Journal of the European Ceramic Society **19** (1999) 1431–1434
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0955-2219/99/$ - see front matter
PII: S0955-2219(98)00456-7

Metalorganic Chemical Vapour Deposition (MOCVD) of Zirconia and Lead Zirconate Titanate Using a Novel Zirconium Precursor

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Abstract

The novel mixed ligand precursor $Zr_2(OPr^i)_6(thd)_2$ (thd=2,2,6,6,-tetramethyl-3,5-heptanedionate) has been used in the deposition of ZrO_2 and $Pb(Zr,Ti)O_3$ thin films by liquid injection metalorganic chemical vapour deposition (MOCVD). Oxide growth was observed over a wide temperature range, from 250°C to at least 600°C. Maximum growth rates of ZrO_2 occurred between 350°C and 550°C, significantly lower than the optimum deposition temperature from the conventional $Zr(thd)_4$ precursor, and in a similar temperature range to optimised oxide growth from $Pb(thd)_2$. Consequently, the use of $Zr_2(OPr^i)_6(thd)_2$ in combination with $Pb(thd)_2$ and $Ti(OPr^i)_2(thd)_2$ leads to the deposition of $Pb(Zr,Ti)O_3$ with improved compositional uniformity. © 1999 Elsevier Science Limited. All rights reserved

Keywords: MOCVD, films, PZT, ZrO_2.

1 Introduction

Thin films of zirconia, ZrO_2, have applications as protective coatings,[1] mirrors,[2] sensors[3] and dielectric films in microelectronics,[4] whilst the related ferroelectric oxide lead zirconate titanate, $Pb(Zr,Ti)O_3$ has large potential applications in infrared devices[5] and non-volatile computer memories.[6,7]

Metalorganic chemical vapour deposition (MOCVD) is an attractive technique for the deposition of these materials,[8,9] offering the potential for large area growth, good composition control and excellent conformal step coverage at dimensions $<2\,\mu$m. The MOCVD technique is also fully compatible with existing silicon CVD processes.

Precursors used for the MOCVD of ZrO_2 and $Pb(Zr,Ti)O_3$ include zirconium alkoxides,[10] zirconium β-diketonates[11] and fluorinated β-diketonates.[12] Although many of the problems associated with the vapour-phase transport of these low vapour pressure precursors can be solved by the use of liquid injection MOCVD,[13] there remain a number of drawbacks associated with their use. For instance, the β-diketonates Zr(acetylacetonate)$_4$ and Zr(trifluoroacetylacetonate)$_4$ lead to carbon or fluorine contamination, respectively,[4] and although higher purity ZrO_2 can be deposited from $Zr(thd)_4$ (thd = 2,2,6,6,-tetramethyl-3,5-heptanedionate),[14] the high thermal stability of the precursor only allows diffusion controlled oxide growth at substrate temperatures >600°C.[15] Whilst suitable for protective coatings, such high deposition temperatures are incompatible with the low growth temperatures (<500°C) required for the majority of microelectronics applications.

The high thermal stability of $Zr(thd)_4$ relative to $Pb(thd)_2$ can also lead to problems during the growth of $Pb(Zr,Ti)O_3$ by liquid injection MOCVD using $Pb(thd)_2$, $Zr(thd)_4$ and Ti $(OPr^i)_2(thd)_2$.[15] The high substrate temperatures required to optimise oxide deposition from $Zr(thd)_4$ (i.e. > 550°C) result in loss of lead from the film by desorption. The use of increased Zr precursor flow rates or increased evaporator temperatures to enhance Zr incorporation at lower substrate temperatures leads either to the blocking of reactor lines with $Zr(thd)_4$ or the decomposition of $Pb(thd)_2$ in the evaporator.

Therefore alternative zirconium oxide precursors are required, which are more volatile than $Zr(thd)_4$ and which also have a lower thermal stability, more compatible with $Pb(thd)_2$. Although zirconium alkoxides, $Zr(OR)_4$ ($R = Pr^i$, Bu^t), are significantly

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*To whom correspondence should be addressed. Fax: +44-(0)163-871-8259; e-mail: tony@inorg.demon.co.uk less thermally stable and more volatile than $Zr(thd)_4$ they contain a highly positively charged Zr(IV) centre with an incomplete coordination sphere. This renders them highly sensitive to air and moisture and susceptible to pre-reaction in the MOCVD reactor. Their reactivity may also lead to a reduced shelf-life in solution-based liquid injection MOCVD applications.

The addition of the bidentate/chelating thd ligand to $Zr(OR)_4$ increases the coordinative saturation around the Zr centre and may be expected to render the compound less moisture sensitive. We have therefore investigated mixed alkoxide/β-diketonate complexes of Zr as precursors for the MOCVD of ZrO_2,[15,16] an approach which aims to combine the advantages of good ambient stability associated with Zr β-diketonates with the lower thermal stability and increased volatility of $Zr(OR)_4$ precursors. A complex with the stoichiometry '$Zr(OPr^i)_2(thd)_2$' was used successfully for deposition of ZrO_2,[15] however NMR studies indicated that '$Zr(OPr^i)_2(thd)_2$' exists as a mixture of monomers and dimers in solution, and the alkoxide bridged dimer $Zr_2(OPr^i)_6(thd)_2$ was subsequently isolated from solution and characterised by X-ray crystallography[16,17] (see Fig. 1).

In this paper we describe the successful use of $Zr_2(OPr^i)_6(thd)_2$ for the deposition of ZrO_2 and $Pb(Zr,Ti)O_3$ by liquid injection MOCVD, and show how this novel source represents a significant improvement over conventional $Zr(thd)_4$ and $Zr(OR)_4$ precursors.

2 Experimental

2.1 Precursor synthesis and characterisation

$Zr_2(OPr^i)_6(thd)_2$ was synthesised by a procedure described fully elsewhere,[17] involving the addition of thdH (1 mol equivalent) to $Zr(OPr^i)_4$ (1 mol equivalent) in n-hexane. Removal of volatiles *in vacuo* gave $Zr_2(OPr^i)_6(thd)_2$ as a crystalline solid (m.pt. 160–163°C). The purity of the precursor was confirmed by proton NMR spectroscopy and microanalysis.

In contrast to $Zr(OR)_4$ compounds, $Zr_2(OPr^i)_6(thd)_2$ is only slightly air sensitive and thermogravimetric analysis data, shown in Fig. 2, indicates that of $Zr_2(OPr^i)_6(thd)_2$ is more volatile than $Zr(thd)_4$, evaporating at approx. 100°C lower temperature.

Thin films of ZrO_2 were deposited by liquid injection MOCVD using a 0·1 molar solution of $Zr_2(OPr^i)_6(thd)_2$ in tetrahydrofuran (THF). The films were deposited over the temperature range 250–600°C on to Si(100) single crystal substrates using an MOCVD reactor described elsewhere.[15] The growth conditions are summarised in Table 1.

The $Pb(Zr,Ti)O_3$ thin films were grown in a commercial liquid injection MOCVD reactor. Precursor solutions were held in separate reservoirs and mixed prior to injection into the evaporator. A full summary of growth conditions is given in Table 2.

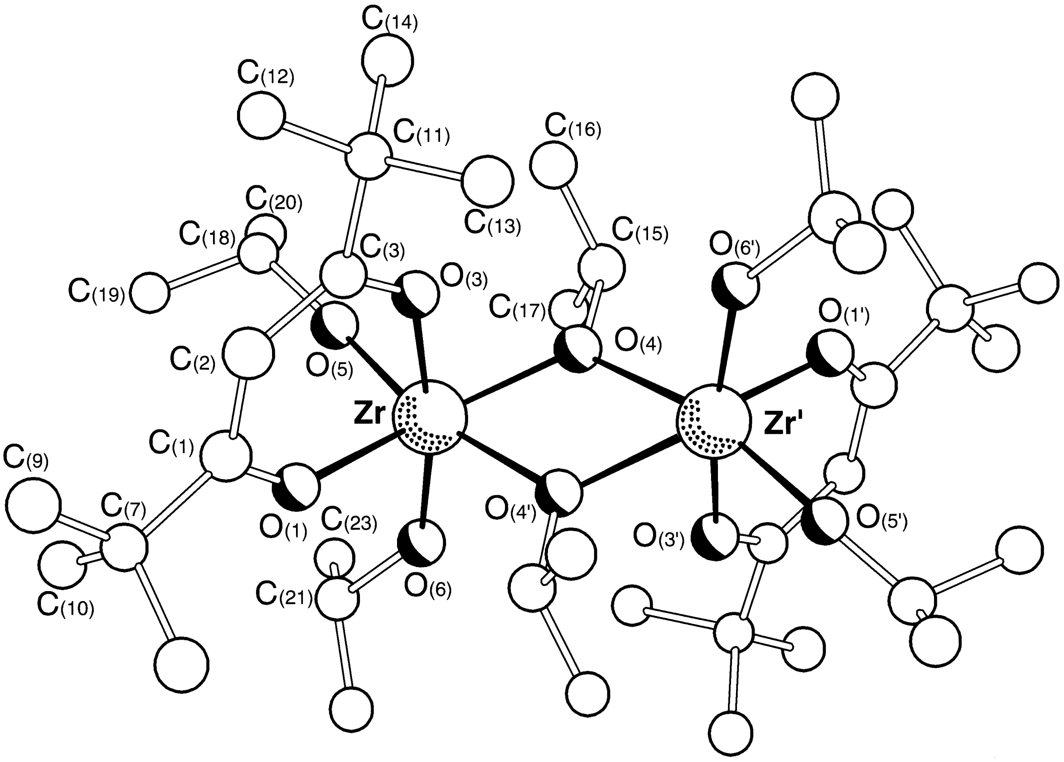


Fig. 1. Molecular structure of $Zr_2(OPr^i)_6(thd)_2$.[17]

3 Results and Discussion

The $Zr_2(OPr^i)_6(thd)_2$ precursor allows the deposition of ZrO_2 over a wide range of substrate temperatures, from 250°C up to at least 650°C. The atomic composition of films grown at various substrate temperatures was determined by Auger electron spectroscopy, which showed that the films were of comparable purity to those deposited from the commonly used precursor $Zr(thd)_4$.[14] The only detectable impurity was trace carbon at levels of between 2 and 5 at%. The amount of carbon incorporation in the films was found to be a function of growth conditions, decreasing at higher growth temperature and higher oxygen flow rates. This can be readily ascribed to incomplete combustion of the alkoxide or β-diketonate ligands, due either to a lack of thermal energy or lack of available oxygen at low oxygen flow rates.[18]

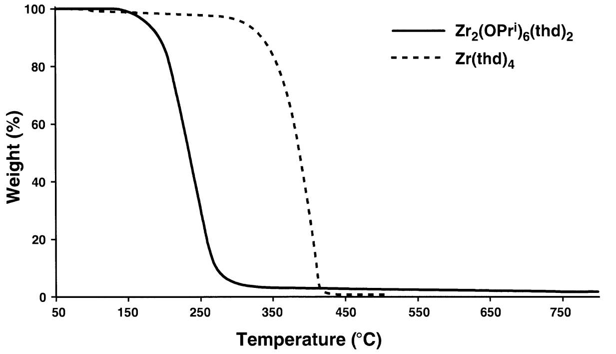


Fig. 2. Comparative TGA data for $Zr_2(OPr^i)_6(thd)_2$ and $Zr(thd)_4$ (analyses carried out under nitrogen).

Table 1. Growth conditions used for the MOCVD of ZrO_2 thin films using $Zr_2(OPr^i)_6(thd)_2$

Reactor pressure	1000 mbar
Substrates	Si(100)
Precursor solution injection rate[a]	3·5 $cm^3\ h^{-1}$
Argon flow rate	3000–4000 $cm^3\ min^{-1}$
Oxygen flow rate	1000–2000 $cm^3\ min^{-1}$
Evaporator temperature	200°C
Substrate temperature	500–600°C
Typical film growth rate	0·2 $\mu m\ h^{-1}$

[a] 0·1 molar solution in THF.

Table 2. Growth conditions used for the MOCVD of $Pb(Zr,Ti)O_3$ films using $Pb(thd)_2$, $Zr_2(OPr^i)_6(thd)_2$ and $Ti(OPr^i)_2(thd)_2$

Reactor pressure	3·5 mbar
Substrates	Si(100)
Precursor solution injection rate[a]	1 $cm^3\ min^{-1}$
Nitrogen flow	500 $cm^3\ min^{-1}$
Oxygen flow rate	500 $cm^3\ min^{-1}$
Evaporator temperature	220°C
Substrate temperature	525°C
Typical film growth rate	2 $\mu m\ h^{-1}$

[a] Solution concentrations: $Pb(thd)_2$ 0·25 molar; $Zr_2(OPr^i)_6(thd)_2$ 0·1 molar; $Ti(OPr^i)_2(thd)_2$ 0·4 molar.

The variation in ZrO_2 growth rate with substrate temperature for $Zr_2(OPr^i)_6(thd)_2$ is shown in Fig. 3, in which a comparison is also made with oxide growth from $Zr(thd)_4$ and $Pb(thd)_2$, used under similar growth conditions on the same reactor. These data show that $Zr_2(OPr^i)_6(thd)_2$ deposits ZrO_2 over a much wider temperature range than $Zr(thd)_4$. The onset of diffusion-controlled growth from $Zr_2(OPr^i)_6(thd)_2$ occurs at approx. 450°C, some 100°C lower than from $Zr(thd)_4$ and this can be readily attributed to the reduced thermal stability of $Zr_2(OPr^i)_6(thd)_2$ relative to $Zr(thd)_4$. Significantly, the optimum temperature range for oxide deposition from $Pb(thd)_2$ on the same reactor is in the region of 450–500°C (see Fig. 3), which indicates that $Zr_2(OPr^i)_6(thd)_2$ is a more suitable precursor than $Zr(thd)_4$ for the MOCVD of $Pb(Zr,Ti)O_3$ at low/moderate substrate temperature (450–550°C). However, the high growth rates observed at more elevated substrate temperatures also suggest that $Zr_2(OPr^i)_6(thd)_2$ is suited for the MOCVD of ZrO_2 and yttria-stabilised ZrO_2 protective coatings.

$Zr_2(OPr^i)_6(thd)_2$ was successfully used in combination with $Pb(thd)_2$ and $Ti(OPr^i)_2(thd)_2$ for the liquid injection MOCVD of $Pb(Zr,Ti)O_3$ at a substrate temperature of 525°C. In contrast to $Zr(thd)_4$, the $Zr_2(OPr^i)_6(thd)_2$ precursor showed no tendency to block reactor delivery lines. The $Pb_{1\cdot1}(Zr_{0\cdot75}Ti_{0\cdot25})_{0\cdot9}O_3$ films showed very high

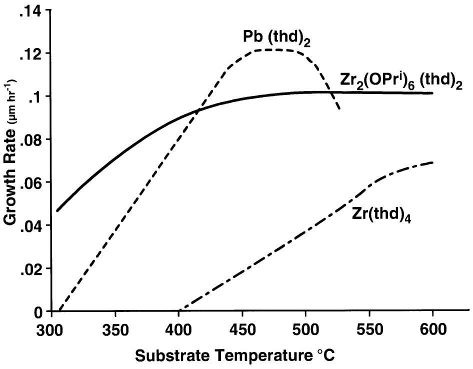
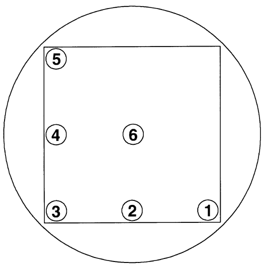


Fig. 3. Variation of metal oxide growth rate with substrate temperature for the precursors; $Zr_2(OPr^i)_6(thd)_2$, $Zr(thd)_4$ and $Pb(thd)_2$.



Point	$\frac{Zr}{Zr+Ti}$	$\frac{(Zr+Ti)}{Pb}$
1	0.43	0.85
2	0.39	0.84
3	0.37	0.80
4	0.39	0.85
5	0.43	0.86
6	0.41	0.84

Fig. 4. Compositional uniformity across a 3″ wafer of a $Pb(Zr,Ti)O_3$ film grown using $Pb(thd)_2$, $Zr_2(OPr^i)_6(thd)_2$ and $Ti(OPr^i)_2(thd)_2$ (figures in at% film thickness 0·2 μm).

compositional uniformity, in which the ratios Pb/(Zr + Ti) and Zr/Ti varied by ± 4% across a 3″ wafer (see Fig. 4). The $Pb(Zr,Ti)O_3$ films also had excellent surface morphology.

4 Conclusions

The novel precursor $Zr_2(OPr^i)_6(thd)_2$ has more convenient physical properties than conventional Zr sources, being less air-sensitive than $Zr(OR)_4$ compounds and more volatile than $Zr(thd)_4$. $Zr_2(OPr^i)_6(thd)_2$ leads to the deposition of ZrO_2 over a wider temperature range than $Zr(thd)_4$ and is more compatible with the commonly used lead source $Pb(thd)_2$, allowing the deposition of high uniformity $Pb(Zr,Ti)O_3$ films by liquid injection MOCVD.

Acknowledgements

The authors are grateful to Dr. G. W. Critchlow (University of Loughborough, UK) for provision of the AES data, and to Professor W. Rees Jr (Georgia Institute of Technology, USA) for the TGA analysis. Part of the work was funded by the Department of Trade and Industry under the Teaching Company Scheme. H.O.D. is a Teaching Company Associate (Imperial College).

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