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Metal–organic chemical vapour deposition of lead scandium tantalate: chemical issues and precursor selection

Anthony C. Jones ^{a,*}, Timothy J. Leedham ^a, Hywel O. Davies ^b, Kirsty A. Fleeting ^b, Paul O'Brien ^{1,b}, Michael J. Crosbie ^c, Peter J. Wright ^c, Dennis J. Williams ^c, Penelope A. Lane ^c

^a Inorgtech Limited, 25 James Carter Road, Mildenhall, Suffolk IP28 7DE, UK

^b Department of Chemistry, Imperial College of Science Technology and Medicine, London SW7 2AZ, UK

^c Defence Evaluation and Research Agency, St. Andrews Road, Great Malvern, Worcestershire WR14 3PS, UK

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Abstract

MOCVD is a promising technique for the deposition of the pyroelectric oxide lead scandium tantalate, $Pb(Sc_{0.5}Ta_{0.5})O_3$. In order to exploit the full potential of the method, it is important to identify the optimum combination of precursors so that process parameters and film properties are optimised. In this paper, issues involved in the selection of suitable Pb, Sc and Ta precursors are discussed and the molecular design of new Ta and Sc sources is described. It is shown how the use of carefully matched precursors allows the growth of $Pb(Sc_{0.5}Ta_{0.5})O_3$ in the required perovskite phase at low substrate temperatures. ©2000 Elsevier Science Ltd All rights reserved.

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1. Introduction

Thin films of the ferroelectric oxides $Pb(Zr,Ti)O_3$, $Pb(Mg,Nb)O_3$ and $Pb(Sc_{0.5}Ta_{0.5})O_3$ have important applications in pyroelectric [1], and piezoelectric devices [2]. Various techniques have been used for the deposition of such oxides, including reactive sputtering [3], sol–gel deposition [4,5] and metal–organic chemical vapour deposition (MOCVD) [6–8]. Of these techniques, MOCVD offers the most flexible approach, having the advantages of large area deposition capability, good composition rates, and excellent conformal step coverage at device dimensions less than 2 μ m, which is particularly important in microelectronics applications.

An essential requirement for successful MOCVD is the availability of suitable precursors with the appropriate physical properties for transport and reactivity for deposition. There must be an adequate temperature window between precursor vaporisation and decomposition, and for most electronics applications oxide deposition is limited to temperatures in the region of 500°C, to prevent degradation of the underlying silicon circuitry and metal interconnects.

The most accessible and widely used precursors for ferroelectric oxide MOCVD are metal alkoxides and β-diketonates [9], which generally have quite low equilibrium vapour pressures, typically in the order of 1 Torr at 200°C. In order to overcome this inherent involatility, liquid injection MOCVD, in which a solution of the precursor is injected into a heated evaporator, is now widely used [10,11]. This approach minimises thermal degradation of precursors, but leads to the added requirements that the precursor must be stable for long periods in solution, and must not react with other precursors in the solution. Precursor solutions should also evaporate at a common temperature without decomposition, otherwise blockages will eventually occur in the evaporator. Ideally, the separate precursors should also decompose to deposit oxide film in a similar temperature regime in order to optimise film uniformity. Although acceptable MOCVD performance and high quality ferroelectric films can often be obtained using existing precursors, in the case of more complex oxides it is sometimes necessary to 'tailor' the precursor to improve compatibility with other precursors and to optimise process parameters such as precursor evaporation temperature and oxide deposition temperature. In this paper we discuss one approach to the selection

^{*} Corresponding author. Fax: +44-163-871-8259; e-mail: tony@ inorgtech.co.uk

¹ Also corresponding author.

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Fig. 1. Molecular structures of some lead, scandium and tantalum compounds used in this study. (1) $Pb(thd)_2$, (2) $Ta(OR)_4(thd)$, (3) $Sc(thd)_3$, (4,5) $Sc(tmod)_3$. In the solid state $Sc(tmod)_3$ exists as a mixture of meridional and facial isomers (4) and (5). In solution the statistically preferred facial isomer predominates.

and design of precursors for the deposition of $Pb(Sc_{0.5}-Ta_{0.5})O_3$ by liquid injection MOCVD. $Pb(Sc_{0.5}Ta_{0.5})O_3$ is a sensitive pyroelectric oxide with a high figure of merit which has applications in uncooled thermal imaging, including night sight technologies and fire detection [12].

2. Precursor selection

2.1. Pb precursors

Although PbO and Pb(Zr,Ti)O₃ can be deposited using lead alkyls or alkoxides such as tetraethyllead, PbEt₄, lead *tert*-butoxide, Pb(OBu^t)₂, and triethyllead neopentoxide, Et₃Pb(OCH₂C(CH)₃), their high toxicity and reactivity, coupled with their high volatility, make them difficult to handle and extremely hazardous to use in liquid injection MOCVD.

In contrast, lead β -diketonates are less toxic and have lower vapour pressures, which minimises the toxic release hazard. Therefore the following precursors have all been used in MOCVD: Pb(thd)₂ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate), Pb(acetylacetonate)₂, Pb(hexafluoroacetylacetonate)₂, Pb(fod)₂ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate) [6]. The fluorine-containing compounds Pb(hfac)₂ and Pb(fod)₂ can lead to high levels of fluorine contamination in the oxide films, decomposing above 300°C to form a PbF₂ phase [6]. Consequently, the most volatile of the non-fluorine containing precursors Pb(thd)₂ is at present the precursor of choice for the MOCVD of lead oxide based ferroelectrics Pb(Zr,Ti)O₃ and Pb(Sc_{0.5}Ta_{0.5})O₃.

Pb(thd)₂ is a monomeric molecule [13], see Fig. 1, which gives it a reasonably high vapour pressure for a β -diketonate compound of 0.1 Torr at 128°C. In liquid injection MOCVD [11], an evaporator temperature of 200°C is sufficient to give

acceptable PbO growth rates at substrate temperatures above 400°C, with maximum growth rates occurring in the region 450–500°C [11]. However, at evaporator temperatures greater than 250°C, Pb(thd)₂ begins to decompose to deposit an oxide residue, and at substrate temperatures greater than 500°C desorption of PbO from the substrate occurs. Therefore, for the growth of Pb(Sc_{0.5}Ta_{0.5})O₃ with good uniformity, it is necessary to identify the Sc and Ta sources which most closely match the evaporation and deposition characteristics of Pb(thd)₂.

2.2. Sc precursors

The choice of Sc precursor is more limited than that of Pb, with the available Sc sources being restricted to β -diketonates such as Sc(thd)₃. This molecule is monomeric [14] with octahedral coordination at the metal atoms, see Fig. 1, and it deposits oxide films over a conveniently wide temperature regime of 450 to at least 600°C (see Fig. 2), showing reasonable overlap with the Pb(thd)₂ oxide deposition zone (450–500°C) [15]. However, Sc(thd)₃ is significantly less



Fig. 2. Variation in oxide growth rate with substrate temperature for $Sc(thd)_3$, $Sc(tmod)_3$ and $Sc(mhd)_3$.

volatile than Pb(thd)₂, and consequently the evaporator temperature must be approximately 300°C to obtain adequate Sc_2O_3 growth rates. This can lead to decomposition of the Pb(thd)₂ and the Ta alkoxide precursors, and so a more volatile Sc oxide source than Sc(thd)₃ would be very desirable.

Asymmetric β -diketonate ligands R'C(O)CHC(O)R", containing two different R groups, such as tmod (2,2,7-trimethyloctane-3,5-dionate) and mhd (6-methylheptane-2,4dionate) (see Fig. 3) have been shown to influence significantly the volatility of yttrium β -diketonates [16]. The lack of symmetry and increased disorder associated with the tmod and mhd ligands can be expected to disrupt the molecular packing of the metal β -diketonates, thereby increasing the precursor vapour pressure [16]. We have therefore investigated the sterically hindered scandium β -diketonates $Sc(tmod)_3$ and $Sc(mhd)_3$ as alternatives to $Sc(thd)_3$, and a schematic of the Sc(tmod)₃ structure is shown in Fig. 1. TGA data for the various Sc β -diketonates, shown in Fig. 4, indicate that $Sc(tmod)_3$ and $Sc(mhd)_3$ both evaporate at lower temperature than $Sc(thd)_3$. The residues of between 5 and 10 wt.% remaining after the evaporation of $Sc(tmod)_3$ and $Sc(mhd)_3$ are not intrinsic features, and arise from slight sample decomposition due to the presence of trace oxygen and moisture during analysis of very small samples (ca. 10 mg).

Both $Sc(tmod)_3$ and $Sc(mhd)_3$ were shown to deposit oxide over a wide temperature range (Fig. 2), fully compatible with the oxide deposition temperature from Pb(thd)₂. In



Fig. 3. β -diketone ligands used to influence the volatility of Sc(β -diketonate)₃ complexes.



Fig. 4. Typical TGA data for some *tris*- β -diketonates of scandium: (a) [Sc(thd)₃], (b) [Sc(mhd)₃], (c) [Sc(tmod)₃]. Sample weight ca. 10 mg, Pt cell, argon atmosphere, heating rate 20°C min⁻¹.



Fig. 5. Variation in growth rate with substrate temperature for Ta alkoxides: (a) $Ta(OEt)_5$, (b) $Ta(OMe)_4(thd)$, (c) $Ta(OEt)_4(thd)$, (d) $Ta(OPr^i)_4(thd)$.

particular, the new $Sc(tmod)_3$ source looks to be ideally suited to the MOCVD of $Pb(Sc_{0.5}Ta_{0.5})O_3$, however the tmodH ligand is significantly more expensive than thdH which may somewhat limit the utility of $Sc(tmod)_3$ as an alternative to $Sc(thd)_3$.

2.3. Ta precursors

The selection of a suitable Ta source presents a major challenge in the MOCVD of Pb(Sc_{0.5}Ta_{0.5})O₃. There are no tantalum β -diketonates available, and the simple alkoxide precursor Ta(OEt)₅ has a significantly lower thermal stability than Sc(thd)₃, which leads to oxide deposition in a different temperature regime, and also gives rise to decomposition of Ta(OEt)₅ in the evaporator and reactor inlet pipes at the temperatures used to evaporate Sc(thd)₃.

However, the thermal stability of tantalum alkoxide precursors can be increased by the insertion of β -diketonate groups, or by altering the alkoxide group. For instance, the oxide deposition temperature is higher for Ta(OEt)₄(thd) than for Ta(OEt)₅ and increases in the order Ta(OPrⁱ)₄(thd) < Ta(OEt)₄(thd) < Ta(OMe)₄(thd) [17], as shown by the growth rate data in Fig. 5. These precursors are monomeric (Fig. 1) and are less air sensitive than the parent alkoxides. It has also been shown that Ta(OR)₄(thd) compounds undergo significantly less decomposition than Ta(OEt)₅ in the evaporator at temperatures greater than 200°C [17]. Therefore Ta(OEt)₄(thd) and Ta(OMe)₄(thd) can be selected as most compatible with Sc(thd)₃ and Pb(thd)₂ for Pb(Sc_{0.5}Ta_{0.5})O₃ growth.

3. MOCVD of Pb(Sc_{0.5}Ta_{0.5})O₃

The application of $Pb(Sc_{0.5}Ta_{0.5})O_3$ in pyroelectric devices has been restricted by the high temperatures (>1000°C) usually required to synthesise the desired perovskite phase and to eliminate the pyrochlore phase, with its poor dielectric properties, which tends to form at low temperature. Although $Pb(Sc_{0.5}Ta_{0.5})O_3$ in the perovskite phase has been grown at low temperature by sol-gel techniques [18,19], there have been relatively few reports of successful MOCVD studies. Early studies [20] reported that a processing temperature of 800°C and a post growth anneal were required to obtain the perovskite phase. More recent studies [21] have shown that $Pb(Sc_{0.5}Ta_{0.5})O_3$ in the perovskite phase can be grown in one step at temperatures as low as 600°C. However, in both of these studies conventional MOCVD was employed, in which the Pb, Sc and Ta precursors were held in bubblers at relatively high source temperatures, leading to the possibility of source decomposition with time.

In order to avoid source decomposition we have employed liquid injection MOCVD, and $Pb(Sc_{0.5}Ta_{0.5})O_3$ films have been successfully grown at substrate temperatures of between 400 and 600°C using a single solution of $Pb(thd)_2$, $Sc(thd)_3$ and $Ta(OEt)_4(thd)$, dissolved in tetrahydrofuran (THF) [22]. This precursor combination was selected initially as the best compromise between precursor availability and cost and MOCVD performance.

At substrate temperatures of 500°C and below the material was found to be a mixture of the perovskite and pyrochlore phases. Increasing the substrate temperature led to increasing amounts of the perovskite phase, and at 600°C the perovskite phase was found to be predominant (see Fig. 6). These low growth temperatures are fully compatible with device fabrication requirements, indicating that the use of liquid injection MOCVD techniques, together with the use of carefully selected precursors, should lead to increased exploitation of this important technology.

4. Conclusions

Careful selection and molecular design of the Pb, Sc and Ta precursors have allowed us to match more closely the physical properties of each precursor, and to achieve oxide growth in a similar temperature regime. The use of the precursor combination Pb(thd)₂, Sc(thd)₃ and Ta(OEt)₄(thd) has allowed the growth of Pb(Sc_{0.5}Ta_{0.5})O₃ in the required perovskite phase at substrate temperatures as low as 600°C.

5. Experimental

5.1. Precursor synthesis

The β -diketones thdH, tmodH and mhdH used in this study were purchased from Lancaster synthesis. Pb(thd)₂ was synthesised by the addition of Na(thd) to PbCl₂ in aqueous methanol [13]. The Sc β -diketonates Sc(thd)₃, Sc(tmod)₃ and Sc(mhd)₃ were synthesised by the reaction of Sc(NO₃)₃(H₂O)_x with the sodium salts of the respective β diketonates (3 mol equivalents, prepared in situ by reaction of NaOH with the β -diketone in aqueous methanol) [23]. After isolation of the solid products by filtration, the Sc β diketonates were dried overnight and then purified by vacuum



Fig. 6. X ray diffraction data for $Pb(Sc_{0.5}Ta_{0.5})O_3$ grown at 600°C using $Pb(thd)_2$, $Sc(thd)_3$ and $Ta(OEt)_4(thd)$. Pe diffraction peaks from perovskite phase, Pt diffraction peaks from platinum substrate.

sublimation. Each compound was fully characterised by ¹H NMR, ¹³C{¹H} NMR, mass spectroscopy, and microanalysis, and full details are given elsewhere [14].

 $Ta(OR)_4$ (thd) compounds were prepared from the reaction between $Ta(OR)_5$ and 1 mol equivalent of thdH in *n*hexane solvent. After removal of the solvent and volatiles in vacuo, the $Ta(OR)_4$ (thd) products were purified by vacuum distillation. The synthesis and characterisation of $Ta(OR)_4$ (thd) compounds are described more fully elsewhere [24].

5.2. Growth of single oxide films

PbO, Sc_2O_3 and Ta_2O_5 films were deposited on Si(100) substrates at 1000mbar, using a liquid injection MOCVD reactor described elsewhere [11]. The films were grown from individual solutions of the Pb, Sc and Ta oxide precursors dissolved in THF. The growth conditions are summarised in Table 1.

5.3. Growth of $Pb(Sc_{0.5}Ta_{0.5})O_3$ films

Thin films of $Pb(Sc_{0.5}Ta_{0.5})O_3$ were deposited onto Pt(111) substrates by the evaporation of a single solution of precursors in THF using an MOCVD reactor described in detail elsewhere [11]. An evaporator temperature of 300°C

Table	1	

Growth conditions	used for c	leposition of	of single	e metal	oxides '
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Precursor	THF solution concentration (molar)	Injection rate $(cm^3 h^{-1})$	Evaporator temperature (°C)
$Pb(thd)_2$	0.16	1	200
$Sc(thd)_3$,	0.1	2	300
$Sc(tmod)_3$	0.1	2	300
$Sc(mhd)_3$	0.1	2	300
$Ta(OR)_4(thd)$	0.1	2	225

^a Reactor pressure 1000 mbar, substrate Si(100), Ar flow rate 4000 cm³ min⁻¹, oxygen flow rate 1000 cm³ min⁻¹.

Table 2 Growth conditions used for deposition of $Pb(Sc_{0.5}Ta_{0.5})O_3$ from a single precursor solution

Reactor pressure (mbar)	1000		
Substrate	Pt(111)		
THF solution composition (%)	$Pb(thd)_2$ 35.5, $Sc(thd)_3$ 32.25,		
	Ta(OEt) ₄ (thd) 32.25		
Solution injection rate $(cm^3 h^{-1})$	2		
Argon flow rate $(cm^3 min^{-1})$	4000		
Oxygen flow rate $(cm^3 min^{-1})$	1000		
Evaporator temperature (°C)	300		
Substrate temperature (°C)	450-600		
Film growth rate ($\mu m h^{-1}$)	0.1-1		

was used to prevent condensation of the least volatile precursor $Sc(thd)_3$, and minimal decomposition of $Pb(thd)_2$ and $Ta(OEt)_4(thd)$ was observed. A full summary of growth conditions is given in Table 2.

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References

- N.M. Shorrocks, S.G. Porter, R.W. Whatmore, A.D. Parsons, J.N. Gooding, D.J. Pedder, Proc. SPIE 1320 (1990) 88.
- [2] D.L Polla, Microelectron. Eng. 29 (1995) 51.

- [3] S. Krupanidhi, N. Maffeo, M. Sayer, K. El-Assel, J. Appl. Phys. 54 (1983) 6601.
- [4] K.D. Budd, S.K. Dey, D.A. Payne, Proc. Br. Ceram. Soc. 36 (1985) 107.
- [5] B.A. Tuttle, R.W. Schwartz, MRS Bull. 21 (1996) 49.
- [6] C.H. Peng, S.B. Desu, J. Am. Ceram. Soc. 77 (1994) 1799.
- [7] M. Okada, K. Tominaga, T. Araki, S. Katayama, Y. Sakashita, Jpn. J. Appl. Phys. 29 (1990) 718.
- [8] C.J. Brierly, C. Trundle, L. Considine, R.W. Whatmore, F.W. Ainger, Ferroelectrics 91 (1989) 181.
- [9] A.C. Jones, Chem. Vap. Deposition 4 (1998) 169.
- [10] W.S. Rees, in: W.S. Rees (Ed.), CVD of Non Metals, VCH, Weinheim, 1996, Ch. 1, Section 1.5, and references therein.
- [11] A.C. Jones, T.J. Leedham, P.J. Wright, M.J. Crosbie, P.A. Lane, D.J. Williams, K.A. Fleeting, D.J. Otway, P. O'Brien, Chem. Vap. Deposition 4 (1998) 46.
- [12] R.W. Whatmore, S.B. Stringfellow, N.M. Shorrocks, Infrared Technol. XIX (1993) 391.
- [13] M.A. Malik, P.O'Brien, M. Motevalli, A.C. Jones, Polyhedron 18 (1999) 1641.
- [14] K.A. Fleeting, P.O. Brien, H.O. Davies, A.J.P. White, D.J. Williams, A.C. Jones, T.J. Leedham, Chem. Vap. Deposition 5 (1999) 261.
- [15] A.C. Jones, T.J. Leedham, P.J. Wright, M.J. Crosbie, D.J. Williams, P.A. Lane, P. O'Brien, Mater. Res. Soc. Symp. Proc. 495 (1998) 11.
- [16] H.A. Luten, W.S. Rees, V.L. Goedken, Chem. Vap. Deposition 2 (1996) 149.
- [17] M.J. Crosbie, P.J. Wright, D.J. Williams, P.A. Lane, J. Jones, A.C. Jones, T.J. Leedham, P. O'Brien, H.O. Davies, Paper presented at EURO CVD 12, Sitges, Spain, September 5–10, 1999, J. Phys. IV France 9 (1999) PR8-935.
- [18] D. Liu, L. Ma, D.A. Payne, D.D. Viehland, Mater. Lett. 17 (1993) 319.
- [19] D. Liu, D.A. Payne, J. Appl. Phys. 77 (1995) 1458.
- [20] F.W. Ainger, K. Bass, C.J. Brierly, M.D. Hudson, C. Trundle, R.W. Whatmore, Prog. Cryst. Growth Charact. 22 (1991) 183.
- [21] D. Liu, H. Chen, Mater. Lett. 28 (1996) 17.
- [22] M.J. Crosbie, P.A. Lane, P.J. Wright, A.C. Jones, T.J. Leedham, D.J. Williams, C.L. Reeves, submitted to J. Cryst. Growth.
- [23] K.J. Eisentrout, R.E. Sievers, Inorg. Synth. 11 (1978) 94.
- [24] H.O. Davies, T.J. Leedham, A.C. Jones, P. O'Brien, A.J.P. White, D.J. Williams, Polyhedron.