JOURNAL OF
Materials
CHEMISTRY

Synthesis and characterisation of two novel titanium isopropoxides stabilised with a chelating alkoxide: their use in the liquid injection MOCVD of titanium dioxide thin films

Anthony C. Jones,*[a] Timothy J. Leedham,[a] Peter J. Wright,[b] Michael J. Crosbie,[b] Kirsty A. Fleeting,[c] David J. Otway,[c] Paul O'Brien*[c]† and Martyn E. Pemble[d]

[a]*Inorgtech Limited, 25 James Carter Road, Mildenhall, Suffolk, UK IP28 7DE*
[b]*Defence Research Agency, St. Andrews Road, Malvern, Worcestershire, UK WR14 3PS*
[c]*Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY*
[d]*Department of Chemistry, University of Salford, Salford, UK M5 4WT*

The new precursors $[\mathrm{Ti(OPr^i)_3(OCH_2CH_2NMe_2)}]$ **1** and $[\mathrm{Ti(OPr^i)_2(OCH_2CH_2NMe_2)_2}]$ **2** have been prepared and characterised. Compound **1** exists in solution at room temperature as a mixture of monomer and dimer(s), however at elevated temperatures the monomer predominates. Compound **2** exists in solution predominantly as a monomeric complex presumably with pseudo-octahedral coordination at the metal centre. Thin films of TiO_2 have been deposited at 300–450 °C by liquid injection MOCVD using both **1** and **2**. Analysis of the films by Auger electron spectroscopy failed to detect nitrogen although trace carbon was detected at levels of between 2.9 and 7.7%. The potential utility of these modified compounds as precursors to TiO_2 is discussed.

Introduction

Thin films of titanium dioxide (TiO_2) have several potential applications in microelectronics including as an alternative to silicon dioxide (SiO_2) in the gate dielectric of metal oxide semiconductor field effect transistors (MOSFETS).[1,2] Oxides of titanium are important in many ternary perovskites, the best known of which are ferroelectrics such as $BaTiO_3$ and $SrTiO_3$.[3] The related quaternary materials, $[\mathrm{Pb(Zr,Ti)O_3}]$ and $[\mathrm{(Pb,La)(Zr,Ti)O_3}]$, may become particularly important either as infrared detectors (because of their pyroelectric properties) or in next generation non-volatile computer memories (NV FRAMs).[4] Recently there has been a report[5] that the addition of a small percentage of TiO_2 to tantalum oxide leads to a nearly four fold increase in the dielectric constant of the material, offering the potential of improved performance DRAMs. Although this material appears to be a high temperature phase, MOCVD has on occasion been successful in depositing non-equilibrium phases. However the precursor chemistry of titanium is far from well developed.

The MOCVD of TiO_2 and related metal oxides has most often been carried out using titanium tetrachloride, $TiCl_4$[6,7] or titanium alkoxides, $\mathrm{Ti(OR)_4}$ ($\mathrm{R=Et, Pr^i}$).[1,2,4,8,9] There are a number of drawbacks associated with the use of these precursors. The metal halide, $TiCl_4$, can lead to chloride contamination of the films and requires relatively high deposition temperatures (>500 °C), which are incompatible with the processing requirements (<500 °C) for deposition on to pre-processed silicon circuits. Alkoxide precursors such as $\mathrm{Ti(OR)_4}$ have been used for the deposition of TiO_2 films at lower substrate temperatures (<400 °C),[8] but they contain an unsaturated $\mathrm{Ti^{IV}}$ centre which is highly reactive to air and moisture. Such compounds are susceptible to pre-reaction in MOCVD reactors, and stringent precautions are required to prevent deterioration during both storage and use. The significant moisture sensitivity of such $\mathrm{Ti(OR)_4}$ compounds also makes them difficult to use in solution-based liquid injection MOCVD. Such methods are being increasingly used for the deposition of ferroelectric metal oxides, and there is also the possibility of pre-reaction between $\mathrm{Ti(OR)_4}$ and other precursors in solution.

Modified alkoxides of titanium, such as $[\mathrm{Ti(OPr^i)_2(tmhd)_2}]$ (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate), which have an increased coordinative saturation at the metal centre relative to $\mathrm{Ti(OR)_4}$ compounds, have been investigated as alternative precursors in liquid injection MOCVD processes.[10,11] NMR studies[12] have confirmed that $[\mathrm{Ti(OPr^i)_2(tmhd)_2}]$ does not pre-react with the $[\mathrm{Pb(tmhd)_2}]$ or $[\mathrm{Zr(tmhd)_4}]$ precursors used in solution. Consequently $[\mathrm{Ti(OPr^i)_2(tmhd)_2}]$ has been used successfully for the deposition of $[\mathrm{Pb(Zr,Ti)O_3}]$[10] and $[\mathrm{Pb(La,Ti)O_3}]$[11] by liquid injection MOCVD.

Another approach to increasing the coordinative saturation of the metal centre is to use a 'functionalised' alkoxide ligand such as dimethylaminoethoxide, $\mathrm{OCH_2CH_2NMe_2}$ (dmae)[13] which provides an additional Lewis base site able to form chelate rings or to bridge metal centres. This approach has been successfully used by us[14] in the modification of $[\mathrm{Ta(OEt)_5}]_2$ and $[\mathrm{Nb(OEt)_5}]_2$; the addition of 1 mol equivalent of dmae led to the formation of monomeric $[\mathrm{Ta(OEt)_4(dmae)}]$ and $[\mathrm{Nb(OEt)_4(dmae)}]$. These compounds had higher vapour pressures than the dimeric parent alkoxides and have allowed the MOCVD of Ta_2O_5 and Nb_2O_5 films at low temperature (<400 °C).[14] This success has encouraged us to investigate the effect of adding similar functionalised alkoxide ligands to titanium alkoxides. Such compounds are likely to be compatible with $[\mathrm{Ta(OEt)_4(dmae)}]$, and may find an application in the MOCVD of the mixed oxide Ta_2O_5/TiO_2. Although mixed titanium alkoxide/β-diketonate compounds such as $[\mathrm{Ti(OPr^i)_3(acac)}]$ and $[\mathrm{Ti(OPr^i)_2(acac)_2}]$ are known,[15] there are no reports of the equivalent titanium alkoxide/dmae complexes. Here, we report the synthesis and characterisation of the novel precursors $[\mathrm{Ti(OPr^i)_2(dmae)_2}]$ **1** and $[\mathrm{Ti(OPr^i)_3(dmae)}]$ **2** and their use in the growth of TiO_2 films by liquid injection MOCVD.

Experimental

General techniques

Titanium tetraisopropoxide $[\mathrm{Ti(OPr^i)_4}]$ was used as manufactured by Inorgtech Ltd. Dimethylaminoethanol (Hdmae) was

---

†E-mail: p.obrien@ic.ac.uk

obtained from Aldrich Chemical Co. and was dried by storage over molecular sieves and distilled before use. *n*-Hexane (Aldrich) was HPLC grade and used without further purification. NMR spectra were recorded on a JEOL GS 270 MHz or a Bruker AM400 Fourier transform spectrometer, using the proton impurities of the deuterated benzene solvent as a reference and the $^{13}C\{^1H\}$ resonance of the solvent for $^{13}C\{^1H\}$ spectra. All chemical shifts are reported positive to the high frequency of the standard. Elemental microanalysis was performed by the Liverpool University Chemistry Department service.

Auger electron spectroscopy was carried out on a Varian scanning Auger spectrometer. The atomic compositions quoted are from the bulk of the film, free from surface contamination and were obtained by combining AES with sequential argon ion bombardment until comparable compositions were obtained for consecutive data points.

Synthesis and characterisation of $[Ti(OPr^i)_3(dmae)]$ 1 and $[Ti(OPr^i)_2(dmae)_2]$ 2

$[Ti(OPr^i)_4]$ (19.9 g, 0.07 mol) was dissolved in *n*-hexane (120 ml) and Hdmae (6.7 g, 0.075 mol or 13.4 g, 0.15 mol) was added. The solution was refluxed with stirring for 1 h and was then allowed to cool. Removal of all volatiles *in vacuo* gave either $[Ti(OPr^i)_3(dmae)]$ **1** or $[Ti(OPr^i)_2(dmae)_2]$ **2** as colourless oils, which were then purified by vacuum distillation. Yield $[Ti(OPr^i)_3(dmae)]$ **1**: 90% based on $[Ti(OPr^i)_4]$; yield $[Ti(OPr^i)_2(dmae)_2]$ **2**: 80% based on $[Ti(OPr^i)_4]$.

$[Ti(OPr^i)_3(dmae)]$ **1** and $[Ti(OPr^i)_2(dmae)_2]$ **2** were characterised by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, elemental microanalysis and mass spectroscopy, which confirmed the stoichiometry of the complexes.

$[Ti(OPr^i)_3(dmae)]$ 1. Microanalysis. Found: C, 50.1; H, 10.1; N, 4.0. Calc. for $TiO_4NC_{13}H_{31}$: C, 49.9; H, 9.9; N, 4.5%. ^1H NMR (270 MHz, C_6D_6, 25 °C): δ 1.2 [18H, d, $OCH(CH_3)_2$], 2.1 [6H, s, $OCH_2CH_2N(CH_3)$], 2.4 [2H, t, $OCH_2CH_2N(CH_3)_2$], 4.1 [2H, t, $OCH_2CH_2N(CH_3)_2$], 4.7 [broad m, $OCH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (67.94 MHz, C_6D_6, 25 °C): δ 26.5 [$OCH(CH_3)_2$], 46.5 [$OCH_2CH_2N(CH_3)_2$], 62.7 [$OCH_2CH_2N(CH_3)$], 69.5 [$OCH_2CH_2N(CH_3)_2$], 75.8 [$OCH(CH_3)_2$]. Mass spectrometry (EI^+): *m/z* 626 $[Ti_2(OPr^i)_6(dmae)_2]$ (15%), 400 $[Ti(OPr^i)_3(dmae)_2H]$ (70%), 313 $[Ti(OPr^i)_3(dmae)]$ (27%), 254 $[Ti(OPr^i)_2(dmae)]$ (4%), 194 $[Ti(OPr^i)(dmae)]$ (2%).

$[Ti(OPr^i)_2(dmae)_2]$ 2. Microanalysis. Found: C, 49.41; H, 10.15; N, 8.10. Calc. for $TiO_4N_2C_{14}H_{34}$: C, 49.20; H, 10.05; N, 8.20%. ^1H NMR (270 MHz, C_6D_6, 25 °C): δ 1.20 [12H, d, $OCH(CH_3)_2$], 2.15 [12H, s, $OCH_2CH_2N(CH_3)_2$], 2.50 [4H, t, $OCH_2CH_2N(CH_3)_2$], 4.30 [4H, t, $OCH_2CH_2N(CH_3)_2$], 4.85 [2H, hept, $OCH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (67.94 MHz, C_6D_6, 25 °C): δ 27.0 [$OCH(CH_3)_2$], 47.0 [$OCH_2CH_2N(CH_3)_2$], 63.0 [$OCH_2CH_2N(CH_3)$], 71.0 [$OCH_2CH_2N(CH_3)_2$], 76.0 [$OCH(CH_3)_2$]. Mass spectrometry (EI^+): *m/z* 343 $[Ti(OPr^i)_2(dmae)_2H]$ (53%), 342 $[Ti(OPr^i)_2(dmae)_2]$ (15%), 283 $[Ti(OPr^i)(dmae)_2]$ (100%), 254 $[Ti(OPr^i)_2(dmae)]$ (9%), 194 $[Ti(OPr^i)(dmae)]$ (4%), 66 $[Ti(OPr^i)_2]$ (5%).

TiO_2 film growth

The TiO_2 thin films were deposited by liquid injection MOCVD using 0.1 mol dm^{-3} solutions of either $[Ti(OPr^i)_3(dmae)]$ **1** or $[Ti(OPr^i)_2(dmae)_2]$ **2** in tetrahydrofuran (THF). The films were deposited over the temperature range 300–650 °C onto Si(100) single crystal substrates using an MOCVD reactor described elsewhere.[15] The growth conditions used for each precursor are summarised in Tables 1 and 2 together with some analytical results.

Results

Precursor chemistry

^1H NMR, $^{13}C\{^1H\}$ NMR, mass spectroscopy and microanalytical data show that the addition of 1 and 2 mol of Hdmae to $[Ti(OPr^i)_4]$ leads to the formation of the new complexes $[Ti(OPr^i)_3(dmae)]$ **1** and $[Ti(OPr^i)_2(dmae)_2]$ **2**, respectively. Qualitatively, both compounds were observed to be significantly less air and moisture sensitive than the parent alkoxide $[Ti(OPr^i)_4]$. X-Ray absorption experiments[16] indicate that $[Ti(OPr^i)_4]$ is a monomer with four-coordinate Ti in the liquid state. The addition of the chelating ligand acetylacetonate (pentane-2,4-dione, acac) has been shown to give a complex with stoichiometry $[Ti(OPr^i)_3(acac)]$ in which the metal centre is assigned as five co-ordinate. It is therefore likely that $[Ti(OPr^i)_3(dmae)]$ **1** is also five co-ordinate and this is supported by the reduced air/moisture sensitivity compared with $[Ti(OPr^i)_4]$. The NMR spectrum of this compound is clean and suggests that at room temperature, equilibria with other species (*e.g.* disproportionation reactions) are not significant.

$[Ti(OPr^i)_3(dmae)]$ 1

A variable temperature ^1H NMR study of the $[Ti(OPr^i)_3(dmae)]$ complex (Fig. 1) indicates that at 50 °C only a single, presumably monomeric, compound is present. The proton resonances are well defined multiplets, and the coupling constants can be measured. However, the temperature is not quite high enough to completely resolve the $OCH(CH_3)_2$ multiplet at δ 4.7, which limits the accuracy as to which of the coupling constants can be measured. However, both the $OCH_2CH_2NMe_2$ (δ 2.4) and the $OCH_2CH_2NMe_2$ (δ 4.1) triplets are well defined, and have coupling constants of 5.9 Hz. As the temperature is lowered, significant broadening of the proton resonances are observed in the ^1H NMR spectra. The most likely explanation is a dimer–monomer exchange process. At −50 °C each of the chelating dmae ligand proton resonances are split into at least three signals, and the isopropoxide signals into at least two.

Fig. 2 illustrates the three possible parent dimeric forms available for the stoichiometry $[Ti(OPr^i)_6(dmae)_2]$.

The first, (a), is a structure proposed by Saxena *et al.*[17] for the related tris isopropoxide β-diketonate compounds.[18] The dimer is formed *via* bridging isopropoxide ligands. The structure shown is just one of the several geometrical and optical isomers possible for this stoichiometry.

The second, (b), is a symmetric structure, involving deprotonated alkoxy-bridging dmae ligands, and terminal isopropoxide groups.

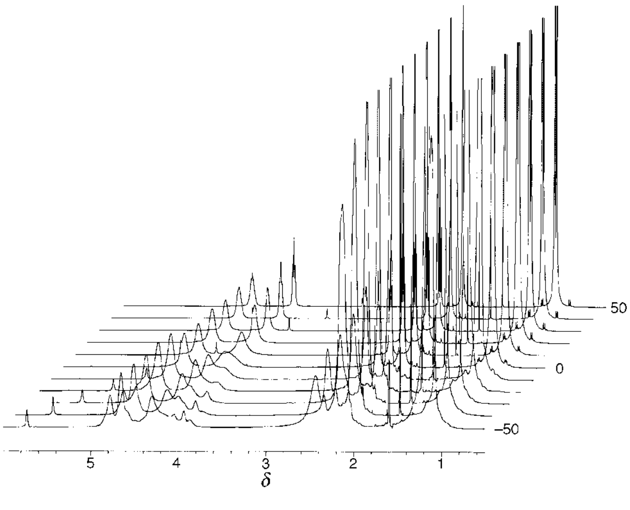


Fig. 1 Variable temperature ^1H NMR spectra of $[Ti(OPr^i)_3(dmae)]$ **1**

Table 1 Growth conditions used to deposit TiO_2,[a] and AES data for TiO_2 films grown using $[Ti(OPr^i)_3(dmae)]$ **1**

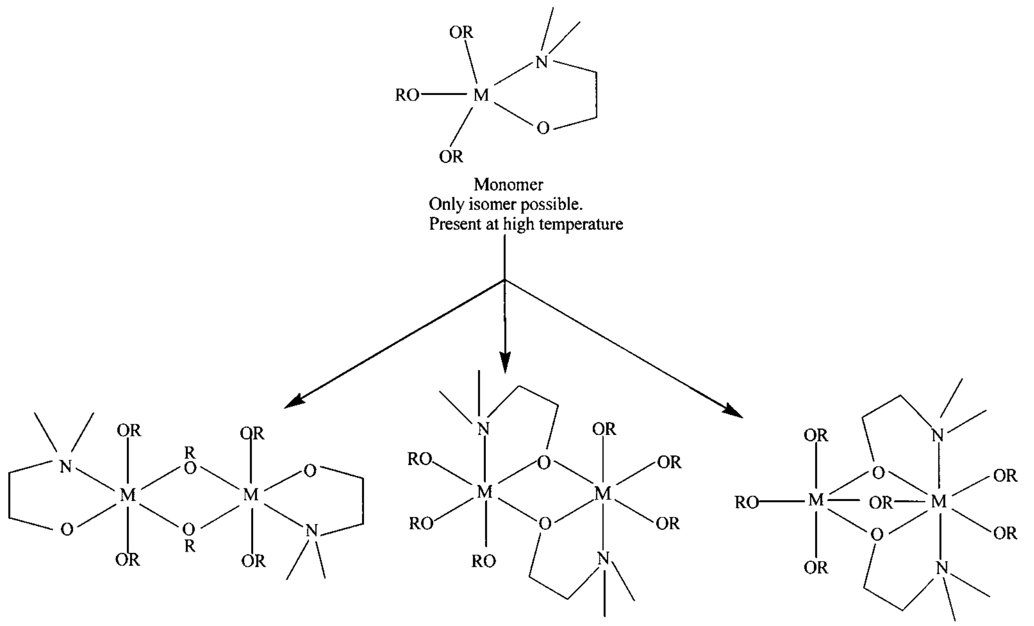
run	reactor pressure/ mbar	argon flow rate/ $cm^3\ min^{-1}$	oxygen flow rate/ $cm^3\ min^{-1}$	substrate temperature/ °C	film thickness[b]/ μm	composition (atom%) Ti	O	C	O/Ti ratio
425	1000	1000	0	400	1.03	35.2	57.1	7.7	1.62
430	50	500	100	400	1.00	33.1	59.3	7.6	1.79
421	1000	1000	200	450	0.13	36.6	60.5	2.9	1.65
424	1000	1000	400	400	0.61	34.2	62.2	3.6	1.82
427	1000	1000	800	400	0.47	34.9	62.1	3.0	1.78

[a]Evaporator temperature = 200 °C; precursor injection rate = 3.5 $cm^3\ h^{-1}$; duration of each run = 90 min; Si(100) substrates. [b]Measured by weighing.

Table 2 Growth conditions used to deposit TiO_2,[a] and AES data for TiO_2 films using $[Ti(OPr^i)_2(dmae)_2]$ **2**

run	reactor pressure/ mbar	argon flow rate/ $cm^3\ min^{-1}$	oxygen flow rate/ $cm^3\ min^{-1}$	substrate temperature/ °C	film thickness[b]/ μm	composition (atom%) Ti	O	C	O/Ti ratio
483	1000	5000	0	400	0.44	35.6	57.7	6.7	1.62
488	1000	3500	1500	400	0.39	35.3	61.6	3.2	1.74
485	100	3000	2000	400	0.35	36.4	60.6	3.1	1.66

[a]Evaporator temperature = 200 °C; precursor injection rate = 3.5 $cm^3\ h^{-1}$; duration of each run = 60 min; Si(100) substrates. [b]Measured by weighing.



(a) Dimer bridged *via* alkoxide groups. One of many possible geometrical and optical isomers.

(b) Dimer bridged *via* dmae ligands. Most likely structure at low temperature.

(c) Dimer based on Zr analogues. Not very likely as Ti prefers coordination of six or less.

Fig. 2 Possible structures of $[Ti(OPr^i)_3(dmae)]$ **1** at low temperature

The third, (c), involves bridging occurring through the chelating alkoxy ligands but with the amine coordinated to the same metal atom. In addition there is one bridging isopropoxide group. This is similar to a structural type that we have demonstrated in related recent work;[19] the crystal structures of $[Zr_2(OPr^i)_6(dmap)_2]$ and $[Zr_2(OPr^i)_6(bdmap)_2]$ (where Hdmap = dimethylaminoisopropanol and Hbdmap = bis(dimethylamino)isopropanol), however the expansion of the titanium coordination sphere, to seven, is unlikely.

At low temperature the most likely structure to be adopted is the symmetrical dimer (b). In this structure steric effects are balanced and the dmae oxygen (the most acidic) and probably able to act as a better ligand to the metal as it is 'supported' by the amine bridges. Although the NMR spectrum becomes complicated as the temperature is lowered, large numbers of new peaks are not apparent and a symmetrical dimeric structure probably predominates. It is important to note that isomers are possible for all of the parent structures proposed, which will account for the other peaks observed. There is no NMR evidence for the formation of disproportionation products such as **2** and the free alkoxide, $[Ti(OPr^i)_4]$.

The mass spectrometry data for **1** demonstrate that in the instrument, the dimer $[Ti_2(OPr^i)_6(dmae)_2]$ and fragments for the monomer are present.

$[Ti(OPr^i)_2(dmae)_2]$ 2

In the case of **2**, the room temperature ^1H NMR data are much more well defined and probably indicate that a single molecular species is formed as the spectra are all well resolved and clean. Compound **2** may be the more promising MOCVD precursor, being less likely than **1** to decompose to give the parent alkoxide during volatilisation. The variable temperature ^1H NMR spectra show no major changes at high or low temperatures, further supporting this argument. The coordination number of **2** is likely to be six in both the liquid and vapour phases. The mass spectrometry data for **2** show a major molecular ion peak for the monomer, and fragments thereof, supporting the arguments that it may be a good MOCVD precursor.

MOCVD results

TiO_2 thin films were successfully deposited from both $[Ti(OPr^i)_3(dmae)]$ and $[Ti(OPr^i)_2(dmae)_2]$ precursors over the temperature range 300–550 °C. The atomic composition of the films was determined by Auger electron spectroscopy (AES) and the films were found to have O/Ti ratios of between 1.62 and 1.82 (Tables 1 and 2). Significantly, nitrogen was not detected in the films (estimated detection limit, 1 atom%), although carbon was detected at levels of 2.9–7 atom%. The carbon is present in the bulk of the film and not as surface contamination. Trace carbon is commonly observed in TiO_2 films grown by MOCVD from Ti–alkoxide precursors[1] and can be attributed to the incomplete decomposition of the metalorganic precursor. There is no evidence that carbon contamination has been increased by the use of THF as solvent in the liquid injection MOCVD process. Consistent with previous MOCVD studies using $[Ti(OR)_4]$ precursors,[1] it was found that the carbon contamination tended to decrease with increasing deposition temperature and was significantly reduced at high oxygen flows (200 cm^3 min^{-1} and above) (see Tables 1 and 2). These trends in carbon contamination can be readily ascribed to the incomplete combustion of the alkoxide ligand, due either to a lack of thermal energy (at low substrate temperatures), or lack of available oxygen at low oxygen flow rates.[1]

The variation in TiO_2 growth rate with substrate temperature for the $[Ti(OPr^i)_3(dmae)]$ **1** and $[Ti(OPr^i)_2(dmae)_2]$ **2** precursors is shown in Fig. 3 and 4, respectively. In each case the maximum growth rate occurs at *ca.* 410 °C, which compares closely with the optimum TiO_2 growth temperature obtained using $[Ti(OPr^i)_4]$ on the same reactor under comparable conditions, and also with the optimum growth temperature of Ta_2O_5 deposited from $[Ta(OEt)_4(dmae)]$.[13] Above substrate temperatures of *ca.* 450 °C, the growth rate falls off quite sharply which suggests that the precursors pre-react to some extent with oxygen. Further evidence for pre-reaction is the observed decrease in growth rate with increasing oxygen flow, which occurs for each precursor, as shown in Fig. 5 and 6. As the vapour pressures of $[Ti(OPr^i)_3(dmae)]$ **1** and $[Ti(OPr^i)_2(dmae)_2]$ **2** have not yet been accurately determined, it is not possible to judge the extent of pre-reaction compared with the standard $[Ti(OPr^i)_4]$ precursor.

Conclusions

Thin films of TiO_2 have been successfully deposited by liquid injection MOCVD using the new precursors $[Ti(OPr^i)_3(dmae)]$ **1** and $[Ti(OPr^i)_2(dmae)_2]$ **2**. The TiO_2 films were deposited at relatively low substrate temperatures (300–550 °C), similar to those utilised for the conventional $[Ti(OPr^i)_4]$ precursor. The TiO_2 films were of comparable purity to films grown by conventional MOCVD using $[Ti(OR)_4]$ precursors, containing trace carbon at levels of 2.9–7.7%. However, in the liquid state, the new precursors are significantly less reactive to air and moisture than conventional $[Ti(OR)_4]$ precursors which should prevent deterioration

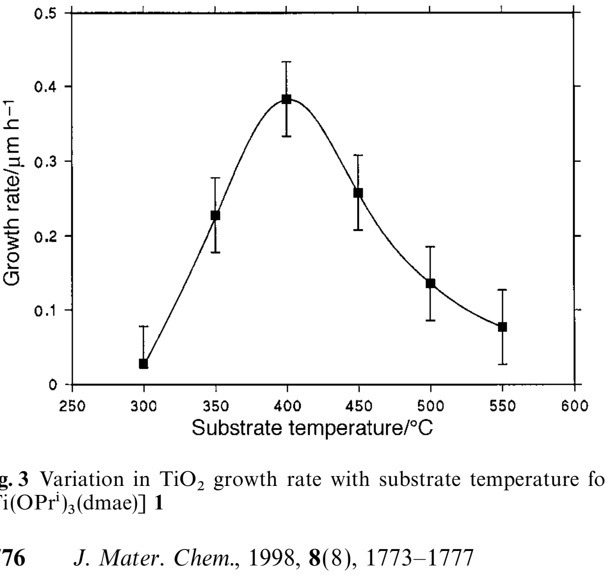


Fig. 3 Variation in TiO_2 growth rate with substrate temperature for $[Ti(OPr^i)_3(dmae)]$ **1**

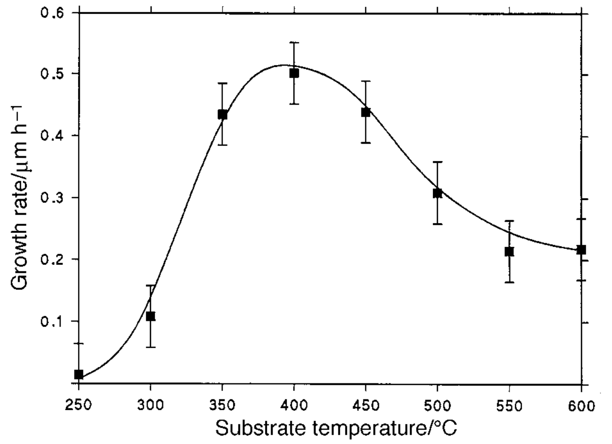


Fig. 4 Variation in TiO_2 growth rate with substrate temperature for $[Ti(OPr^i)_2(dmae)_2]$ **2**

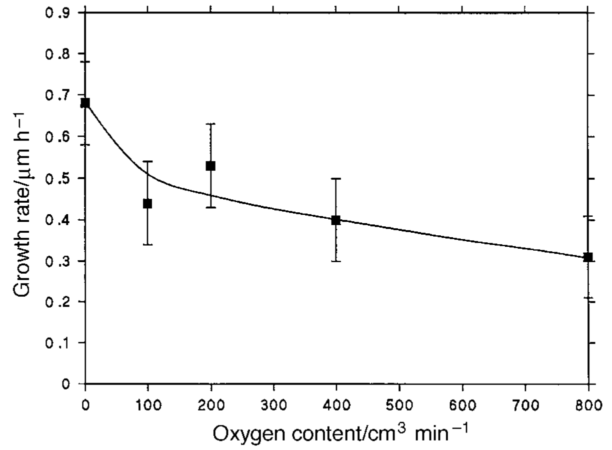


Fig. 5 Variation in TiO_2 growth rate with carrier gas oxygen content for $[Ti(OPr^i)_3(dmae)]$ **1**; argon flow rate = 1 dm^3 min^{-1}

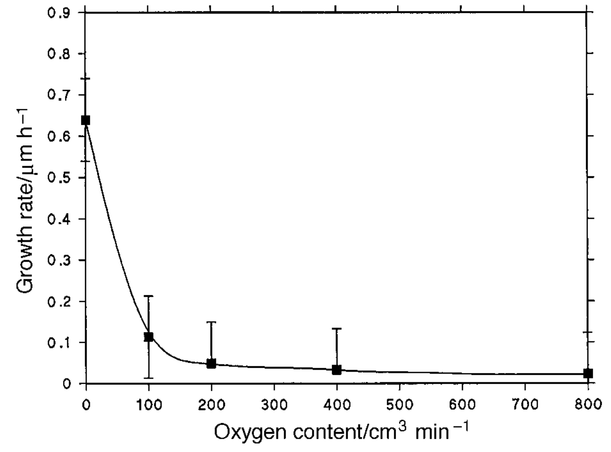


Fig. 6 Variation in TiO_2 growth rate with carrier gas oxygen content for $[Ti(OPr^i)_2(dmae)_2]$ **2**; argon flow rate = 1 dm^3 min^{-1}

during storage and use, especially in liquid injection MOCVD applications.

We would like to thank the EPSRC and Inorgtech Ltd. for a CASE award. We thank Inorgtech Ltd. for the gifts of chemicals used in this study. The authors are grateful to Dr. G. W. Critchlow and Mr. D. Hall (Loughborough Consultants) for provision of the AES data, and to Mr. J. M. Giordanengo (University of Salford) for experimental assistance, and also to Dick Sheppard and Paul Hammerton for VC and VT NMR studies. We are pleased to acknowledge Dr. J. P. Senatur (CNRS, Grenoble) for helpful discussions. P.O.B. is the Sumitomo/STS Professor of Materials Chemistry at Imperial College, and the Royal Society Amersham International Research Fellow (1997/98).

References

1 T. Won, S. Yoon and H. Kim, *J. Electrochem Soc.*, 1992, **139**, 3284.
2 S. A. Campbell, D. C. Gilmer, X.-C. Wang, M.-T. Hsieh, H.-S. Kim, W. L. Gladfelter and J. Yan, *IEEE Trans. Electron. Devices*, 1997, **44**, 104.
3 R. E. Jones, Jr., P. Zurcher, P. Chu, D. J. Taylor, Y. T. Lii, B. Jiang, P. D. Maniar and S. J. Gillespie, *Microelectron. Eng.*, 1995, **29**, 3.
4 C. H. Peng and S. B. Desu, *J. Am. Ceram. Soc.*, 1994, **77**, 1799.
5 R. F. Cava, W. F. Peck, Jr. and J. J. Krajewski, *Nature* (*London*), 1995, **377**, 215.
6 K. S. Yeung and Y. W. Lam, *Thin Solid Films*, 1983, **109**, 169.
7 M. K. Akhtar, S. E. Pratsinis and S. V. R. Mastrangelo, *J. Mater. Res.*, 1994, **9**, 1241.
8 M. Yokazawa, H. Iwasa and I. Teramoto, *Jpn. J. Appl. Phys.*, 1968, **7**, 96.
9 Y. Takahashi, K. Tsuda, K. Sugiyama, H. Minoura, D. Makino and M. Tsuiki, *J. Chem. Soc.*, *Faraday Trans.*, 1981, **77**, 1051.
10 J. F. Roeder, B. A. Vaartstra, P. C. Van Buskirk and H. R. Beratan, *Mater. Res. Soc. Symp. Proc.*, 1996, **415**, 123.
11 D. B. Beach and C. E. Vallet, *Mater. Res. Soc. Symp. Proc.*, 1996, **415**, 225.
12 R. A. Gardiner, P. C. Van Buskirk and P. S. Kirlin, *Mater. Res. Soc. Symp. Proc.*, 1994, **335**, 221.
13 W. A. Hermann, N. W. Huber and O. Runte, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 2187.
14 A. C. Jones, T. J. Leedham, P. J. Wright, M. J. Crosbie, D. J. Williams, P. A. Lane and P. O'Brien, *Proceedings of MRS conference*, *Fall 1997*, *Mater. Res. Soc. Symp. Proc.*, vol. 485, in press.
15 C. Sanchez, J. Livage, M. Henry and F. Barbonneau, *J. Non-Cryst. Solids*, 1998, **100**, 65.
16 A. C. Jones, T. J. Leedham, P. J. Wright, M. J. Crosbie, P. A. Lane, D. J. Williams, K. A. Fleeting, D. J. Otway and P. O'Brien, *Adv. Mater.*, *Chem. Vap. Dep.*, 1998, **4**, 46.
17 U. B. Saxena, A. K. Rai, V. K. Mathur, R. C. Mehrotra and D. Radford, *J. Chem. Soc. A*, 1970, 904.
18 A. C. Jones, T. J. Leedham, D. J. Williams, K. A. Fleeting, D. J. Otway and P. O'Brien, *Inorg. Chem.*, 1998, submitted.
19 K. A. Fleeting, A. C. Jones, T. J. Leedham, M. A. Malik, P. O'Brien and D. J. Otway, *Proceedings of MRS conference*, *Fall 1997*, *Mater. Res. Soc. Symp. Proc.*, vol. 485, in press.

Paper 8/02933D; *Received* 20*th April*, 1998