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Exploiting volatile lead compounds as precursors for the atomic layer deposition of lead dioxide thin films

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Abstract

Lead dioxide thin films were grown by atomic layer deposition on Si(100) substrates. Lead diethyl-dithiocarbamate ($\text{Pb}(\text{dedtc})_2$), lead 2,2,6,6-tetramethyl-3,5-heptadione ($\text{Pb}(\text{thd})_2$) and tetraphenyl-lead (Ph_4Pb) were used as lead precursors, and ozone as oxygen source. The depositions were carried out at 300–350 °C, 150–300 °C and 185–400 °C for $\text{Pb}(\text{dedtc})_2$, $\text{Pb}(\text{thd})_2$ and Ph_4Pb , respectively. Attempts to use $\text{Pb}(\text{dedtc})_2$ as a lead-containing precursor for lead oxide thin films resulted in lead sulphate films, which reacted with the substrate and formed lead silicate during annealing. According to X-ray diffraction, films deposited from $\text{Pb}(\text{thd})_2/\text{O}_3$ or from $\text{Ph}_4\text{Pb}/\text{O}_3$ were crystalline either orthorhombic or tetragonal lead dioxide. Surface morphology of the films were characterized by atomic force microscopy while time-of-flight elastic recoil detection analysis was used to analyse stoichiometry and possible impurities.

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1. Introduction

Lead monoxide is an attractive material for applications because of its low electrical conductivity and interesting semiconducting and photoconducting properties, which have been exploited in laser technology and imaging devices [1]. Other applications are in the field of semiconducting gas-sensors for CO_2 [2], lead-containing high-temperature superconducting films [3,4] and high refractive index materials [5]. Lead monoxide films have also been used as anodic material for lithium secondary batteries [6]. Because lead dioxide is a strong oxidizing agent and it has been used as an oxidant [7]. Recently lead dioxide has also been used as thin film form in pH-sensors [8].

Considerable interest has been focused also on ferroelectric materials where lead oxide is the main component in many materials, e.g. PbTiO_3 , $\text{Pb}(\text{Zr,Ti})\text{O}_3$ and $(\text{Pb,Lu})(\text{Zr,Ti})\text{O}_3$. These materials have been frequently investigated due to their electromechanical, dielectric, piezoelectric and pyroelectric

properties [9,10]. Possible applications include, for example, ferroelectric random access memories and electro-optic devices [11,12].

Lead oxide exists in many different forms because lead can adopt either the +2 or +4 oxidation state. Furthermore, the oxides have also many different crystal forms [7] and it is difficult to deposit only a single oxide phase with certain crystal form. Earlier studies have shown that attempts to deposit lead oxide thin films using the metal organic chemical vapour deposition (MOCVD) techniques lead to different lead oxide phases [13–15]. For example, when an excess of oxygen was used in MOCVD, Madsen and Weaver [13] observed a significant amount of PbO_2 . Film deposition temperature was 515 °C and films were deposited on Si from tetraethyl-lead and oxygen. Tokita and Okada [14] used laser-induced MOCVD to grow lead oxide on Si(100). When $(\text{C}_2\text{H}_5)_3\text{PbOCH}_2\text{C}(\text{CH}_3)_3$ was irradiated by 193 nm laser, the film consisted mainly of lead oxide and the dioxide was also observed by X-ray diffraction. Oxygen was used as oxidizing gas. Zhao et al. [15] used 2,2,6,6-tetramethyl-3,5-heptadione lead ($\text{Pb}(\text{thd})_2$) and oxygen to deposit lead oxide on Pt and Ir substrates. On Pt substrates, PbO_2 together with PbO were observed when the deposition temperature was 475 °C. When the temperature was raised to

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500 °C, PbO₂ and Pb₃O₄ were present. On Ir substrate, no PbO₂ was observed but both Pb₃O₄ and metallic Pb were observed by X-ray diffraction.

Lead oxide thin films have been deposited by both physical and chemical deposition methods. Physical vapour deposition methods reported in the literature include pulsed laser-assisted deposition [2,16], spray pyrolysis [5,6], dc and rf magnetron sputtering [17,18], electrodeposition [19] and evaporation [20,21]. Various chemical vapour deposition (CVD) methods have been previously used, including low-pressure chemical vapour deposition (LPCVD) [22–24], metal organic chemical vapour deposition (MOCVD) [13,25], plasma-enhanced chemical vapour deposition (PECVD) [26] and laser-induced CVD [14,27]. Deposition temperature in the LPCVD processes has been in the range of 400–700 °C. MOCVD processes can be operated as low as at 300 °C, while with PECVD, it is possible to process the oxide at 250 °C and with laser-assisted CVD even at 150 °C.

In CVD methods the two most commonly used volatile lead precursors are Pb(thd)₂ [3,15,22,28,29] and tetraethyl-lead [13,26,30]. More recently, the use of tetraethyl-lead has been diminished because of its established toxicity and the use of Pb(thd)₂ has been increased. In addition, other non-fluorinated as well as fluorinated β-diketonate-type precursors have been examined [4,24,31]. Other volatile lead precursors such as PbCl₂ [23] and some alkoxides [14,25] have also been studied.

In the present study, we have deposited lead oxide thin films with atomic layer deposition (ALD) [32,33], also known as atomic layer epitaxy. ALD is a surface-controlled growth method, which relies on alternate pulsing of the gaseous precursors onto the substrate surface. The precursor pulses are separated by inert gas pulses to eliminate gas phase reactions and to remove volatile reaction products. In an ideal case, one monolayer of the first reactant or a distinct fraction thereof is chemisorbed on to the substrate and this layer then reacts with the second precursor pulsed onto the substrate, resulting in the formation of a solid film. This makes the thin film growth process self-limiting and easy to control. The film thickness can be accurately controlled by repeating the reaction cycle until the desired thickness has been achieved. Previously, ALD has been used for the deposition of a variety of thin oxide films [34]. Also some lead-containing thin films, namely PbS [35,36], have been deposited by ALD using PbCl₂, PbBr₂ [37], Pb(thd)₂, lead diethyl-dithiocarbamate (Pb(dedtc)₂) and lead *tert*-butoxide [36] as precursors together with H₂S.

In this study, we have examined the use of tetraphenyl-lead (Ph₄Pb) as a novel volatile organo-lead precursor for ALD. Previously Ph₄Pb has been observed to be more thermally stable than the alkyl-lead derivatives [38]. Deposition parameters such as lead-precursor and ozone pulse durations, substrate and source temperatures were examined in detail. Crystal structure, crystallite orientation, impurities, surface morphologies and stoichiometry of lead oxide thin films were also studied. For comparison, we present also the results obtained by the Pb(thd)₂/O₃ as well as Pb(dedtc)₂/O₃ ALD processes.

2. Experimental details

Pb(dedtc)₂, Pb(thd)₂ and commercial Ph₄Pb (Aldrich Chemical Co., 97%) were used as lead precursors. Pb(dedtc)₂ was synthesized according to Honjo et al. [39] while Pb(thd)₂ was synthesized according to Eisentraut and Sievers [40] and was purified by sublimation. Simultaneous thermo gravimetry/differential thermal analysis (TG/DTA) measurements were used to examine the volatility and thermal stability of the precursors. The measurements were done under reduced pressure in a Seiko Instruments SSC/5200 thermobalance. In order to simulate the ALD deposition conditions, 300–400 Pa pressure and nitrogen (>99.999%) carrier gas were used.

Lead oxide thin films were deposited with ALD in a commercial flow-type F-120 reactor manufactured by ASM Microchemistry Ltd. Film depositions were carried out at 200–300 Pa pressure onto Si(100) substrates (5 × 10 cm²). Ozone was used as oxidizer and it was generated from oxygen (>99.999%) in an ozone generator (Fischer model 502). Nitrogen (>99.999%) was prepared in a nitrogen generator (Nitrox UHPN 3000-1) for use as carrier and purging gas.

Evaporation temperatures for Pb(dedtc)₂, Pb(thd)₂ and Ph₄Pb were 190 °C, 110–115 °C and 165–170 °C, respectively. The effect of deposition temperature on the growth rate was studied in the temperature range of 150–300 °C and 185–400 °C for Pb(thd)₂ and Ph₄Pb, respectively. The lower limit deposition temperatures were chosen based on the evaporation temperatures. Pb(dedtc)₂ deposition was tested in the temperature range of 300–350 °C. Precursor pulsing as well as nitrogen purging times were also studied in order to optimise the conditions for the deposition process. Precursor pulsing times applied were 1.0–3.0 s for both Pb(thd)₂ and Ph₄Pb. Ozone pulses varied between 1.0 and 3.0 s and the nitrogen purging pulses between 1.0 and 2.5 s.

Thicknesses of the deposited lead oxide films were measured by profilometry (Surface Profile Measuring System Dektak from Veeco Instruments) in the case of Pb(thd)₂ and Ph₄Pb, while thickness of the films deposited from Pb(dedtc)₂ were analysed in a Hitachi U-2000 dual-beam spectrophotometer. In the spectrometric method, reflectance spectra were measured and the film thickness was determined by the fitting of the optical spectra as described by Ylilammi and Ranta-Aho [41]. Crystal structure and crystallite orientation of the deposited films were determined by Philips X-ray diffraction (XRD) MPD 1880 using Cu Kα radiation. Atomic force microscopy (AFM) measurements were carried out to determine the surface morphology of the films. All AFM images were recorded with a Nanoscope III atomic force microscope (Digital instruments) operating in tapping mode with a scanning frequency of 1 Hz. Roughness was calculated as root-mean-square (rms) values.

Some selected samples deposited by the Pb(dedtc)₂/O₃ process were annealed in a rapid thermal annealing furnace PEO 601 (ATV Technologie GmbH, Germany). The annealing was performed in a nitrogen atmosphere for 10 minutes at 600, 700, 800 and 1000 °C. The crystal structure and crystallite

orientation of the as-deposited and annealed films were determined by X-ray diffraction as described above.

Stoichiometry and possible impurities were measured by time-of-flight elastic recoil detection analysis (TOF–ERDA) at the Accelerator Laboratory of the University of Helsinki. In this method [42,43], heavy ions are projected into the sample and the signal consists of forward recoiling sample atoms ejected by the ion beam. Both velocity and energy for recoiled atoms are determined using timing gates and a charged particle detector, which makes it possible to separate different masses. For these TOF–ERD measurements, a 53 MeV $^{127}\text{I}^{10+}$ ion beam was used, obtained from a 5 MV tandem accelerator EGP-10-II. Samples were measured at 20° tilt and the recoils were detected at 20° with respect to the incoming beam. Error limit for detected lead and oxygen atoms was 3 at.%.

3. Results and discussion

Precursors were analysed by simultaneous TG/DTA measurements under reduced pressure, and the result of thermal analysis indicated almost complete volatility for all three precursors. Ph_4Pb sublimed in a single step while $\text{Pb}(\text{thd})_2$ sublimed in two steps (Fig. 1). The TG curve onset values for volatilisation were 200–205 °C for Ph_4Pb and 150–155 °C and 230–235 °C for $\text{Pb}(\text{thd})_2$. Previously it has been reported that commercial $\text{Pb}(\text{thd})_2$ sublimes in a single step [29]. However, Nykänen et al. [36] observed the sublimation of $\text{Pb}(\text{thd})_2$ to occur in two steps. The volatility of $\text{Pb}(\text{dedtc})_2$ has been previously studied in connection with the ALD deposition of PbS thin films [36].

First $\text{Pb}(\text{dedtc})_2$ and ozone were used as a precursors for deposition. However, the as-deposited films were orthorhombic lead sulphate according to XRD. Growth rates observed were in the range of 0.8–1.1 Å/cycle depending on the deposition temperature. The lead sulphate films deposited on silicon substrates at 300 and 350 °C were annealed at different temperatures in a nitrogen atmosphere in an attempt to thermally decompose them to lead oxide films. However, no differences to as-deposited films were observed at annealing temperatures of 600 °C, whereas the XRD peak intensities of orthorhombic lead sulphate decreased at 700 °C. According to

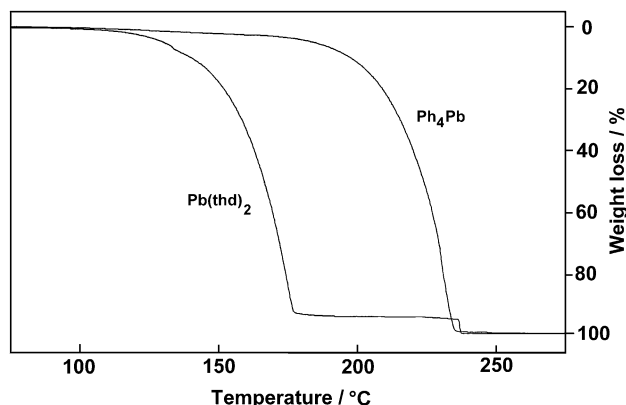


Fig. 1. TG curves for the lead precursors used. Heating rate was 10 °C/min and sample mass ~ 10 mg. Measuring pressure was 300–400 Pa.

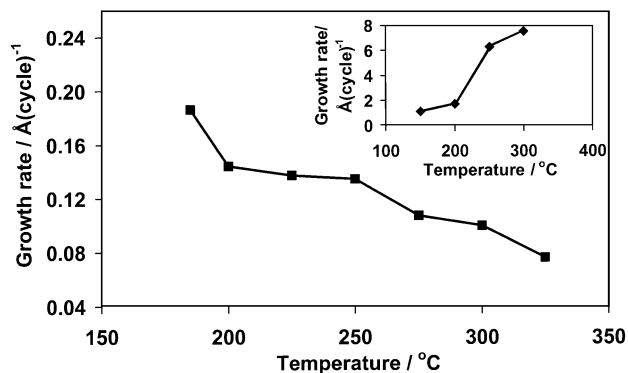


Fig. 2. Growth rate of the PbO_2 thin films from $\text{Ph}_4\text{Pb}/\text{O}_3$ as a function of the deposition temperature. The pulsing time for Ph_4Pb was 1.5 s and for ozone 2.0 s. Inset shows the growth rate of PbO_2 by the $\text{Pb}(\text{thd})_2/\text{O}_3$ process. The pulsing time for $\text{Pb}(\text{thd})_2$ was 1 s and for ozone 1.5 s.

thermo-analytical data lead sulphate remains undecomposed when heated in air up to 960 °C [44]. However, monoclinic PbSiO_3 peaks were observed at annealing temperatures of 800 and 1000 °C indicating that silicon substrate was reacting with the thin film producing silicates.

Pulsing times of the $\text{Pb}(\text{thd})_2$ and Ph_4Pb reactants were optimised in order to verify the self-limiting ALD growth. Growth rate was examined at 2 cm from the leading edge. $\text{Pb}(\text{thd})_2$ pulse times were examined at 150 °C, where the ozone pulse was kept constant at 2.0 s and the $\text{Pb}(\text{thd})_2$ pulse time was varied between 0.6 and 2.0 s. The shortest pulsing time of 0.6 s was clearly insufficient to deposit uniform thin films. However, the films were smooth at the 1.0 s pulsing time and no difference with longer pulsing times were observed.

The effect of the Ph_4Pb pulsing times was examined at 250 °C and 300 °C. Ozone pulse time was kept constant at 2.0 s while the Ph_4Pb pulsing time was varied between 1.0 and 3.0 s. Purge time after the ozone pulse was 2.0 s and after Ph_4Pb pulses 1.0–2.0 s, depending on the Ph_4Pb pulsing time. Growth rate at 300 °C was found to be almost independent of the precursor pulsing time and only small increase in the growth rate from 0.13 to 0.16 Å/cycle was observed at 250 °C.

The growth rates for PbO_2 were determined for $\text{Pb}(\text{thd})_2$ and Ph_4Pb precursors as a function of the substrate temperature. The lowest temperature studied was chosen according to evaporation temperature. The upper limit was tested and for

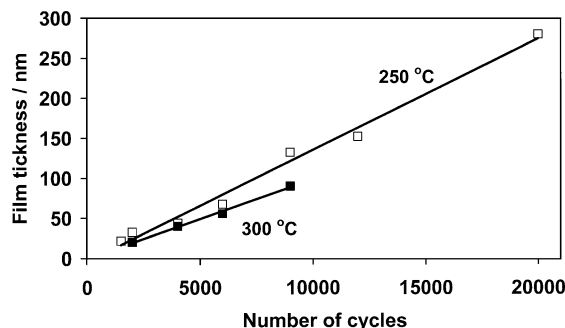


Fig. 3. PbO_2 film thickness as a function of the number of deposition cycles at two different deposition temperatures. Ph_4Pb and O_3 were used as a precursors.

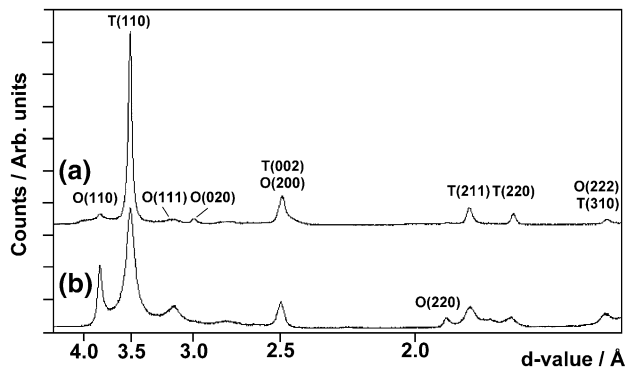


Fig. 4. XRD patterns of PbO_2 films deposited from $\text{Ph}_4\text{Pb}/\text{O}_3$ (a) and $\text{Pb}(\text{thd})_2/\text{O}_3$ (b) at 250 °C and 150 °C, respectively. The thickness was for (a) 70 nm and for (b) 170 nm. Diffraction peaks were identified according to JCPDS [48]. (T=tetragonal, O=orthorhombic).

$\text{Pb}(\text{thd})_2$ the limit was determined by decomposition of the precursor while the upper limit for Ph_4Pb was caused by low deposition rate. To obtain sufficient surface saturation precursor pulse times for $\text{Pb}(\text{thd})_2$ and Ph_4Pb were 1 and 1.5 s, respectively. In the case of $\text{Pb}(\text{thd})_2$, the growth rate increased with the increasing deposition temperature (Fig. 2, inset). Typically, in a β -diketonate ALD process, the growth rate increases when the deposition takes place above the constant growth rate region [45]. A steep thickness profile in the deposited films was observed above 200 °C, indicating thermal decomposition of the $\text{Pb}(\text{thd})_2$ precursor. Growth rate for the $\text{Pb}(\text{thd})_2/\text{O}_3$ process under 200 °C was 1.0–1.5 Å/cycle, but it increased up to 7.6 Å/cycle when the deposition temperature reached 300 °C.

In the case of Ph_4Pb , the growth rate decreased from 0.19 to 0.08 Å/cycle with increasing deposition temperature from 185 to 325 °C (Fig. 2). This phenomenon has previously been observed also with other oxides deposited from organometallic precursors [45]. When organometallic compounds with high reactivity are used, the growth rate mainly depends on the number of –OH groups on the surface, i.e. the adsorption sites available [46]. Higher temperature means less –OH groups and thus less available adsorption sites. In the $\text{Ph}_4\text{Pb}/\text{O}_3$ process, the films were uniform within the entire temperature range. A

Table 1

Results from the TOD–ERD analyses of stoichiometry and impurity levels in the PbO_2 thin films deposited by the $\text{Ph}_4\text{Pb}/\text{O}_3$ and $\text{Pb}(\text{thd})_2/\text{O}_3$ processes onto Si(100) substrates

Process	Deposition temperature (°C)	Pb/O ratio	Carbon (at.%)	Hydrogen (at.%)
$\text{Pb}(\text{thd})_2/\text{O}_3$	150	0.71	1.1 ± 0.5	0.2
$\text{Ph}_4\text{Pb}/\text{O}_3$	250	0.67	0.5 ± 0.2	<0.1

constant growth rate 0.13 Å/cycle was obtained at 200–250 °C. Typically, a low ALD growth rate may be attributed to steric hindrances due to large ligand size of the precursor [47].

For the $\text{Ph}_4\text{Pb}/\text{O}_3$ process, dependence of the film thickness on the number of reaction cycles was measured at 250 and 300 °C. As seen in Fig. 3, a quite linear relationship is observed at both temperatures, enabling a facile process control. Constant growth rate at 250 °C was 0.13 Å/cycle and at 300 °C slightly less on 0.10 Å/cycle.

The crystallinity and orientation of the crystallites were measured by XRD. Thin films deposited by the $\text{Pb}(\text{thd})_2/\text{O}_3$ process were crystalline regardless of the deposition temperature. Below 200 °C the films were polycrystalline containing either orthorhombic (O) or tetragonal (T) lead dioxide (PbO_2). The most intense reflection at 150 °C was tetragonal (110) (Fig. 4). At 200 °C the most intense reflection was orthorhombic (111) and at deposition temperatures above 200 °C the films contained also lead oxides with nonstoichiometric oxygen content between PbO and PbO_2 . According to the literature lead dioxide normally occurs as tetragonal form but also a high-pressure orthorhombic polymorph is known [7]. Lead oxide thin films with lead at the oxidation state +2 have been obtained earlier by CVD from $\text{Pb}(\text{thd})_2$ and oxygen at the deposition temperature of 420 °C [22].

Lead oxide films deposited by the $\text{Ph}_4\text{Pb}/\text{O}_3$ process were polycrystalline containing both orthorhombic and tetragonal lead dioxide phases (Fig. 4). Thus, according to XRD in ALD depositions, only the PbO_2 phase was observed, which is probably due to the strong oxidizer used, i.e. ozone. The most intense reflection was T(110) if films were deposited below 300 °C, whereas the most intense reflection at higher temperatures was O(111). Film thickness was also observed

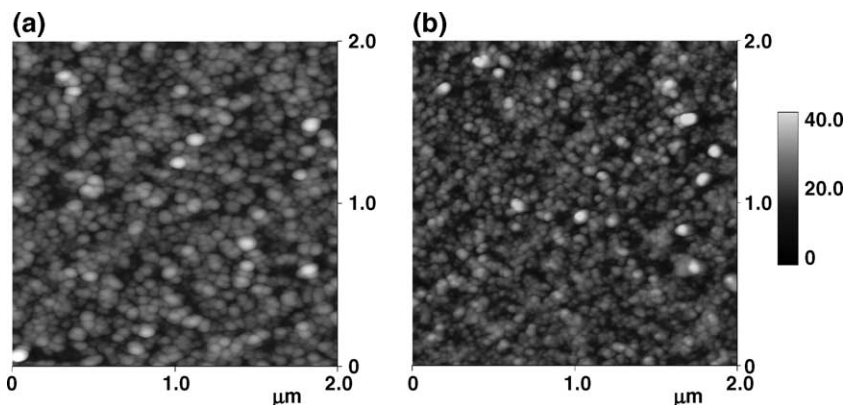


Fig. 5. AFM images of the PbO_2 thin film surfaces deposited from $\text{Ph}_4\text{Pb}/\text{O}_3$ at 250 °C (a) and 300 °C (b). The thicknesses of the measured samples were 130 nm (a) and 90 nm (b). Image size = 2 × 2 μm^2 . Depth scale = 40 nm from black to white.

to affect the crystalline orientations in the $\text{Ph}_4\text{Pb}/\text{O}_3$ process. When film thickness was below 40 nm, both T(110) and O(111) peaks had almost the same intensities.

AFM measurements were carried out in order to analyse the surface morphology of the PbO_2 thin films deposited by the $\text{Ph}_4\text{Pb}/\text{O}_3$ process at 250 and 300 °C. The rms-value slightly decreased when the deposition temperature was decreased from 250 °C to 300 °C as seen in Fig. 5. Rms-value for the 130 nm thick film deposited at 250 °C was 3.9 nm while for the 90 nm thick film deposited at 300 °C the rms-value was slightly higher on 4.6 nm, but considering the lower thickness of the film, the increase is significant.

Stoichiometry and impurity levels of the deposited films were examined by TOF–ERDA for films deposited onto Si(100) substrates. The lead to oxygen ratio was near 0.7 in both cases studied (Table 1). Although XRD results indicated that the films contained only PbO_2 , there could also be other phases present containing less oxygen or amorphous material judging from the TOF–ERDA results (Table 1). Carbon and hydrogen impurity levels were generally quite low. Carbon impurities in the films grown by the $\text{Ph}_4\text{Pb}/\text{O}_3$ process at 250 °C were 0.5 at.% and hydrogen impurities under 0.1 at.%. Impurity levels in the $\text{Pb}(\text{thd})_2/\text{O}_3$ process when deposited at 150 °C were somewhat higher being 1.1 at.% for carbon and 0.2 at.% for hydrogen.

4. Conclusions

In this study, we have demonstrated for the first time the PbO_2 thin film growth by ALD on Si(100) using Ph_4Pb and $\text{Pb}(\text{thd})_2$ precursors together with ozone. Attempts to use $\text{Pb}(\text{dedtc})_2$ as a lead-containing precursor resulted in lead sulphate films, however. A constant growth rate of 0.13 Å/cycle for the $\text{Ph}_4\text{Pb}/\text{O}_3$ process was obtained between 200 and 250 °C. Deposition rate for the $\text{Pb}(\text{thd})_2/\text{O}_3$ process at 200 °C and under was 1.0–1.5 Å/cycle. According to XRD, both $\text{Ph}_4\text{Pb}/\text{O}_3$ and $\text{Pb}(\text{thd})_2/\text{O}_3$ processes yielded crystalline films at all deposition temperatures explored. Because of the use of a strong oxidizer, ozone, the obtained films crystallized predominantly as lead dioxide (PbO_2) phase. According to XRD, the most intense reflection was either tetragonal (111) or orthorhombic (111) PbO_2 depending on the deposition temperature. TOF–ERD analysis indicated that lead to oxygen ratio was for both precursors near 0.7, which is an indication that the films contain also other phases than PbO_2 or amorphous material. Films were smooth and $\text{Ph}_4\text{Pb}/\text{O}_3$ and $\text{Pb}(\text{thd})_2/\text{O}_3$ process contained only 0.5 and 1.1 at.% of C, respectively. Hydrogen impurities were also low being under 0.1 at.% and 0.2 at.% for the $\text{Ph}_4\text{Pb}/\text{O}_3$ and $\text{Pb}(\text{thd})_2/\text{O}_3$ processes, respectively.

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