Polyhedron 177 (2020) 114270

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and characterization of lead (IV) precursors and their conversion to PZT materials through a CVD process



POLYHEDRON

Euk Hyun Kim^a, Cheong Won Moon^b, Jung Gyu Lee^a, Myoung Soo Lah^c, Sang Man Koo^{a,b,*}

^a Department of Chemical Engineering, Hanyang University, Seoul 04763, Republic of Korea

^b Department of Fuel Cells and Hydrogen Technology, Hanyang University, Seoul 04763, Republic of Korea

^c Department of Chemistry, UNIST, Ulsan 44919, Republic of Korea

ARTICLE INFO

Article history: Received 5 September 2019 Accepted 28 November 2019 Available online 16 December 2019

Keywords: Lead precursors β-Ketonate ligand Silylamides MOCVD process PZT materials

ABSTRACT

New Pb(IV) precursors for lead zirconate titanate (PZT) thin films were synthesized, and their solid-state structures were elucidated by single-crystal X-ray crystallography. First, tetraphenyl lead (Ph₄Pb) was synthesized from the reaction of PbCl₂ with the Grignard reagent, PhMgBr, by a published method. Two of the phenyl ligands in Ph₄Pb were replaced by bromines, and then were substituted with bis (trimethylsilyl)amides (btsa) to yield Ph₂Pb(btsa)₂ (1), or with 2,2,6,6-tetramethyl-3,5-heptadiketonate (thd) ligands to yield Ph₂Pb(thd)₂ (2). Single crystals of these two new Pb(IV) precursors were obtained by recrystallization in hexane, and their chemical compositions were characterized by FT-IR and ¹H NMR. In TG analyses, both compounds exhibited sharp decomposition curves, with major mass losses in the region of 200–250 °C. PZT films were fabricated from one of the newly prepared Pb(IV) precursors by an MOCVD process involving Ti(OⁱPr)₄ and Zr(OPr)₄, and the development of the perovskite phase with temperature was monitored by a XRD method.

© 2019 Elsevier Ltd. All rights reserved.

1. Introduction

Lead zirconate titanates (PZT, Pb(Zr_xTi_{1-x})O₃) are well-known ferroelectric materials based on the perovskite structure, and are of great interest for microelectronic applications such as pyroelectric and piezoelectric devices, actuators, thermal image sensors, non-volatile memory systems and optical waveguides [1,2]. Various techniques for the preparation of PZT thin films have been employed, such as reactive magnetron sputtering, multi-ion-beam sputtering, spin coating, sol-gel processing, and pulsed laser ablation [3–7]. For thin-film applications, the formation of crystalline single-phase materials at low temperatures is desired. Chemical routes such as sol-gel processing and MOCVD offer advantages over physical deposition techniques, and have attracted wide interest.

Among various chemical routes, liquid delivery metalorganic chemical vapor deposition (LD-MOCVD) is regarded as one of the most suitable techniques for the formation of PZT thin films due to its good step coverage, high deposition rate, large area uniformity and high throughput [8–10]. In the LD-MOCVD process, pre-

* Corresponding author. E-mail address: sangman@hanyang.ac.kr (S.M. Koo). cursors are dissolved in a solvent, and a controlled amount of the solution is injected into a flash evaporator. The evaporated gas mixture is introduced into a deposition chamber, and a film is deposited on a substrate, as in an ordinary CVD process.

One of the challenges in LD-MOCVD is the need for suitable precursors that have convenient vapor pressures at moderate temperatures, decompose at modest temperatures and are stable during storage. Organometallic compounds have been found to satisfy most of these demands, as the physical and chemical properties of such precursors can be changed through the tailoring of the organic ligands. Various organometallic precursors, including metal alkoxides, beta-diketonates and aminoalcohols, have been used for the MOCVD of TiO₂ and ZrO₂ [8–12]. However, there are few precursors for lead sources that exhibit both high reactivity at low temperatures and long-term stability in solution-based processes. Aside from lead precursors that are frequently used for the growth of PZT thin films, such as tetraethyllead $(Pb(C_2H_5)_4)$ and Pb $(thd)_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptadiketonate), most of the Pb precursors developed so far have inadequate vapor pressures for the CVD process compared to Ti and Zr sources, due to their polymeric structure of lead (II) compound [13].

In this study, we describe the preparation of a new series of lead (IV) precursors containing phenyl ligands and the fabrication of ferroelectric $Pb(Zr_xTi_{1-x})O_3$ thin films by LD-MOCVD. For the syn-



thesis, Ph₂PbBr₂ was obtained as an intermediate through the bromination of Ph₄Pb. It is known that the introduction of phenyl ligands onto the lead center (Ph₂Pb²⁺) stabilizes the resulting compounds in the solution and renders them less toxic than their aliphatic counterparts [14]. Thus, the volatility or thermal behavior of lead precursors could be markedly enhanced by the substitution of the two bromines of Ph₂PbBr₂ with bis(trimethylsilyl)amide (btsa) or 2,2,6,6-tetramethyl-3,5-heptadiketonate (thd) ligands. The newly prepared lead precursors were characterized by FT-IR, ¹H NMR, TGA and single-crystal X-ray crystallography. PZT films were then fabricated by LD-MOCVD at 550 or 700 °C on a Si wafer, and the development of PZT phases was investigated by XRD, SEM and AFM methods.

2. Experimental section

2.1. General methods

All reactions were carried out in a dry nitrogen atmosphere by standard Schlenk techniques, unless otherwise noted. Hexane, toluene, diethyl ether and tetrahydrofuran (THF) were distilled from sodium and benzophenone, and were stored under dry nitrogen. Chloroform was distilled with calcium hydride prior to use. Anhydrous alcohols were also stored under dry nitrogen with a 4 Å molecule sieve (baked at 250 °C, 2 h). Lead chloride (PbCl₂, Daejung Chemicals), phenyl magnesium bromide (PhMgBr, 3 M in diethyl ether, Aldrich), titanium isopropoxide (Ti(OⁱPr)₄, 97%, Aldrich) and zirconium propoxide (Zr(OPr)₄, 70 wt% in *n*-propanol, Aldrich) were purchased and used without further purification. Deuterated benzene and chloroform for NMR measurements were used as received. The synthesized precursors were characterized by FT-IR (ABB, FTLA 2000), ¹H NMR (Varian, Mercury 300, 300 MHz) and TGA (TA Instrument, SDT Q600). The structures of the synthesized compounds were investigated by single-crystal X-ray crystallography (Bruker, Smart CCD 1000). The fabricated PZT films were analyzed by XRD (Rigaku, MiniFlex 600) at 40 kV, 15 mA, along with SEM (Jeol JEM-6340F) and AFM (Park Systems, XE-100) methods.

2.2. Syntheses

2.2.1. Preparation of tetraphenyl lead, Ph₄Pb

Tetraphenyl lead (Ph₄Pb) was prepared by a previously described method with some modifications [15]. 10.0 g of lead chloride (PbCl₂, 35.9 mmol) was dispersed in 30 mL of anhydrous diethyl ether. Then 1.0 equivalent of anhydrous iodo-benzene (C₆H₅I, 4.0 mL, 35.9 mmol.) was injected into the dispersed solution. With vigorous stirring, 12.0 mL of phenyl magnesium bromide solution (3.0 M in diethyl ether, 107.7 mmol.) was slowly added using a cannula, maintaining inert atmosphere. After addition of phenyl magnesium bromide, the reaction mixture was refluxed for 8 h. Excess de-ionized (DI) water was slowly and cautiously added into the stirring solution to remove unreacted phenyl magnesium bromide. By heating the reaction medium, most of diethyl ether was removed by evaporation. The gray precipitates were washed with an excess amount of DI-water and dried in vacuum. The obtained powder was re-dissolved in a minimal amount of anhydrous chloroform, and the resulting solution was filtered. Clear solution was then stored in -30 °C refrigerator for 3 days and the crystalline product of tetraphenyl lead was finally obtained after filtration (yield: 70%).

Anal. FT-IR (KBr, cm⁻¹): 3060 m, 3036 m, 1473 s, 1425 s, 1057 m, 1016 m, 991 s, 725 vs, 694 vs.

¹H NMR (CDCl₃, 25 °C, ppm): 7.53 (m, 4H, Ph), 7.26 (m, 4H, Ph), 7.24 (m, 2H, Ph).

2.2.2. Preparation of diphenyl dibromo lead, Ph₂PbBr₂

Diphenyl dibromo lead (Ph₂PbBr₂) was prepared by a published procedure with some modifications [16]. First, 3.00 g of Ph₄Pb (5.8 mmol) was dissolved in 75 mL of anhydrous chloroform. The solution was cooled down to -64 °C in a chloroform/liquid-N₂ mixture bath, and 0.6 mL of bromine (Br₂, 11.6 mmol) was injected into the solution with a syringe. Upon thawing of the reaction bath, the reaction mixture was stirred for 4 h at room temperature, and the color of the solution changed from red to white. The resulting solution was filtered to remove by-products. The filtered product was washed with anhydrous benzene and anhydrous diethyl ether several times, and was air-dried (yield: 80%).

Anal. FT-IR (KBr, cm⁻¹): 3068 vw, 3049 vw, 1558 m, 1471 s, 1439 s, 1321 w, 984 s, 717 vs, 673 s.

¹H NMR analysis for Ph₂PbBr₂ could not be carried out because Ph₂PbBr₂ is insoluble in most NMR solvents.

2.2.3. Preparation of diphenyl di{bis(trimethylsilyl)amide} lead, Ph₂Pb {N(SiCH₃)₂}₂ (1)

A 1.28-g sample of lithium bis(trimethylsilyl)amide (btsa, 7.6 mmol) was dissolved in anhydrous hexane, and 2.00 g of diphenyl dibromo lead (Ph₂PbBr₂, 3.8 mmol) was added. After being stirred for 12 h, the reaction mixture was filtered, and the filtered product was washed with methanol to remove the residual lithium btsa salt. After the filtrate was reduced to 10 mL, it was stored at -20 °C overnight, and the crystalline product of Ph₂Pb{N(SiCH₃)₂}₂ was obtained in cold hexane (yield: 80%).

Anal. FT-IR (KBr, cm^{-1}): 3064 w, 2951 m, 2895 m, 1572 w, 1475 w, 1431 m, 1248 s, 933 vs, 858 vs, 837 vs, 721 s, 669 s, 617 m.

¹H NMR (CDCl₃, 25 °C, ppm): 7.68 (d, 4H, Ph), 7.47 (t, 4H, Ph), 7.36 (t, 2H, Ph), 0.17 (s, 36H, Si(C**H**₃)₃). CCDC-1582108.

2.2.4. Preparation of diphenyl di(2,2,6,6-tetramethyl-3,5-heptadiketonate) lead, Ph₂Pbthd₂ (**2**)

First, 0.78 mL of 2,2,6,6-tetramethyl-3,5-heptadiketonate (thdH, 7.6 mmol) and 0.18 g of sodium hydride (NaH, 7.60 mmol) was added to 100 mL of anhydrous toluene. After the solution was stirred for several hours, 2.00 g of diphenyl dibromo lead (Ph_2PbBr_2 , 3.8 mmol) was added, and the mixture was stirred for 12 h at room temperature. The reaction mixture was filtered, the filtrate was stored at -20 °C overnight, and the crystalline product of Ph_2 -Pbthd₂ was obtained after the filtration (yield: 80%).

Anal. FT-IR (KBr, cm⁻¹): 3070 w, 3057 w, 2962 m, 2930 m, 1564 s, 1496 s, 1435 s, 1387 s, 1356 s, 1219 s, 1182 s, 1124 s, 1018 m, 993 m, 945 m, 868 s, 793 m, 735 s, 687 s, 602 m.

¹H NMR (CDCl₃, 25 °C, ppm): 7.61 (d, 4H, Ph), 7.43 (t, 4H, Ph), 7.31 (t, 2H, Ph), 5.52 (s, 2H, COCHCO), 1.08 (s, 18H, CC(CH₃)₃). CCDC-1582107.

2.3. Fabrication of a PZT film through the MOCVD process

Before deposition of PZT film, TiO_2 layer was prepared on Si wafer for bottom layer of PZT film. Si wafer was washed with acetone and ethanol to remove organic impurities on the wafer and dried prior to use. 1.0 mL of $Ti(O^iPr)_4$ was used as Ti precursor, the deposition time was 10 min. The temperatures of canister and oven were 50 °C and 500 °C, respectively.

For the preparation of the PZT source for the MOCVD process, 1.0 g of Pb precursor **2** was dissolved with 0.5 M equivalent of Ti $(O^{i}Pr)_{4}$ (0.20 mL) and $Zr(OPr)_{4}$ (70 wt% in *n*-PrOH, 0.30 mL) in 5.0 mL of butyl ether and 0.4 mL of tetraglyme. The canister and line temperatures were set to 175 and 220 °C, respectively, and the oven temperature was 550 or 700 °C. To control the flow rate, 10 sccm of argon gas was used, and the operating pressures ranged from 2 to 15 torr. The reaction time was 1 h, and there was no additional sintering process. After the MOCVD process, the crystallinity of the PZT-coated on Si wafer was characterized by an XRD method, and its surface morphology was characterized by SEM and AFM methods.

2.4. Crystallographic data collection and refinement of the structure

The crystal data, experimental details and refinement results for Pb(IV) precursors **1** and **2** are listed in Table 1. Crystals of precursors **1** and **2** were coated with paratone oil, and the diffraction data were measured at 298 K and 173 K, respectively, with Mo K α radiation on an X-ray diffraction camera system with an imaging plate equipped with a graphite crystal incident beam monochromator. RapidAuto software [S1] was used for data collection and data processing. The structures were solved by a direct method and refined by a full-matrix least-squares calculation with the SHELXTL software package [S2].

S1. Rapid Auto software, R-Axis series, Cat. No. 9220B101, Rigaku Corporation.

S2. G. M. Sheldrick, *SHELXTL-PLUS, Crystal Structure Analysis Package*; Bruker Analytical X-Ray; Madison, WI, USA, **1997**.

3. Results and discussion

3.1. Synthesis and characterization of Pb(IV) precursors

Ph₄Pb was obtained from the reaction of PbCl₂ with the Grignard reagent (PhMgBr) and iodobenzene by a previously described process [15]. Ph₂PbBr₂ was prepared of Ph₄Pb via liquid bromine at -64 °C in a chloroform/liquid-N₂ mixture bath by a modified

Table 1

	Crystal o	data and	structure	refinement	of Pb	(IV)	precursors:	precursors	1	and	2.
--	-----------	----------	-----------	------------	-------	------	-------------	------------	---	-----	----

- (a) 2 PbCl₂ + 4 PhMgBr \rightarrow Ph₄Pb + Pb + 2 MgBr₂ + 2 MgCl₂
- (b) $Ph_4Pb + 2 Br_2 \rightarrow Ph_2PbBr_2 + 2 PhBr$
- (c) $Ph_2PbBr_2 + 2 Li(btsa) \rightarrow Ph_2Pb(btsa)_2$ (1) + 2 LiBr
- (d) $Ph_2PbBr_2 + 2 Na(thd) \rightarrow Ph_2Pb(thd)_2$ (2) + 2 NaBr

Scheme 1. Synthetic routes for the two Pb (IV) precursors 1 and 2.

bromination of published method [16]. Two new Pb(IV) precursors were synthesized by the ligand displacement reaction of Ph₂PbBr₂ with two equivalents of the monodentate ligand, bis(trimethylsilyl)amide (btsa, N{SiMe₃}₂), for precursor **1**, and two equivalents of the bidentate ligand, 2,2,6,6-tetramethyl-3,5-heptadiketonate (thd), for precursor **2**, as shown in Scheme 1. The ligand displacement reactions of Ph₂PbBr₂ proceeded readily at room temperature through the use of alkali salts of the corresponding ligands, and the reactions generated insoluble by-products, alkali metal bromides (LiBr or NaBr), in organic solvents. The newly synthesized Pb(IV) precursors (1 and 2) easily dissolved in most organic solvents. In contrast. Ph₄Pb is partially soluble only in CHCl₃, and Ph₂PbBr₂ is insoluble in most organic solvents. Therefore, the degree of ligand displacement reaction for Pb(IV) precursors **1** and **2** could be monitored by the disappearance of the insoluble Ph₂PbBr₂ in an organic medium, such as toluene and hexane.

The two Pb(IV) precursors were characterized by FT-IR and ¹H NMR spectrometry as well as TGA. The FT-IR spectra for both Pb (IV) precursors exhibited the characteristic absorption peaks at

	Precursor 1	Precursor 2		
Empirical formula	$C_{24}H_{46}N_2Si_4Pb$	C ₃₄ H ₄₈ O ₄ Pb		
Formula weight	682.18	727.91		
Temperature (K)	173(2)	298(2)		
Wavelength (Å)	0.71073	0.71073		
Crystal system	Monoclinic	Monoclinic		
Space group	$P2_1/c$	$P2_1/c$		
a (Å)	13.332(3)	17.387(4)		
b (Å)	11.743(2)	9.6407(19)		
c (Å)	20.392(4)	21.209(4)		
$A(^{\circ})$	90	90		
β(°)	90.56(3)	102.31(3)		
$\gamma(\circ)$	90	90		
Volume (Å ³)	3192.6(11)	3473.4(12)		
Z	4	4		
Density (calculated)	1.419 Mg/m ³	1.392 Mg/m ³		
Abs. coeff. (mm^{-1})	5.448	4.889		
F(0 0 0)	1368	1464		
Crystal size	$0.30 \times 0.25 \times 0.24 \ mm^3$	$0.75 \times 0.55 \times 0.24 \text{ mm}^3$		
Theta range for data collection	3.05–27.45°	3.19–27.48°		
Index ranges	$-17 \le h \le 17$	$-22 \leq h \leq 22$		
	$-15 \le k \le 15$	$-12 \le k \le 11$		
	$-26 \leq l \leq 26$	$-27 \le l \le 27$		
Reflections collected	30,018	32,372		
Independent reflections	7278 [R(int) = 0.0428]	7933 [R(int) = 0.1471]		
Completeness to theta = 27.45°	99.80%	99.50%		
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents		
Max. and min. transmission	0.3547 and 0.2918	0.3866 and 0.1206		
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²		
Data/restraints/parameters	7278/0/292	7933/48/396		
Goodness-of-fit on F ²	1.039	1.013		
Final R indices [I > 2sigma(I)]	$R_1 = 0.0218$	$R_1 = 0.0838$		
	$wR_2 = 0.0475$	$wR_2 = 0.1934$		
R indices (all data)	$R_1 = 0.0266$	$R_1 = 0.1013$		
	$wR_2 = 0.0494$	$wR_2 = 0.2267$		
Extinction coeff.	-	0.0061(7)		
Largest diff. peak/hole	1.166/-0.833 e Å ⁻³	3.560/-2.880 e Å ⁻³		

3058, 1569, 1474, 1439, 984, 717 and 673 cm⁻¹ from the stretching vibrations of the two phenyl groups. It was noticeable that the v(C=C) stretching vibrational peak from the phenyl groups in precursors **1** and **2** had red-shifted from 1600 cm⁻¹ (in free phenyl groups) to 1569 cm⁻¹, due to the weakening of the C=C bond energy by the electron withdrawal from the Pb(IV) center. For precursor **1**, the absorption peaks of v(C-H) and v(Si-C) stretching vibrations from the monodentate btsa ligands were observed at 2951, 2895 cm⁻¹ and 1248 cm⁻¹, respectively, and those of v(Si-N) and v(Si-C) bending vibrations appeared at 933 cm⁻¹ and 837 cm⁻¹, respectively. For the bidentate β -ketonate ligands in precursor **2**, the peak from C=O stretching vibrations had red-shifted from 1604 cm⁻¹ (in free thdH) to 1564 cm⁻¹, due to the formation of a six-membered ring between a lead atom and the β -ketonate ligands.

The ¹H NMR spectra of Pb(IV) precursors **1** and **2** exhibited typical split resonance peaks from phenyl protons, ranging between 7.3 and 7.7 ppm. For precursor **1**, an additional singlet peak was observed at 0.17 ppm from the two Si(CH₃)₃ units in the btsa ligand, exhibiting an up-field shift compared to 0.38 ppm for the Sr(btsa)₂ complex [17]. For precursor **2**, two singlet absorption peaks appeared at 5.52 and 1.08 ppm, corresponding respectively to protons of C(=O)CHC(=O) and the two C(CH₃)₃ units in the β -ketonate ligands, also displaying a slight up-field shift from 5.72 and 1.17 ppm for thdH. These up-field shifts in the positions of the proton peaks for both the btsa and β -ketonate ligands in the two Pb(IV) precursors might have been induced by shielding effects, probably due to the electron-donating abilities of phenyl ligands.

3.2. Single-crystal X-ray structures for Pb(IV) precursors

Single-crystal X-ray diffraction analyses revealed that precursors **1** and **2** both crystallized in the monoclinic space group $P2_1/c$. The ORTEP diagrams of the two precursors are shown in Fig. 1. As shown in Fig. 1a, precursor **1** existed as a slightly distorted tetrahedral structure, in which the two btsa and two phenyl ligands were coordinated to the central Pb(IV) atom. As shown in Table 2, the C-Pb-C bond angle between the two phenyl ligands around the metal center was 101.80(10)°, while the N-Pb-N bond angle between the two btsa ligands around the metal center was 109.93(8)°. The four C-Pb-N bond angles between the phenyl and btsa ligands around the metal center were $105.01(9)^\circ$, $105.18(9)^\circ$, $116.68(9)^\circ$ and $118.56(9)^\circ$. The average distances for the two Pb-N and two Pb-C bonds were 2.167(2) and 2.214(3) Å, respectively.

In precursor **2**, the lead atom was coordinated to two bidentate β-ketonate ligands and two phenyl ligands, forming a slightly distorted octahedral geometry. The C-Pb-C angle between the two phenyl groups around the Pb atom was 163.9(3)°, deviating from that of the ideal octahedral structure (180°). In addition, the two inter O-Pb-O angles between the two β-ketonate ligands on the equatorial plane of the octahedral geometry also exhibited severely distorted values of 80.7(2) and 124.3(2)°, while the intra O-Pb-O angles of the β -ketonate ligands were 77.2(2) and 77.7 (2)°. The distances of the two Pb–C bonds from the phenyl groups were 2.134(7) and 2.173(9) Å, similar to previously reported values [18], while those of the four Pb–O bonds from the β -ketonate ligands were 2.243(3), 2.253(5), 2.422(8) and 2.429(6) Å. The two different set values of the Pb-O bonds may indicate that the distorted structure was due to the anisotropic bidentate chelation of the β -ketonate ligands to the metal center. These results differed from those for Pbthd₂, where the bond lengths of the four Pb-Os were similar: 2.303 Å of Pb(1)–O(1) versus 2.287 Å of Pb(1)–O(2) [19].



Fig. 1. ORTEP diagrams of the two Pb(IV) precursors: (a) precursor 1 and (b) precursor 2.

3.3. Conversion to PZT thin films (by the LD-MOCVD process)

Fig. 2 exhibited TGA curves for the two lead precursors **1**, Ph₂Pb (btsa)₂, and **2**, Ph₂Pb(thd)₂. The curve pattern for the precursor **1** shows that the weight decrease starts at 230 °C and finally ends at below 300 °C. The pattern for precursor **2** looks quite similar to that of Pb(thd)₂ [8], although the window for the sublimation for precursor **2** appears to be wider than precursor **1**—The weight change occurred from 220 °C to a temperature slightly above 300 °C. The sublimation points of precursors **1** and **2** were found to be higher than the transition temperatures for other diphenyl lead (IV) derivatives (Ph₂PbX₂); for example, Ph₄Pb (m.p. 229.5 °C) [20], Ph₂PbBr₂ (decomposition at 248 °C) [21], and Ph₂-Pb(OAc)₂ (m.p. 208.5 °C) [22]. The final residues of precursors **1** and **2** were 4.6% and 5.5%, respectively, after the decomposition of the samples under aerobic conditions during the TGA measurements.

Precursor **2** was chosen as a precursor for the fabrication of PZT thin films by the LD-MOCVD process, due to its higher volatility and better stability than those of precursor **1**. Butyl ether was used as a main solvent for mixing PZT precursors and facilitating liquid delivery, and a small amount (0.5 mL) of tetraglyme was used as a thermal stabilizer for its high boiling point (~275 °C). Unlike the

Table 2 Bond lengths (Å) and angles (°) of Pb (IV) precursors 1 and 2.

Precursor 1		Precursor 2		
Average bond length (Å) Average bond angle (°)		Average bond length (Å)	Average bond angle (°)	
Pb(1)-N(1) 2.168(2) Pb(1)-N(2) 2.166(2) Pb(1)-C(13) 2.219(2) Pb(1)-C(19) 2.209(3)	C(13)-Pb(1)-C(19) 101.80(10) C(13)-Pb(1)-N(1) 105.18(9) C(13)-Pb(1)-N(2) 118.56(9) C(19)-Pb(1)-N(1) 116.68(9) C(19)-Pb(1)-N(2) 105.01(9) N(1)-Pb(1)-N(2) 109.93(8)	Pb(1)-C(1) 2.134(7) Pb(1)-C(7) 2.173(9) Pb(1)-O(1) 2.243(6) Pb(1)-O(2) 2.429(6) Pb(1)-O(3) 2.422(8) Pb(1)-O(4) 2.253(5)	$\begin{array}{c} C(1)-Pb(1)-C(7) \ 163.9(3) \\ C(1)-Pb(1)-O(1) \ 94.9(3) \\ C(1)-Pb(1)-O(2) \ 89.7(2) \\ C(1)-Pb(1)-O(3) \ 87.4(3) \\ C(1)-Pb(1)-O(4) \ 98.1(2) \\ C(7)-Pb(1)-O(1) \ 97.8(3) \\ C(7)-Pb(1)-O(2) \ 83.4(3) \\ C(7)-Pb(1)-O(2) \ 83.4(3) \\ C(7)-Pb(1)-O(3) \ 84.5(3) \\ C(7)-Pb(1)-O(2) \ 77.7(2) \\ O(1)-Pb(1)-O(3) \ 157.89(19) \\ O(1)-Pb(1)-O(3) \ 124.3(2) \\ O(2)-Pb(1)-O(3) \ 124.3(2) \\ O(2)-Pb(1)-O(4) \ 157.7(2) \\ O(3)-Pb(1)-O(4) \ 77.2(2) \\ \end{array}$	



Fig. 2. TGA curves for the two Pb(IV) precursors: (a) precursor 1 and (b) precursor 2.

case of PZT films fabricated with $Pb(C_2H_5)_4$ [23,24], an additional oxygen source such as O_2 or ozone gas was not needed, due to the availability of the thd ligands as an oxygen source.

We note that the initial decomposition temperature of Pb(thd)₂ on a heated substrate is known to be 350 °C at vacuum) [9]. Considering low boiling points of Ti(OⁱPr)₄ (232 °C at 1 atm.) and Zr (OPr)₄ (208 °C at 0.1 torr) as well as TGA curve of precursor **2**, the sublimation of three molecular sources-Pb(thd)₂, Ti(OⁱPr)₄, Zr (OPr)₄, occurred initially at low temperature range between 200 and 300 °C without any structural decomposition. Then the decomposition of alkoxide ligands in titanium isopropoxides and zirconium propoxides should be followed, while maintaining the structural integrity of Ph₂Pb(thd)₂. Finally, the assembly to multimetallic cluster species containing lead, titanium, and zirconium would be taken placed, resulting the formation of PZT phase upon sintering. Further study will be necessary to elucidate the exact decomposition process for the deposition of PZT films.

Fig. 3 exhibits the XRD patterns for standard PbZr_{0.5} $T_{0.5}O_3$ phase and the PZT films grown at 500 and 700 °C in this study, respectively. As shown in Fig. 3, the X-ray diffraction peaks from a fabricated PZT film prepared at 700 °C were observed at 21.9° (1 0 0), 31.0° (1 0 1), 39.0° (1 1 1), 45.2° (2 0 0), and 51.2° (2 1 0). At 700 °C, no peak from pyrochlore phase, or unconverted metal oxide, such as lead, zirconium and titanium oxide, was observed, indicating the formation of fully developed PZT phase with a (1 0 1) preferred orientation. In a meanwhile, the XRD pattern of a PZT film prepared at 550 °C shows no discernible diffraction



Fig. 3. XRD spectra of PZT thin films; (a) standard PbZr_{0.5}Ti_{0.5}O_3 (JCPDS 14-0031), (b) prepared at 550 °C and (c) 700 °C.

peaks, indicating the amorphous nature of a fabricated film at this temperature.

Okamura et al. investigated the relationship between the position of diffraction peaks in the resulting PZT phases and the ratios of Ti to Zr [25]. They found that two XRD peaks at 22.0° (100) and 31.1° (1 0 1) were shifted to lower angles (21.6° and 30.7°) when the ratio of Ti/Zr decreased from 1 to 0.2, while the direction of peak shift was reversed to higher angles (22.4° and 31.4°) when the ratio of Ti/Zr increased from 1 to 5. When the ratio was 1, two diffraction peaks appeared at 22.0° and 31.1°. Based on this result, it could be concluded that PZT film obtained in this study should have the Ti/Zr ratio of 0.8, because two XRD peaks from (1 0 0) and (1 0 1) were observed at 21.9° and 31.0°. Okamura et al. also examined the effect of the PT/(PZ + PT) ratio on the type of PZT phases formed (such as orthorhombic, rhombohedral, and tetragonal phases). They discovered that the orthorhombic phase of PZT was first formed, when the PT/(PZ + PT) ratio was between 0 and 0.1. Next, the conversion of the PZT phase to rhombohedral was observed when the PT/(PZ + PT) ratio was increased from 0.1 to 0.4. Finally, the transformation to tetragonal PZT was occurred as the PT/(PZ + PT) ratio exceeded to 0.4. Considering the Ti/Zr ratio of 0.8 (which corresponds to the PT/(PZ + PT) ratio of 0.4, the phase of PZT film fabricated in this study should be tetragonal with the expected lattice parameters of a = b = 4.061 Å, c = 4.097 Å, respectively. The calculated tetragonality value (c/a) was 1.009.

It has been known that the orientation of deposited PZT films could be controlled by growth and crystallization conditions such as chemical composition of substrates and crystal lattice matching between PZT phase and substrate. Dormans et al. reported the relationship between the chemical composition of substrate and the preferred orientation of resulting PZT film deposited using MOCVD method [26]. They investigated the deposition of PZT thin films using triethyllead tert-butoxide and titanium and zirconium tetra-butoxides as precursors and observed that ferroelectric PZT films with good crystallinity of preferred (0 0 1) orientation were obtained at 700 °C, when a (1 1 1)-Pt coated oxidized (1 1 0) Si was used as a substrate. Veith's group also reported that (1 0 0)oriented PZT thin films were produced using a classical thermal CVD process [27]. They employed quasi single-source precursor solutions, prepared by mixing two mixed bimetallic species of Pb-Ti and Pb-Zr complexes. After chemical vapor deposition on Pt-Ti-SiO₂-Si substrates and subsequent thermal treatment, transparent PZT thin films exhibiting (1 0 0)-oriented perovskite phase were obtained. In the other hand, Zhou et. al obtained PZT films with different preferred orientation on a TiO₂-Si substrate using sol-gel process [28]. Highly preferred (1 0 1) orientation PZT thin film was produced on the well crystallized TiO₂ insulator layer which was deposited by MOCVD method. Bai et al. fabricated $PbZr_{0.5}Ti_{0.5}O_3$ thin films on (1 0 1) and (1 1 0) $RuO_2/SiO_2/Si$ (0 0 1) substrate respectively by MOCVD, and noticed that preferred orientation of fabricated PZT films were decided from unit cell matching between PZT layer and substrate, even though the chemical compositions of substrates are identical [29]. When a PZT thin film layer was grown on a (1 0 1)-textured RuO₂ bottom electrode layer, PZT phase with predominant (0 0 1) orientation was observed, while a PZT layer deposited on (1 1 0)-textured RuO₂ presented a randomly oriented PZT phase with a mixed (001)-(111)-(110) polycrystalline structure. Based on the above results, it should be reasonable that highly (1 0 1)-oriented directional growth was observed on fabricated PZT thin films on a TiO-Si substrate used in this study.

The surface morphologies of PZT thin films prepared at 550 or 700 °C were characterized by SEM and AFM methods. As can be seen in Fig. 4, the PZT thin film prepared at 550 °C consisted of large numbers of small grains, coinciding with the amorphous feature shown in the XRD pattern. On the other hand, the crystalline



Fig. 4. SEM (bar = 1 μ m) and AFM images of PZT thin films prepared at (a) 550 °C and (b) 700 °C.

size of PZT thin film prepared at 700 °C was found to be 13.1 nm by calculating with Debye-Scherrer equation using a 31.0° (1 0 1) peak in XRD spectrum. In a meanwhile, the RMS roughness value of the same deposited PZT film was obtained from the result of AFM image analysis, as shown in Fig. 4. The estimated average grain size of the deposited PZT film at 700 °C was 22.18 nm. It appears that there might be no apparent relationship between the size of primary particles from XRD analysis and grain sizes obtained from RMS roughness value using AFM analysis. Nishida et. al investigated the PZT film growth using the RF plasmaassisted CVD [30]. They found that the RMS roughness values of PZT film grown at 550 °C increased from 10 nm to 50 nm as the thickness of deposited film increased from 46 nm to 400 nm. From the result of SEM image analysis, the average size of secondary particles, obtained from counting sizes of 20 particles, in deposited PZT film at 700 °C was 195(±46) nm. Veith et. al reported that they observed SEM images of PZT thin films with a smooth surface with grain sizes between 100 nm and 500 nm, after heat treatment at 700 °C [27]. It seems that the agglomeration of several primary particles to the secondary particles occurred in a deposited film.

4. Conclusion

We successfully synthesized a new series of lead (IV) precursors for the fabrication of ferroelectric Pb(Zr,Ti)O₃ thin films by LD-MOCVD. Ph₄Pb is a thermally stable and volatile precursor, but due to the absence of an oxygen source, Ph₄Pb is not fully converted to PbO, inhibiting the fabrication of a PZT film of conformal composition. Therefore, two of its phenyl ligands were substituted with monodentate bis(trimethylsilyl)amide or bidentate 2,2,6,6tetramethyl-3,5-heptadiketonate for the synthesis of Pb(IV) precursors **1** and **2**. These precursors were purified by recrystallization in an anhydrous solvent, and were characterized by FT-IR, ¹H NMR and TGA. In the TGA, precursors 1 and 2 evaporated at 272 °C and 262 °C, respectively, under atmospheric pressure without any thermal decomposition, demonstrating their applicability as precursors for MOCVD. The monomeric structures of precursors 1 and 2 were defined by single-crystal X-ray crystallography. Ph₂Pbthd₂ was chosen as a precursor for the fabrication of PZT thin films, due to its higher volatility and better stability. The perovskite PZT thin films were successfully deposited on a silicon wafer at 700 °C by the LD-MOCVD process. XRD, SEM and AFM methods were used to characterize the crystallinity and surface morphology of the PZT thin films.

5. Contributions of author

First author and corresponding author are mainly contributed and all other authors are contributed partially for preparing this manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was supported by the Converging Research Center Program through the Ministry of Science, ICT and Future Planning, Korea (2013K000156), and by the Technology Innovation Program (10052730, Rutile TiO₂ Powder Manufacturing Technology by TiCl₄ Oxidation) funded by the Ministry of Trade, Industry & Energy (MI, Korea).

Appendix A. Supplementary data

CCDC 1582107 and 1582108 contain the supplementary crystallographic data for precursors 1 and 2. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- D.W. Richerson, Modern Ceramic Engineering Properties, Processing, and Use in Design, second ed., CRC Press, 1992.
- [2] Z. Ou, C. Lu, A. Yang, H. Zhou, Z. Cao, R. Zhu, Sens. Actuators, A 290 (2019) 8, https://doi.org/10.1016/j.sna.2019.03.008.
- [3] Y. Wang, H. Cheng, J. Yan, N. Chen, P. Yang, F. Yang, J. Ouyang, Materialia 5 (2019), https://doi.org/10.1016/j.mtla.2019.100228 100228.
- [4] D.M. Kim, C.B. Eom, V. Nagarajan, J. Ouyang, R. Ramesh, V. Vaithyanathan, D.G. Schlom, Appl. Phys. Lett. 88 (2006), https://doi.org/10.1063/1.2185614 142904.
- [5] L. Jian, A.S. Kumar, C.S.C. Lekha, S. Vivek, I. Salvado, A.L. Kholkin, S.S. Nair, Nano-Struct. Nano-Objects 18 (2019), https://doi.org/10.1016/ j.nanoso.2019.100272 100272.
- [6] C.C. Leu, C.P. Hsu, C.G. Hong, C.T. Hu, J. Mater. Chem. 21 (2011) 12991, https:// doi.org/10.1039/c1jm11464f.
- [7] Y.D. Maio, J.P. Colombier, P. Cazottes, E. Audouard, Opt. Lasers Eng. 50 (2012) 1582, doi: j.optlaseng.2012.05.022.
- [8] J.S. Zhao, D.Y. Park, M.J. Seo, C.S. Hwang, Y.K. Han, C.H. Yang, K.Y. Oh, J. Electrochem. Soc. 151 (2004) C283, https://doi.org/10.1149/1.1676711.
- [9] D.H. Kim, W.Y. Yang, S.W. Rhee, J. Electrochem. Soc. 150 (2003) C516, https:// doi.org/10.1149/1.1584441.
- [10] D. Xie, R. Li, X. Han, Y. Ruan, T.L. Ren, L.T. Liu, Integr. Ferroelectr. 100 (2008) 114, https://doi.org/10.1080/10584580802540538.
- [11] M.V. Baryshnikova, L.A. Filatov, A.S. Petrov, S.E. Alexandrov, Chem. Vap. Dep. 21 (2015) 327, https://doi.org/10.1002/cvde.201507187.

- [12] M.A. Cameron, S.M. George, Thin Solid Films 348 (1999) 90, https://doi.org/ 10.1016/S0040-6090(99)00022-X.
- [13] R.J. Puddephatt, G.H. Thistlethwaite, J. C. S. Dalton Trans. (1972) 570, https:// doi.org/10.1039/DT9720000570.
- [14] U. Tuncel, W.J. Clerici, R.O. Jones, Hear. Res. 166 (2002) 113, https://doi.org/ 10.1016/S0378-5955(02)00303-9.
- [15] H. Gilman, L. Summers, R.W. Leeper, J. Org. Chem. 17 (1952) 630, https://doi. org/10.1021/jo01138a018.
- [16] G. Grüttner, Ber. Dtsch. Chem. Ges. 51 (1918) 1298, https://doi.org/10.1002/ cber.19180510216.
- [17] S.M. George, B.K. Park, C.G. Kim, T.M. Chung, Eur. J. Inorg. Chem. 2014 (2014) 2002, https://doi.org/10.1002/ejic.201301296.
- [18] C. Schneider, M. Drager, J. Organomet. Chem. 415 (1991) 349, https://doi.org/ 10.1016/0022-328X(91)80135-7.
- [19] M.A. Malik, P. O'Brien, M. Motevalli, A.C. Jones, T. Leedham, Polyhedron 18 (1999) 1641, https://doi.org/10.1016/S0277-5387(99)00043-1.
- [20] E.C. Juenge, D. Seyferth, J. Org. Chem. 26 (1961) 563, https://doi.org/10.1021/ jo01061a067.
- [21] S.N. Bhattacharya, A.K. Saxena, J. Indian, Chem. Sect. A: Inorg. Phys. Theor. Anal. 17A (1979) 307.
- [22] A.W. Krebs, M.C. Henry, J. Org. Chem. 28 (1963) 1911, https://doi.org/10.1021/ jo01042a513.
- [23] Y. Sakashita, H. Segawa, K. Tominaga, M. Okada, J. Appl. Phys. 73 (1993) 7857, https://doi.org/10.1063/1.353936.
- [24] C.Y. Pan, Y.L. Chen, D.S. Tsai, Mater. Res. Soc. 17 (2002) 1536, https://doi.org/ 10.1557/JMR.2002.0228.
- [25] S. Okamura, R. Takeuchi, T. Shiosaki, Jpn. J. Appl. Phys. 41 (2002) 6714, https:// doi.org/10.1143/JJAP.41.6714.
- [26] G.J.M. Dormans, M. de Keijser, P.J. van Veldhoven, Chem. Mater. 5 (1993) 448, https://doi.org/10.1021/cm00028a009.
- [27] M. Veith, M. Bender, T. Lehnert, M. Zimmer, A. Jakob, Dalton Trans. 40 (2011) 1175, https://doi.org/10.1039/C0DT00830C.
- [28] C. Zhou, P. Peng, Y. Yang, T. Ren, in: 2011 6th IEEE International Conference on Nano/Micro Engineered and Molecular Systems, 2011, p. 134. doi: 10.1109/ NEMS.2011.6017313.
- [29] G.R. Bai, A. Wang, I.F. Tsu, C.M. Foster, O. Auciello, Integr. Ferroelectr. 21 (1998) 291, https://doi.org/10.1080/10584589808202071.
- [30] K. Nishida, K. Shirakata, M. Osada, T. Katoda, J. Cryst. Growth 272 (2004) 789, https://doi.org/10.1016/j.jcrysgro.2004.08.084.