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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 (Pb(dedtc)₂), lead 2,2,6,6-tetramethyl-3,5-heptadione (Pb(thd)₂) and tetraphenyl-lead (Ph₄Pb) 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 Pb(dedtc)₂, Pb(thd)₂ and Ph₄Pb, respectively. Attempts to use Pb(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 Pb(thd)₂/O₃ or from Ph₄Pb/O₃ 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 CO₂ [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. PbTiO₃, Pb(Zr,Ti)O₃ and (Pb,La)(Zr,Ti)O₃. 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 PbO₂. 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 (C₂H₅)₃PbOCH₂C(CH₃)₃ was irritated 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 (Pb(thd)₂) and oxygen to deposit lead oxide on Pt and Ir substrates. On Pt substrates, PbO₂ together with PbO were observed when the deposition temperature was 475 °C. When the temperature was raised to
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 pulse 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 Ykilammi 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 $^{127}$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$_4$Pb sublimed in a single step while Pb(thd)$_2$ sublimed in two steps (Fig. 1). The TG curve onset values for volatilisation were 200–205 °C for Ph$_4$Pb and 150–155 °C and 230–235 °C for Pb(thd)$_2$. Previously it has been reported that commercial Pb(thd)$_2$ sublimes in a single step [29]. However, Nykänen et al. [36] observed the sublimation of Pb(thd)$_2$ to occur in two steps. The volatility of Pb(dedtc)$_2$ has been previously studied in connection with the ALD deposition of PbS thin films [36].

First Pb(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 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 Pb(thd)$_2$ and Ph$_4$Pb reactants were optimised in order to verify the self-limiting ALD growth. Growth rate was examined at 2 cm from the leading edge. Pb(thd)$_2$ pulse times were examined at 150 °C, where the ozone pulse was kept constant at 2.0 s and the Pb(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$_4$Pb pulsing times was examined at 250 °C and 300 °C. Ozone pulse time was kept constant at 2.0 s while the Ph$_4$Pb pulsing time was varied between 1.0 and 3.0 s. Purge time after the ozone pulse was 2.0 s and after Ph$_4$Pb pulses 1.0–2.0 s, depending on the Ph$_4$Pb 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 Pb(thd)$_2$ and Ph$_4$Pb 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
Pb(thd)$_2$ the limit was determined by decomposition of the precursor while the upper limit for Ph$_4$Pb was caused by low deposition rate. To obtain sufficient surface saturation precursor pulse times for Pb(thd)$_2$ and Ph$_4$Pb were 1 and 1.5 s, respectively. In the case of Pb(thd)$_2$, the growth rate increased with the increasing deposition temperature (Fig. 2, inset). Typically, in a $\beta$-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 $^\circ$C, indicating thermal decomposition of the Pb(thd)$_2$ precursor. Growth rate for the Pb(thd)$_2$/O$_3$ process under 200 $^\circ$C was 1.0–1.5 Å/cycle, but it increased up to 7.6 Å/cycle when the deposition temperature reached 300 $^\circ$C.

In the case of Ph$_4$Pb, the growth rate decreased from 0.19 to 0.08 Å/cycle with increasing deposition temperature from 185 to 325 $^\circ$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 Ph$_4$Pb/O$_3$ process, the films were uniform within the entire temperature range. A constant growth rate 0.13 Å/cycle was obtained at 200–250 $^\circ$C. Typically, a low ALD growth rate may be attributed to steric hindrances due to large ligand size of the precursor [47].

The crystallinity and orientation of the crystallites were measured by XRD. Thin films deposited by the Pb(thd)$_2$/O$_3$ process were crystalline regardless of the deposition temperature. Below 200 $^\circ$C the films were polycrystalline containing either orthorhombic (O) or tetragonal (T) lead dioxide (PbO$_2$). The most intense reflection was observed at 150–200 $^\circ$C was tetragonal (110) (Fig. 4). At 200 $^\circ$C the most intense reflection was orthorhombic (111) and at deposition temperatures above 200 $^\circ$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 Pb(thd)$_2$ and oxygen at the deposition temperature of 420 $^\circ$C [22].

In the case of Ph$_4$Pb/O$_3$, the crystallinity and orientation 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 $^\circ$C, whereas the most intense reflection at higher temperatures was O(111). Film thickness was also observed

<table>
<thead>
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<th>Process</th>
<th>Deposition temperature ($^\circ$C)</th>
<th>Pb/O ratio</th>
<th>Carbon (at.%)</th>
<th>Hydrogen (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(thd)$_2$/O$_3$</td>
<td>150</td>
<td>0.71</td>
<td>1.1±0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Ph$_4$Pb/O$_3$</td>
<td>250</td>
<td>0.67</td>
<td>0.5±0.2</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

Table 1

Results from the TOD–ERD analyses of stoichiometry and impurity levels in the PbO$_2$ thin films deposited by the Ph$_4$Pb/O$_3$ and Pb(thd)$_2$/O$_3$ processes onto Si(100) substrates.
to affect the crystalline orientations in the Ph₄Pb/O₃ process. When film thickness was below 40 nm, both T(111) and O(111) peaks had almost the same intensities.

AFM measurements were carried out in order to analyse the surface morphology of the PbO₂ thin films deposited by the Ph₄Pb/PbO₂ process at 250 and 300 °C. The rms-value slightly decreased as 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 the film, the increase is significant.

Conclusions

In this study, we have demonstrated for the first time the Ph₄Pb/PbO₂ thin film growth by ALD on Si(100) using Ph₄Pb and Pb(thd)₂ precursors together with ozone. Attempts to use Pb(dedtc)₂ as a lead-containing precursor resulted in lead sulphate films, however. A constant growth rate of 0.13 Å/cycle for the Ph₄Pb/PbO₂ process was obtained between 200 and 250 °C. Deposition rate for the Pb(thd)₂/O₃ process at 200 °C was 0.5 at.% and hydrogen impurities under 0.1 at.%. Impurity levels in the Pb(thd)₂/O₃ process when deposited at 150 °C were somewhat higher being 1.1 at.% for carbon and 0.2 at.% for hydrogen.

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