5 and 6 adopt a common 8-coordinate dodecahedral geometry in the solid state with pseudo-D<sub>2d</sub> symmetry (Fig. 1b-d). Although there are some minor variations in the relevant Zr-O and Zr-N interactions and across the various C-O and C-N bonds within the amidate ligands, these measurements are closely comparable for all three compounds and lie within the ranges observed in the only previous directly comparable homoleptic zirconium(iv) amidate, the tetrakis(N-(2,6-dimethylphenyl)C-tert-butylamidate) zirconium described by Schafer and co-workers.<sup>17b</sup> Although this previously described species displayed a similar 8-coordinate geometry, it was also noted to adopt a sterically disfavoured N-cis configuration of the amidate ligands, which was ascribed to the additional stability arising from  $\pi$ -stacking interactions of the *N*-ortho-xylyl substituents. Although compounds 2, 5 and 6 lack the potential for similar stabilising interactions, the coordination geometry about zirconium in all three compounds is closely comparable to this earlier structure and any minor variations may be simply attributed to the differing steric profiles of the N- and C-bonded amidate alkyl residues.17b

#### Thermal analysis

Thermogravimetric analysis (TGA) was performed on compounds **1–6** (shown for compounds **2**, **5** and **6** in Fig. 2).

The thermal decomposition of the heteroleptic species, compound 1, was essentially complete at temperatures less than 400 °C, but provided a residual mass significantly in excess of that expected for  $ZrO_2$  (318 (1) versus 123.2 g mol<sup>-1</sup> for  $ZrO_2$ ). Although the homoleptic amidate derivatives 2-6 displayed similar two stage thermal profiles, with an onset of decomposition ca. 150 °C, the differing N- and C-substitution patterns provided significant variability in both the apparent mode of decomposition and the nature of the ultimate involatile residue. While the residual mass of compound 2 (106.74 g mol<sup>-1</sup>) was indicative of some whole molecule volatility, the residues resulting from the decomposition of compounds 3 (167 g mol<sup>-1</sup>) and 4 (199.22 g mol<sup>-1</sup>) were much higher than that expected for  $ZrO_2$  (123.2 g mol<sup>-1</sup>). In contrast, the breakdown of compounds 5 (124 g mol<sup>-1</sup>) and 6 (129 g mol<sup>-1</sup>) provided stable residual masses, which were effectively commensurate with the formation of zirconium dioxide. For both of these latter compounds decomposition was essentially complete at 350 °C and occurred as apparent two-step processes. While compound 5 provided an initial mass loss event corresponding to ca. 7% mass between 100 °C and 290 °C, a similar but more clearly defined separation of decomposition steps was observed for compound 6. In this case an initial mass loss of ca. 16% had been observed by 200  $^\circ C$ prior to more rapid weight loss across an approximate 25 °C window, which we suggest represents the operation of several synchronous processes (vide infra).

Further insight into the nature of these thermal processes was provided by a series of decomposition reactions performed on compounds **2**, **5** and **6**. Guided by the decomposition temperatures indicated by the TGA data, samples (*ca.* 0.1 g) of each compound were heated (**2**, **5**, 400 °C; **6** 350 °C) under a static vacuum in an apparatus which allowed the trapping of any volatile products into the d<sub>8</sub>-toluene solvent contained within a J. Youngs NMR tube cooled to -78 °C. Subsequent appraisal of the resultant solutions by <sup>1</sup>H NMR spectroscopy highlighted a number of features common to all three decomposition reactions. The <sup>1</sup>H NMR spectrum resulting from the gaseous by-products of the decomposition of compound **6** is illustrated in Fig. 3a. The multiplets at  $\delta$  5.71 and 4.98 ppm and



Fig. 2 Thermogravimetric analysis of compounds 2, 5 and 6.

the doublet at  $\delta$  1.56 ppm were readily assigned as the respective methine, methylene and methyl resonances of propylene while the heptet and doublet signals at  $\delta$  1.75 and 0.63 ppm respectively confirmed the production of isobutyronitrile as a further volatile product of thermal decomposition. In accord with the generalised decomposition pathway depicted in Scheme 1, the generation of these small molecule species was also accompanied by the evolution of significant quantities of the protonated N-isopropylisobutyramide ligand precursor, which was observed to co-condense along with sublimed quantities of intact compound 6 onto the cold walls of the heated silica tube projecting from the tube furnace (see Fig. 3b). Analogous decomposition of compounds 2 and 5 similarly resulted in the evolution of the free amide precursors alongside gaseous 2-methylpropene and isobutyronitrile (2) and propene and pivalonitrile (5) respectively. On the basis of these empirical observations and the TGA data described above we, thus, propose that the thermolysis of compounds 2, 5 and 6 occurs by the common mechanism illustrated in schematic form as Scheme 1 and, for the specific case of compound 6, as shown in Scheme 3. Under this regime, the initial mass loss processes highlighted in the thermogravimetric analyses may be rationalised as a consequence of  $\beta$ -hydride elimination and alkene generation from the N-alkyl residue of the relevant amidate ligand. Zirconium oxide formation may then result from a sequence of amidate protonation and nitrile elimination steps reminiscent of the long established thermal behaviour of wholly organic amides.<sup>14</sup> The observed variations in thermal stability of the homoleptic zirconium amidate species are, thus, a reflection of the compounds' relative facility toward N-alkyl β-hydride elimination and subsequent nitrile extrusion corresponding to the C-alkyl amidate residue.

#### Thin film deposition

Based on its sharper and slightly lower decomposition temperature (Fig. 2) and its apparent rational decomposition pathway, compound 6 was identified as the most promising precursor to carry forward for AACVD studies. Precursor solutions (0.05 M) were prepared by dissolving the chosen compound in toluene and deposition was carried out under hot wall conditions onto both silica-coated glass and quartz substrates in the temperature range 350–600 °C for 60 minutes using nitrogen as a carrier gas. The as-deposited films were optically clear but presented a very pale brown colouration (see Fig. S20, ESI†). Post deposition annealing by heating of the samples to 600 °C in air for a further 60 minutes, however, provided completely transparent and colourless films which were well adhered to the substrate and could not be removed by Scotch tape. The maximum thicknesses of the annealed films deposited on quartz were determined with ellipsometry using Complete Ease software (J.A Woollam Co., Inc.). These results (Fig. 4) highlight that the film thickness increases with increasing temperature between 400 and 550 °C, suggesting that film growth occurs under kinetic control between these temperatures and with surface-based reactions incorporating the rate determining step of the growth process. A resultant Arrhenius plot for this regime allowed an estimation





Fig. 3 <sup>1</sup>H NMR spectra ( $d_8$ -toluene, 298 K) of (a) the volatile products resulting from the *in vacuo* thermal decomposition of compound **6** highlighting the formation of propene and isobutyronitrile; (b) the solid condensate products resulting from the thermal decomposition of compound **6**, primarily a mixture of sublimed compound **6** and the *N*-isopropylisobutyramide pro-ligand; (c) the *N*-isopropylisobutyramide pro-ligand; (d) compound **6**.



 $\label{eq:scheme3} \begin{array}{l} \mbox{Scheme 3} & \mbox{Postulated mechanism for the thermal decomposition of compound $\mathbf{6}$.} \end{array}$ 

of the activation barrier toward this process as 42.60  $\pm$  10.23 kJ mol<sup>-1</sup>. In contrast, at temperatures above 550 °C the film thickness is observed to decline in an effectively linear fashion suggesting that, at these higher temperatures, film growth by AACVD is likely to be mass transport limited as result of competitive gas phase reactions.

 $ZrO_2$  may exist in one of four basic crystalline polymorphs (monoclinic, orthorhombic, cubic, or tetragonal) or as a mixture of polymorphs. For example, a mixture of monoclinic and either orthorhombic or tetragonal phases is generally found in CVD  $ZrO_2$  thin films.<sup>8b</sup> Analysis of the non-annealed films deposited from compound **6** at 400, 450, 500, 550 and 600 °C by micro-X-ray diffraction (Micro-XRD), indicated that all the

samples aside from the film prepared at 400 °C displayed maxima associated with the presence of the cubic phase of zirconia (ICDD 04-016-6178). The sample prepared at 550 °C also produced reflections consistent with the production of monoclinic ZrO<sub>2</sub> (Baddeleyite, ICDD 01-083-0943), while the samples deposited at temperatures of 500 °C or lower displayed an additional unidentified peak at a  $2\theta$  value of  $46^{\circ}$ . Notably this latter peak, which we tentatively suggest is a consequence of the incorporation of a metalorganic by-product of the precursor decomposition, was observed to persist even after post deposition annealing at 600 °C. The identification of the baddelevite phase, however, was further confirmed by analysis of the film deposited at 550 °C by Raman spectroscopy (Fig. S24, ESI<sup>†</sup>) while the films, irrespective of annealing, were found to be non-conducting (four-point probe analysis). Optical analysis of the annealed films deposited on quartz substrates confirmed the high optical transparency of the films across all visible wavelengths (Fig. S22, ESI<sup>†</sup>) and Tauc plots (Fig. S23, ESI<sup>†</sup>) derived from these data indicated band gaps of 5.7–5.8 eV consistent with the presence of ZrO<sub>2</sub>.

The morphology of the as-deposited films on  $SiO_2$ -coated glass was analysed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) (Fig. 5a and b). Both microscopic techniques highlighted a smooth and largely featureless coverage of the substrate by the films with a few small lumps included across the surface. Cross sectional SEM images corroborated the estimated film thicknesses illustrated in Fig. 4 and revealed that the films comprised of densely packed microscopic particulates with a sharp interface to the silica

Paper



Fig. 4 Film thickness (nm) determined by ellipsometry *versus* temperature (°C) for annealed zirconia thin films grown on quartz substrates by AACVD from compound **6**.



Fig. 5 (a) AFM image for film grown at 500 °C from complex **6**; (b) cross section SEM image (80° specimen tilt,  $100\,000\times$  magnification) of film grown at 500 °C from complex **6**; plan view SEM images of sample annealed at 600 °C; (c)  $1300\times$  magnification; (d)  $6000\times$  magnification.

substrate surface. Although the films were observed to remain well adhered to the substrate after annealing at 600  $^{\circ}$ C, microscopic analysis revealed the formation of multidirectional cracks which emanated from the larger particulates embedded in the film (Fig. 5c and d). We suggest this latter observation is a consequence of differential thermal expansion between the zirconia films and the glass substrate.

Examination of the film composition was undertaken by X-ray photoelectron spectroscopy (XPS) which was carried out on both as-deposited films grown at 500 °C and those which were subsequently annealed in air at 600 °C. All the samples studied provided very similar spectra and Fig. 6 illustrates typical XPS depth profiles of (a) an as-deposited and (b) an annealed zirconia film. These data provided evidence for adventitious carbon contamination on the film surfaces. The bulk composition of

the films, however, is notably consistent through the entire depth profile and indicates that AACVD utilising compound **6** as a single source precursor provides zirconia films which are remarkably uncontaminated by carbon within the detection limits of the instrumentation (>0.1 at%, Fig. S34, ESI†). In this regard, it is further notable that no elements other than zirconium and oxygen could be detected throughout the bulk of the coatings to the interface with the silica-coated glass substrate. Comparison of the oxygen to zirconium ratios highlighted that the annealed samples had a stoichiometry which was effectively  $ZrO_2$ , whereas the as-deposited samples were slightly sub-stoichiometric with average compositions between  $ZrO_{1.8}$  and  $ZrO_{1.9}$ . Although the presence of lower oxidation state zirconium centres could not be discriminated in the XPS data, the undetectable levels of carbon incorporation and this





Fig. 6 XPS depth profiles of (a)  $ZrO_2$  film deposited from compound **6** at 500 °C; (b)  $ZrO_2$  film deposited from compound **6** at 500 °C and subsequently annealed at 600 °C in air.

slight sub-stoichiometry in oxygen, lead us to postulate that the light colouration associated with the as-deposited films arises from the presence of zirconium colour centres rather than any contaminating impurity.

## Conclusion

In summary, we present a series of homoleptic zirconium amidate derivatives that display notably specific and predictable mechanisms of thermal decomposition at temperatures lower than 400 °C. One of these derivatives, tetrakis(N-isopropyl-isobutyramidato)zirconium (6) has been assessed as a single source precursor to ZrO<sub>2</sub> thin films by an aerosol assisted CVD process. Although the resultant films are crystalline for all deposition temperatures above 400 °C, the films display a minor sub-stoichiometry in oxygen. Compositional analysis, however, within the detection limits of XPS, indicated that the as-deposited films comprised zirconium and oxygen as the sole constituent atoms. We suggest that his latter observation, together with the specificity of the decomposition pathways, demonstrate not only the potential of zirconium amidate derivatives to act as true single source precursor reagents to zirconium oxide but also that metal amidate species in general hold much broader and, as yet, untapped potential as a class of easily synthesised and readily manipulable oxide precursor reagents. We are continuing to examine these possibilities and we will describe our observations in future publications.

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