

Triethyllead *tert*-Butoxide, a New Precursor for Organometallic Chemical Vapor Deposition of Lead Zirconate Titanate Thin Films

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The deposition of lead zirconate titanate ($PbZr_xTi_{1-x}O_3$) thin films by organometallic chemical vapor deposition (OMCVD) is reported using the new precursor triethyllead *tert*-butoxide (TELBUT) together with titanium *tert*-butoxide (TTB) and zirconium *tert*-butoxide (ZTB). TELBUT and the analogous compound triethyllead isopropoxide were synthesized and were found to be thermally stable at room temperature but decomposed when exposed to daylight; for TELBUT the photolysis products are different for the pure compound and solutions in toluene- d_8 . TELBUT started to decompose exothermically around 138 °C in a differential scanning calorimeter, giving metallic lead. OMCVD experiments showed that, in the absence of additional oxygen, TELBUT gave metallic lead. Lead titanate ($PbTiO_3$) could be formed at temperatures between 550 and 700 °C in the presence of oxygen and titanium tetraisopropoxide. Without oxygen, only lead and titanium dioxide were formed. $PbZr_xTi_{1-x}O_3$ thin films were deposited using TTB, ZTB, and TELBUT in the presence of oxygen at 700 °C. Ferroelectric films with good crystallinity and high values for the polarization were obtained with this new precursor system.

Introduction

The perovskite $PbZr_xTi_{1-x}O_3$ has found wide and increasing use because of its dielectric, ferroelectric, electrooptic, piezoelectric, and pyroelectric properties. With recent advances in the technology of thin films, these properties have been used for the fabrication of surface acoustic wave devices, thermal and ultrasonic thermal-image sensors, electrooptic switches and modulators, and nonvolatile memories (for a recent overview see ref 1).

The films have been deposited by most of the techniques currently available, including various forms of evaporation, sputtering, laser ablation, spin-coating, and chemical vapor deposition (CVD).² CVD is regarded as one of the most promising techniques because it is IC-compatible and combines the advantages of a high throughput with uniform growth and good step coverage over large areas. For the growth of oxidic thin films it has the additional advantage that high oxygen pressures can be employed during deposition. One of the problems in CVD is the search for suitable precursors that have convenient vapor pressures at moderate temperatures, decompose at modest temperatures but are stable on storage. Organometallic compounds have been frequently found to satisfy most of these demands. Also, the physical and chemical properties of such precursors can be changed by tailoring the organic ligands.

Organometallic CVD (OMCVD) of the lead-based perovskites $PbTiO_3$,³⁻¹¹ $PbZr_xTi_{1-x}O_3$,¹²⁻¹⁷ (Pb, La) TiO_3 ,¹⁸

and $PbSc_xTa_{1-x}O_3$ ⁸ has been reported using various precursor systems. The most frequently used precursors for the growth of $PbZr_xTi_{1-x}O_3$ are tetraethyllead ($Pb(C_2H_5)_4$, TEL), titanium tetraisopropoxide ($Ti(O^iC_3H_7)_4$, TIP), and zirconium *tert*-butoxide ($Zr(O^iC_4H_9)_4$, ZTB), which all have relatively high vapor pressures. Alternative precursors include other alkoxides, alkyls, and substituted β -diketonates.

The complex chemistry in OMCVD involves reactions of precursors and interactions with reaction products, both at the growing surface and in the gas phase. The growth of PZT from TEL, TIP, and ZTB can be qualitatively

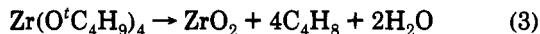
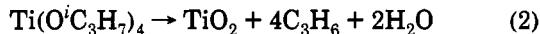
- (4) Kwak, B. S.; Boyd, E. P.; Erbil, A. *Appl. Phys. Lett.* 1988, 53, 1702.
- (5) Yoon, S.-G.; Kim, H.-G. *J. Electrochem. Soc.* 1988, 135, 3137.
- (6) Okada, M.; Watanabe, H.; Murakami, M.; Tomita, K. *J. Ceram. Soc. Jpn. Int. Ed.* 1988, 96, 676.
- (7) Okada, M.; Takai, S.; Amemiya, M.; Tominaga, K. *Jpn. J. Appl. Phys.* 1989, 28, 1030.
- (8) Bierley, C. J.; Trundle, C.; Considine, L.; Whatmore, R. M.; Ainger, F. W. *Ferroelectrics* 1989, 91, 181.
- (9) Swartz, S. L.; Seifert, D. A.; Noel, G. T.; Shrout, T. R. *Ferroelectrics* 1989, 93, 37.
- (10) De Keijser, M.; Dormans, G. J. M.; Cillessen, J. F. M.; De Leeuw, D. M.; Zandbergen, H. W. *Appl. Phys. Lett.* 1991, 58, 2636.
- (11) Dormans, G. J. M.; De Keijser, M.; Larsen, P. K. *Integr. Ferroelectrics* 1992, 2, 297.
- (12) Okada, M.; Tominaga, K.; Araki, T.; Katayama, S.; Sakashita, Y. *Jpn. J. Appl. Phys.* 1990, 29, 718.
- (13) Sakashita, Y.; Ono, T.; Segawa, H.; Tominaga, K.; Okada, M. *J. Appl. Phys.* 1991, 69, 8352.
- (14) Funakubo, H.; Imashita, K.; Kieda, N.; Mizutani, N. *J. Ceram. Soc. Jpn.* 1991, 99, 248.
- (15) Kashihara, K.; Itoh, H.; Tsukamoto, K.; Akasaka, Y. *Extended Abstr. 1991 Int. Conf. Solid State Dev. Mater. Yokohama* 1991, 192.
- (16) Petuskey, W. T.; Richardson, D. A.; Dey, S. K. *Proc. 3rd Int. Symp. Integrated Ferroelectrics, Colorado Springs* 1991, 571.
- (17) Dormans, G. J. M.; De Keijser, M.; Van Veldhoven, P. J. *Mater. Res. Soc. Proc.* 1992, 243, 203.
- (18) Tominaga, K.; Miyajima, M.; Sakashita, Y.; Segawa, H.; Okada, M. *Jpn. J. Appl. Phys.* 1990, 29, L1874.

(1) Swartz, S. L.; Wood, V. E. *Condens. Matter News* 1992, 1, 4.

(2) Roy, R. A.; Etzold, K. F.; Cuomo, J. J. *Mater. Res. Soc. Symp. Proc.* 1990, 200, 141.

(3) Kojima, M.; Okuyama, M.; Nakagawa, T.; Hamakawa, Y. *Jpn. J. Appl. Phys.* 1983, 22 (Suppl. 22-2), 14.

described by the overall reactions⁶



These reactions show that TEL is oxidized by oxygen to form lead oxide, whereas the alkoxides of titanium and zirconium decompose to form their oxides even in the absence of oxygen. In all reactions volatile byproducts are formed, some of which, like water, can interact with the undecomposed precursors. Of course, these reactions give only a simplified picture. For example, it has been reported¹⁹ that the decomposition of TEL in the presence of oxygen initially gives ethyl radicals which oxidize subsequently. Salooja²⁰ reported the formation of CO and CO₂ as the main reaction products for the oxidation of TEL by oxygen in a flow system. Furthermore, we have observed that, when using ZTB and TIP, a rapid transalcoholysis of the ligands occurs which results in the formation of titanium butoxide and zirconium propoxide species. The former type is likely to possess a vapor pressure comparable with that of ZTB and TIP. However, zirconium propoxides are known to have very low vapor pressures and to oligomerize easily forming a solid deposit in the vapor transport lines of the OMCVD system. Therefore, this transalcoholysis not only demands separate transport lines to feed TIP and ZTB to the reactor cell but also might give undesirable homogeneous gas-phase reactions, complicating the deposition process. For this reason, it is beneficial to use precursors with identical alkoxide groups. The *tert*-butoxides were chosen here because of their relatively high vapor pressures.

A complication of the deposition chemistry is the well-known sensitivity of these alkoxides to water. Even minute traces of water can be sufficient to initiate the autocatalytic decomposition of the alkoxides.²¹ Hence, the reaction product water itself could give rise to undesirable homogeneous gas-phase reactions. The formation of water will be further enhanced by the oxidation of the hydrocarbon byproducts. This latter contribution might be suppressed by avoiding the use of additional oxygen. However, for the deposition of lead oxide using TEL as the lead precursor, Okada et al.⁷ showed that an excess of oxygen is needed, even if the deposition takes place in the presence of oxygen-containing alkoxide precursors.

To suppress the extra generation of water, it would be desirable to use a lead precursor that forms lead oxide directly by thermolysis rather than by oxidation. Possible candidates include those containing direct Pb-O bonds, such as alkoxides and β -diketonates. Because of the aforementioned problem of ligand exchange between the precursors, it is preferable to use a lead alkoxide with ligands identical to those of the titanium and zirconium precursors, e.g., lead di-*tert*-butoxide, Pb(O'C₄H₉)₂. This compound has already been used for the OMCVD of lead-based ferroelectric thin films.⁸ However, it is a solid with a low vapor pressure and, therefore, has to be evaporated at temperatures of about 120 °C. Also, it readily decom-

poses to the somewhat less volatile Pb₄O(O'C₄H₉)₆ around the sublimation temperature.²² On the other hand, the *tert*-butoxides of zirconium and titanium are liquids which can be used at evaporation temperatures at, or just above, room temperature. Therefore, it would be desirable to have a lead precursor containing at least one alkoxide ligand and a vapor pressure that allows evaporation at convenient temperatures.

For this purpose, the precursors Pb(C₂H₅)₃(OR), with R = 'C₃H₇ or 'C₄H₉, were synthesized. The latter precursor was used in combination with TIP to deposit PbTiO₃. In combination with TTB and ZTB it was used to deposit PbZr_xTi_{1-x}O₃ thin films: a precursor system in which all alkoxide ligands are identical so that transalcoholysis will not lead to unwanted predeposition.

Experimental Section

The compounds Pb(C₂H₅)₃(OR) with R = 'C₃H₇ or 'C₄H₉ were synthesized via Pb(C₂H₅)₃Cl, either by direct reaction with the appropriate NaOR or by initial reaction with NaOCH₃ to form Pb(C₂H₅)₃(OCH₃) followed by a transalcoholysis with the appropriate alcohol.²³ Although Pb(C₂H₅)₃(O'C₃H₇) could transalcoholize during OMCVD if used in combination with TTB and/or ZTB, it was prepared to compare its decomposition chemistry with that of Pb(C₂H₅)₃(O'C₄H₉) (TELBUT). Both compounds distill as clear, colorless liquids at 42–44 °C/4 Pa and 45–47 °C/2.5 Pa for O'C₃H₇ and O'C₄H₉, respectively.

Neither compound was pyrophoric but both rapidly decomposed upon exposure to the atmosphere. Exposure to daylight through borosilicate glass led to the decomposition of both compounds. With rigorous exclusion of light, both compounds are thermally stable at room temperature. For Pb(C₂H₅)₃(O'C₃H₇) the photolysis led to a pale-yellow, crystalline precipitate. The photolysis of TELBUT was much slower and gave colorless crystals, accompanied by a considerable buildup of pressure. The resulting liquids contained TEL and the respective Pb(OR)₂ compound. Analysis of the gaseous products showed only *n*-butane from Pb(C₂H₅)₃(O'C₃H₇), whereas *n*-butane, ethane, and ethene were evolved from TELBUT. This indicates a different mechanism for the two photolyses. When performed in toluene-*d*₈, the same products were obtained except that no ethane or ethene was generated from TELBUT; neither were any deuterated products formed.

Because the compounds were colorless but decomposed upon exposure to daylight passing through borosilicate glass, it was thought likely that they would show some absorption in the near UV. The absorption spectrum of Pb(C₂H₅)₃(O'C₃H₇) showed two weak absorptions of equal intensity at 220 and 240 nm; that of TELBUT was dominated by a peak at 215 nm, although upon dilution a small shoulder appeared at 295 nm. These spectra do not explain the observed photosensitivity, nor the difference therein between the two compounds.

The thermal stability of TELBUT was estimated using differential scanning calorimetry (DSC). The sample showed exothermic events beginning at 138 °C and gave small initial peaks around 170 °C, and the principal exotherm peaked at 230 °C. The enthalpy of the decomposition process was 165 kJ/mol. The sample also showed an endotherm at the melting point of metallic lead (323 °C). These data suggest that the thermal stability of TELBUT is similar to that of TEL and that the maximum safe working temperature is around 50 °C. It also shows that metallic lead is a principal product of its thermal decomposition.

Thin films were deposited in a small-scale vertical OMCVD reactor with rf heating at reduced reactor pressure. The system is described in detail elsewhere.¹⁰ Substrates used were (111)-Pt-coated oxidized (100)Si wafers. TELBUT was thermostated at 20 °C. For the deposition of PbTiO₃, TIP was used as titanium

(19) Egerton, A.; Smith, F. L. *Philos. Trans. R. Soc. London* 1935, 234, 507.

(20) Salooja, K. C. *J. Inst. Petroleum* 1967, 53, 208.

(21) Bradley, D. C. *Philos. Trans. R. Soc. London, A* 1990, 330, 167.

(22) Papiernik, R.; Hubert-Pfalzgraf, L. G.; Massiani, M. C. *Polyhedron* 1991, 10, 1657.

(23) Davies, A. G.; Puddephat, R. J. *J. Chem. Soc. C* 1967, 2663.

precursor, thermostated at 18 °C. The total flow rate was 0.5 standard L/min (SLM) of dried nitrogen and 0.1 SLM of oxygen at a reactor pressure of 2000 Pa.

The $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ thin films were deposited in a stainless steel reactor chamber with wafer rotation on 10-cm-diameter (111)-Pt-coated oxidized (100)Si wafers. The reactor pressure was kept at 133 Pa to suppress homogeneous gas-phase reactions and to improve layer homogeneity. The total flow rate consisted of 0.5 SLM of dried nitrogen carrier gas and 0.1 SLM of oxygen. The titanium and zirconium precursors used were TTB and ZTB, respectively; both were kept at 20 °C. TELBUT was thermostated at 50 °C, and its vapor transport line was heated to slightly above 50 °C. Depositions were performed for 60 min at a typical deposition rate of 200 nm/h.

The films were analysed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The composition and thickness of the films was determined using X-ray fluorescence (XRF). With a special software package it was possible to calculate the number of metal atoms per unit area with an accuracy of ~2%. Layer thicknesses were calculated from these values by assuming a density of 8×10^{22} atoms/cm².

The electrical characteristics of the layers were measured after gold top electrodes of various areas were sputter-deposited through a shadow mask onto the $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ film. Part of the $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ film was etched away in order to contact the common platinum bottom electrode. Hysteresis curves were measured using a Sawyer-Tower circuit with a sine wave at a frequency of 1 kHz. Small signal dielectric properties were measured using an impedance analyzer.

Results

Influence of Oxygen. One of the incentives for the use of TELBUT was the possibility to form lead oxide without the need for extra oxygen. Therefore, initial OMVCD was performed using only TELBUT. Thereafter it was used in combination with TIP as the titanium precursor both with and without additional oxygen. All depositions were performed at temperatures between 550 and 700 °C.

The deposition rates using TELBUT were ~25% of those obtained with TEL under similar conditions.¹⁰ Hence, assuming a similar decomposition efficiency, the vapor pressure of TELBUT is estimated to be 9 Pa at 20 °C, approximately one-quarter of that of TEL.

XRD analysis showed that in the presence of oxygen TELBUT reacts to form lead oxide as the only crystalline phase; without oxygen only metallic lead was obtained, which readily reacted with the platinum coating to form a PbPt alloy at the deposition temperature.

OMVCD using TELBUT and TIP in the presence of oxygen gave single-phased PbTiO_3 films at all temperatures used with properties similar to those obtained when using TEL.^{10,11} However, in the absence of oxygen, no PbTiO_3 was formed, but TiO_2 and the PbPt alloy mentioned above were obtained. This shows that even in the presence of TiO_2 and the byproducts from the decomposition of TIP, metallic lead is formed upon decomposition of TELBUT. Lead then reacts with platinum to form PbPt rather than to react with TiO_2 to form PbTiO_3 . This result is consistent with our earlier experiments using TEL, but conflicts with those of Kwak *et al.*⁴ who reported the formation of PbTiO_3 from TEL and TIP without extra oxygen.

In conclusion, these experiments show that the thermal decomposition of TELBUT during OMVCD leads to the same product as during DSC (see Experimental Section), namely metallic lead. Additional oxygen is needed to form the oxide. A similar observation has been made for the lead compound $\text{Pb}(\text{O}'\text{C}_4\text{H}_9)_2$.²¹

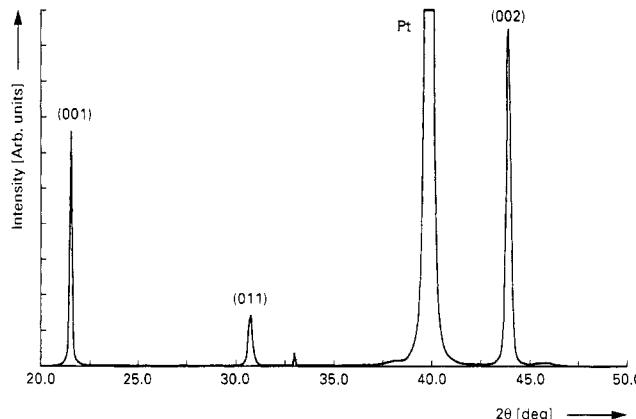


Figure 1. X-ray diffraction pattern of a 260-nm-thick $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ film with $x = 0.78$ deposited at 700 °C on a (111)-Pt-coated oxidized (100)Si substrate. The only phase observed is that of the perovskite-type $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$. The film has a preferred (00l) orientation.

Growth of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$. To evaluate the use of TTB and TELBUT as alternative titanium and lead precursors for the growth of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ thin films, they were used together with ZTB under conditions similar to those employed to deposit $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ from TEL, TIP, and ZTB.¹⁷ For this reference set of precursors the composition of the films in terms of the ratio $\text{Pb}/(\text{Ti} + \text{Zr})$ was found to be stoichiometric (i.e., $\text{Pb}/(\text{Ti} + \text{Zr}) = 1$) at 700 °C within a large interval of precursor gas-phase ratios.^{24,25} At this temperature, the deposition leads directly to the formation of a well-crystallized perovskite-type film and no postanneal is needed. Therefore, $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ thin films were also deposited at 700 °C with the new precursor set TELBUT, TTB, and ZTB.

Films with various zirconium fractions ($x = \text{Zr}/(\text{Zr} + \text{Ti})$) were deposited on (111)-Pt-coated oxidized Si(100) substrates by changing the flows of TTB and ZTB while keeping all other parameters constant. The zirconium fraction x was found to be nearly identical to the gas-phase zirconium fraction, as calculated from the vapor pressures and flow rates of ZTB and TTB.

A potential risk of using organometallics as precursors in CVD is the incorporation of carbon into the films from the organic ligands. The films were examined by Auger electron spectroscopy (AES) for the presence of carbon. Although the analysis is complicated by the near coalescence of the Auger lines of lead and carbon, careful examination of the spectra revealed that the carbon contamination is below the detection limit of 0.5 at. %.

Figure 1 shows a typical example of the XRD pattern of a $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ film with $x = 0.78$, which corresponds to a composition on the rhombohedral side of the PbTiO_3 - PbZrO_3 phase diagram. The only phase observed is perovskite-type $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$. The structure can be indexed by a (pseudo)cubic structure with a lattice constant of 4.112 Å, a value somewhat smaller than that of ceramic $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ of this composition (4.120 Å).²⁶ The XRD pattern shows that the film is strongly preferred (00l) orientated with a minor contribution from (011).

(24) Dormans, G. J. M.; De Keijser, M.; Van Veldhoven, P. J. *J. Cryst. Growth* 1992, 123, 537.

(25) De Keijser, M.; Dormans, G. J. M.; Van Veldhoven, P. J.; Larsen, P. K. Presented at the 4th Int. Symp. on Integrated Ferroelectrics, Monterey, 1992 (to be published in *Integr. Ferroelectrics*).

(26) Jaffe, B.; Roth, R. S.; Marzullo, S. *J. Res. Natl. Bur. Stand.* 1955, 55, 239.

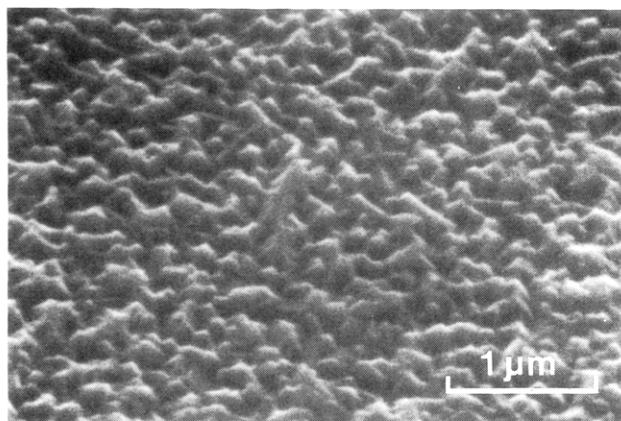


Figure 2. SEM micrograph of a 260-nm-thick $PbZr_xTi_{1-x}O_3$ film with $x = 0.78$ deposited at 700 °C on a (111)Pt-coated oxidized (100)Si substrate.

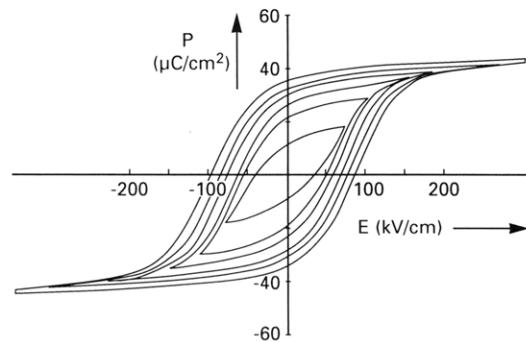


Figure 3. Hysteresis curves of $PbZr_xTi_{1-x}O_3$ with $x = 0.78$, deposited at 700 °C on a (111)Pt-coated oxidized (100)Si substrate, as a function of switching field. The layer thickness is 260 nm. A saturation of the loops is observed at 200 kV/cm (5.2 V). The coercive field strength is 71 kV/cm, the remanent and saturation polarizations are 35 and 42 μ C/cm², respectively.

oriented crystals. This result is comparable to what has been observed for films deposited using TEL, TIP, and ZTB.¹⁷

Figure 2 shows the surface morphology of a representative film. It shows that the films are well crystallized causing some surface roughness. However, cross-sectional SEM (not shown) reveals that the films are dense.

Electrical Results. A representative example of the ferroelectric behavior of these films is given in Figure 3 for a layer with $x = 0.78$ and a thickness of 260 nm. It shows hysteresis loops as a function of applied switching field. At 200 kV/cm (5.2 V) the hysteresis curve is saturated. A further increase of the switching field only results in a slight increase of both the remanent polar-

ization (P_r) and the coercive field strength (E_c), probably due to an increased leakage current. For the saturated loop the value for E_c is 71 kV/cm. The value for P_r is 35 μ C/cm² and the saturation polarization (P_s) is 42 μ C/cm². A lowering of the zirconium content gives a significant increase of E_c , whereas the value for P_r tends to increase slightly. This is similar to observations for films deposited with the reference set of precursors TEL, TIP, and ZTB.²⁵ The values for P_r and P_s of our OMCVD deposited $PbZr_xTi_{1-x}O_3$ thin films are close to those found for bulk $PbZr_xTi_{1-x}O_3$ ceramics. On the other hand, the values for E_c are considerably higher than reported for bulk ceramics but in line with those reported for other $PbZr_xTi_{1-x}O_3$ thin films. The high values for E_c of the thin films are attributed to the presence of electrode interface effects.

The dielectric constant (ϵ_r) and the loss tangent ($\tan \delta$) of the film with $x = 0.78$ were measured at frequencies between 5 and 10⁵ Hz. The dielectric constant is nearly independent of frequency with $\epsilon_r = 750$. The loss tangent is ~0.045 and increases at higher frequencies due to resistive losses in the electrical measurement circuit. The ac resistivity of the film (at 1 kHz) is ~8 × 10⁷ Ω cm. Similar results are obtained for the layers with other Zr fractions. Only ϵ_r is found to depend on x : a maximum value of 900 is obtained near the morphotropic phase boundary ($x = 0.53$). These dielectric properties are in line with those expected for $PbZr_xTi_{1-x}O_3$ thin films on platinum coated silicon substrates and show that very good ferroelectric layers can be deposited with TELBUT as a lead precursor.

Conclusions

The new lead precursors triethyllead *tert*-butoxide (TELBUT) and triethyllead isopropoxide were synthesized. TELBUT is found to be a convenient liquid lead precursor which is thermally stable below 50 °C. Its vapor pressure is about a quarter of that of tetraethyllead (TEL). This and the fact that TELBUT is not pyrophoric and rapidly decomposes upon exposure to the atmosphere make TELBUT a precursor which is easier and safer to handle than TEL. Its sensitivity to light could be used in photoenhanced OMCVD.

Similar to what is found for TEL, the experiments have shown that the thermal decomposition of TELBUT leads to the formation of metallic lead rather than lead oxide and that $PbTiO_3$ is formed only for depositions using TELBUT in combination with TIP in the presence of oxygen. Ferroelectric $PbZr_xTi_{1-x}O_3$ thin films of high quality can be deposited using the all butoxide precursor system TELBUT/TTB/ZTB.