Metalorganic Chemical Vapor Deposition of Lead Titanate

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In this study, the metalorganic chemical vapor deposition (MOCVD) of lead titanate ($PbTiO_3$) was studied using the metalorganic precursors lead bis(tetramethylheptadionate) ($Pb(thd)_2$) and titanium ethoxide ($Ti(OEt)_4$). The structure, composition, and thickness of the resulting films were studied and correlated with the experimental processing parameters. Optical and electrical properties were obtained for the lead titanate films on sapphire and platinum-coated silicon, respectively. Several important processing issues are also addressed including the existence of a high-temperature self-limiting reaction regime for high reproducibility of film stoichiometry and also the stability of the ruthenium oxide-coated silicon substrates in the MOCVD process environment which are candidate electrode materials.

Introduction

Lead titanate ($PbTiO_3$) based ceramics have been well-known for their interesting piezoelectric, pyroelectric, ferroelectric, and electrooptic properties. In recent years, the thin-film forms of $PbTiO_3$ (PT) and PT-derived materials such as lead zirconate titanate (PZT) and lanthanum-doped PZT (PLZT) have generated considerable interest due to their potential application in nonvolatile ferroelectric RAMs. Lead titanate thin films also find applications in optoelectronic devices, sensors, and transducers.

While many processing techniques are available to synthesize lead titanate thin films, metalorganic chemical vapor deposition (MOCVD) is a promising technique for several reasons: the equipment is relatively simple, step coverage is superior to all other processes, compositional control is extremely flexible, and the process can be incorporated into large-scale processing. In this study, the deposition behavior of $PbTiO_3$ was investigated using the metalorganic precursors, lead bis(tetramethylheptadionate) ($Pb(thd)_2$) and titanium ethoxide ($Ti(OEt)_4$) which have not been widely used in the literature. In addition to investigating the general deposition behavior and film properties, we have also demonstrated the existence of a high-temperature process window for controlling the film composition and have also addressed some stability problems regarding the use of ruthenium oxide substrates in the MOCVD environment.

Experimental Procedure

The metalorganic precursors chosen for the MOCVD of lead titanate were lead bis(tetramethylheptadionate) ($Pb(thd)_2$) as lead source and titanium ethoxide ($Ti(OEt)_4$) as titanium source; both were obtained from Strem Chemicals, Inc. $Pb(thd)_2$ is one of the more desirable metalorganic chemical lead sources offering volatility, low toxicity, environmental stability, and the ability to produce contamination-free films.[1] Titanium isopropoxide ($Ti(OPr^i)_4$) is the most commonly used precursor in the literature for the MOCVD of $PbTiO_3$.[2-5] Other results we have obtained have shown that titanium ethoxide (($TiOEt)_4$) is also a viable titanium source, being easily vaporized and pyrolyzed without any resulting contamination (i.e., no carbon in the films) as determined by Auger electron spectroscopy (AES) depth profiling.[6] Titanium ethoxide has a high vapor pressure at relatively low temperatures also; its boiling point at 1 atm is 122 °C.[7]

The substrates used in this study include sapphire, as well as multilayer structures consisting of $Pt/Ti/SiO_2/Si$ and $RuO_2/SiO_2/Si$, which will be referred to as platinum (Pt) and ruthenium oxide (RuO_2) substrates, respectively. The single-crystal sapphire (Al_2O_3) substrates were oriented within a 30° cone of the *c* axis and were used to produce clean XRD charts and obtain optical properties.

The platinum and ruthenium oxide substrates were investigated also because these are typical electrode materials used for ferroelectric films. Platinum is the conventional choice that has been used for electrodes; these substrates were obtained from Sharp, Inc., Japan. Ruthenium oxide has recently gained recognition for exhibiting superior fatigue properties compared to platinum electrodes and for this reason was included in our study.[8,9] The RuO_2 substrates were processed in-house.

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(1) Nyman, M. D. Synthesis and Characterization of Precursors for Chemical Vapor Deposition of Metal Oxide Thin Films. M.S. Thesis, Virginia Polytechnic Institute & State University, Blacksburg, VA, 1992.
(2) Kwak, B. S.; Boyd, E. P.; Erbil, A. Metalorganic Chemical Vapor Deposition of $PbTiO_3$ Thin Films. *Appl. Phys. Lett.* **1988**, *53*, 1702–04.
(3) Swartz, S. L.; Seifert, D. A.; Noel, G. T. Characterization of MOCVD $PbTiO_3$ Thin Films. *Ferroelectrics* **1989**, *93*, 37–43.
(4) Shimizu, M.; Katayama, T.; Fujimoto, M.; Shiosaki, T. Growth of $PbTiO_3$ by Photo-MOCVD. *SPIE v.1519 International Conference on Thin Film Physics and Applications* **1991**, 122–127.
(5) Gao, Y.; Bai, G.; Merkle, K. L.; Shi, Y.; Chang, H. L. M.; Shen, Z.; Lam, D. J. Microstructure of $PbTiO_3$ Thin Films Deposited on (001) MgO by MOCVD. *J. Mater. Res.* **1993**, *8*, 145–153.
(6) Hendricks, W. C.; Sie, J.; Peng, C. H.; Desu, S. B. Metalorganic Chemical Vapor Deposition (MOCVD) of Titanium-Based Ferroelectric Thin Films. *Mater. Res. Symp. Proc.* **1992**, *310*, 241–247.
(7) *Dictionary of Organic Compounds*, 5th ed.; Chapman and Hall: New York, 1982; Vol. 5, p 5772.
(8) Kwok, C. K.; Vijay, D. P.; Desu, S. B.; Parikh, N. R.; Hill, E. A. Conducting Oxide Electrodes for Ferroelectric Thin Films. *Proceedings of the 4th ISIF (Monterrey, CA, 1992)* 412.
(9) Yoo, I. K.; Desu, S. B. Fatigue Modeling of Lead Zirconate Titanate (PZT) Thin Films. *Mater. Sci. Eng. B* **1992**, *13*, 319–322.

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Table 1. Optimum $PbTiO_3$ MOCVD Parameters for T_d = 550 °C

total pressure, p	6 Torr
dilute gas flow rate, f_{O_2}	550 sccm
Ti bubbler temp, T_{b,TiO_2}	114 °C
Pb bubbler temp, $T_{b,Pb}$	140 °C
Pb carrier gas flow rate	50 sccm
Ti carrier gas flow rate	5 sccm

The hot-wall CVD reactor consisted of a 2 in. (5.08 cm) diameter stainless steel tube with a 30.5 cm heated zone. The films were deposited using the conventional hot-wall CVD technique using bubblers to deliver the precursor vapors. Nitrogen was used as the carrier gas; dry oxygen was used as the diluent gas. Both were monitored and controlled by means of a mass flow controller.

Approximately 0.85 g of fresh $Pb(thd)_2$ was used at the start of each run. Titanium ethoxide, in contrast, may be left inside the bubbler for approximately 10 CVD runs if stored under vacuum. Significant vapor pressures may be obtained for many runs beyond this number, but the volatility and hence the vapor partial pressure obtained may not be consistent as the precursor begins to degrade.

Substrates were placed on a tilted susceptor at equal spacings in the hot zone of the reactor; these positions were 9.0, 13.0, 17.0, and 21.0 cm from the reactor entrance and are referred to as positions 2–5, respectively.

A microbalance was used to determine the deposition rates. XRD (Cu Kα) was performed on all of the samples deposited. SEM was used to investigate the surface morphology, and EDS was used to determine the Pb/Ti ratio. Optical properties of the films on sapphire were studied using reflectance and transmittance UV–vis–NIR spectrophotometry. Electrical properties on the Pt and RuO_2 substrates were investigated using standard RT-66A test equipment.

Results and Discussion

It was found that reproducible lead titanate films of excellent composition and structure which were optically specular and transparent could be produced using a deposition temperature, T_d, of 550 °C and the experimental parameters given in Table 1.

However, once these guidelines were established, the importance of the effects that result from slight changes in these experimental parameters regarding the composition, deposition rate (thickness), and crystal structure were examined. Consecutive deposition with identical parameters generally resulted in compositional variation of less than 5%.

In Figure 1, parts a and b, the variation in thickness profile and composition profile, respectively, are shown for three different titanium bubbler temperatures, holding all other parameters unchanged. The titanium bubbler temperature was found to be more important than any other single factor in controlling the film composition at the temperature studied.

The existence of unreacted PbO in films that are stoichiometric overall provides evidence that the individual oxides, PbO and TiO_2 are deposited separately and subsequently react on the substrate to produce $PbTiO_3$. Hence at high enough deposition rates of the individual oxides, the formation rate of lead titanate is limited by the reaction rate of the constituent oxides.

The depositions described previously were all conducted at a total pressure of 6 Torr. The effect of total pressure was investigated by deposition at p = 4 Torr and p = 8 Torr using conditions for which favorable results were obtained at 6 Torr. These results are given for the composition profile and thickness profile in Figure 2. The deposition rate increased by as much as

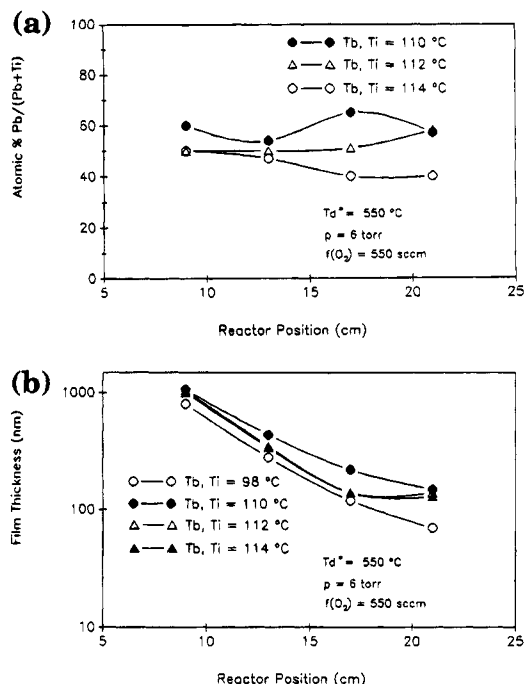


Figure 1. Variation in (a) the composition profile and (b) the deposition rate profile that result from changes in the titanium bubbler temperature.

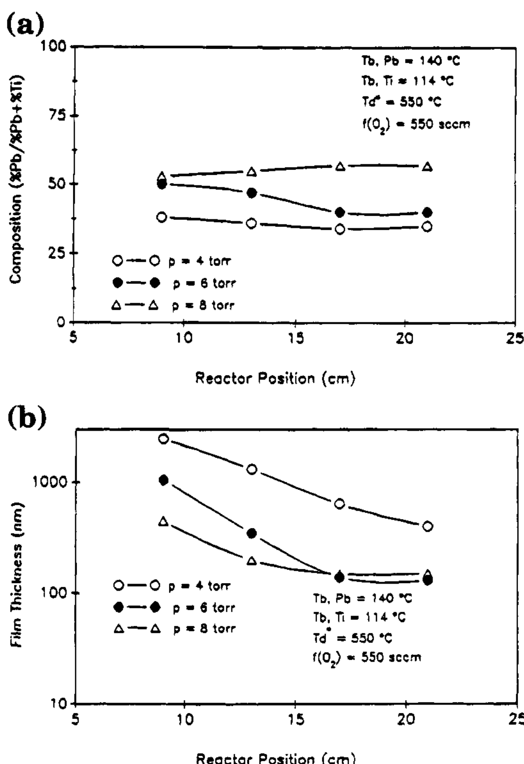


Figure 2. Variation in (a) the composition profile and (b) the deposition rate profile that result from changes in the total reactor pressure.

4 times by decreasing the pressure from 8 to 4 Torr, with the deposition profiles for 6 Torr intermediate between the other two. The explanation for this behavior lies in the composition profiles for each set of data. As the pressure increases from 4 to 6 Torr and then 8 Torr, the composition changes from being Ti-rich to stoichiometic and finally Ti-deficient. Thus, the titanium deposition rate seems to be controlling the overall deposition rate to a large degree. The most probable

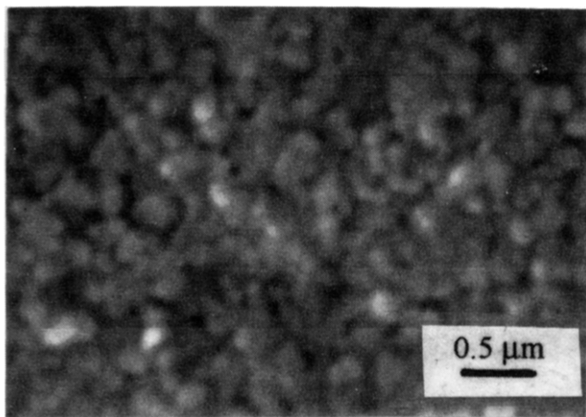


Figure 3. Typical surface morphology of the $PbTiO_3$ films grown on RuO_x substrate viewed using SEM.

explanation is that the titanium vaporization rate is very sensitive to the total pressure in the bubbler which is generally close to the total pressure in the reactor.

The typical surface morphology for $PbTiO_3$ films grown on ruthenium oxide is given in Figure 3; this film was deposited according to the conditions given in Table 1. The films deposited at this temperature (550 °C) are generally smooth and fine-grained and appear mirror-like and transparent to the eye. The microstructure of the lead titanate on platinum and sapphire (not shown) were found to be nearly identical to that observed on ruthenium oxide.

Use of High-Temperature Deposition Regime. It was previously shown that the deposition behavior, especially regarding the composition of the films, is sensitive to the experimental parameters at a temperature of 550 °C as a consequence of the resulting variability of the composition of the gas stream. However, in a paper by de Keijser et al.,[10] it was shown that for the MOCVD of PZT, as the deposition temperature is increased to 600 °C, a process window develops where a range of gas stream compositions will result in stoichiometric PZT. For PZT, stoichiometric is defined as having the ratio of A-site cations to B-site cations in the perovskite structure equal to 1:1. In other words, the films have 50 mol % PbO. Oxygen is assumed to exist in the proper ratio as is generally the case for reasonably low deposition rates.

The existence of a process window was confirmed for lead titanate also in the hot-wall reactor used in this study. $PbTiO_3$ was deposited on sapphire using a lead source temperature of 150 °C and a titanium source temperature of 115 °C. The reactor temperature was increased to 650 °C and the oxygen diluent gas flow rate was increased to 850 sccm to account for the higher depletion rate of the gas stream at the higher temperature. Each of the samples were placed in the reactor at different positions and hence different temperatures, yet each was found to contain 50% PbO within the experimental accuracy of the EDS detector as can be seen in Figure 4b. The only effect which can be seen in Figure 4a is a substantial increase in the deposition rate (thickness). To confirm that the process is insensitive to disturbances in the experimental conditions, the

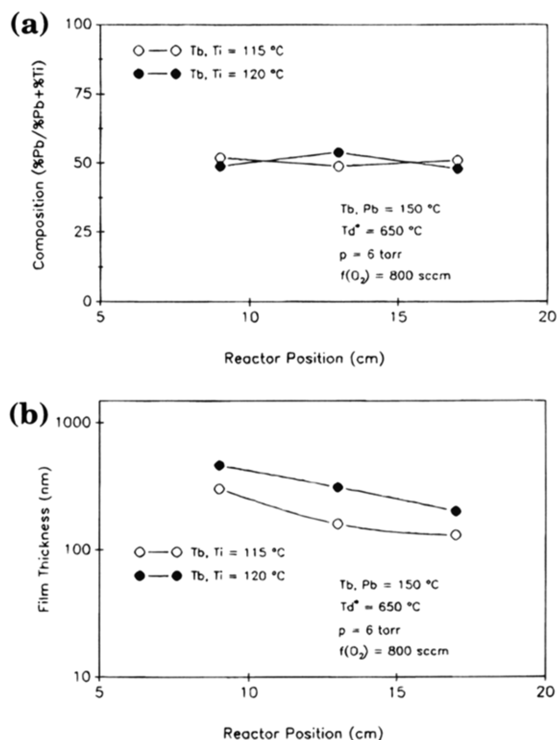


Figure 4. Improvement in experimental reproducibility as a result of the use of the high-temperature regime is observed by comparing these profiles of (a) the composition and (b) the deposition rate for various titanium bubbler temperatures with their counterparts in Figure 1.

titanium bubbler temperature was increased to 120 °C, an increase of 5 °C, which is more than the entire range of titanium bubbler temperatures studied previously. These films were also found to be nearly stoichiometric as is seen in Figure 4b. Consequently, it can be concluded that the main effect of increasing the titanium ethoxide partial pressure by increasing the titanium bubbler temperature is to increase the overall deposition rate while leaving the composition unchanged. The XRD patterns for a typical high-temperature run on sapphire are given in Figure 5. Only in position 2, where the temperature is relatively low and the deposition rate is very high, was any excess PbO phase observed in the XRD patterns.

The surface morphology of the films deposited at this temperature shows a fine-grained microstructure characteristic of a high nucleation rate resulting from the increased deposition temperature (Figure 6). In addition, these films were found to be transparent and specular from UV−vis−NIR spectrophotometery.

The process window exists for the CVD of these lead-based compounds because PbO is much more volatile than the lead titanate or PZT, especially as the temperature exceeds 600 °C. As long as a sufficient quantity of lead precursor is available such that PbO deposits in excess of that required to form the stoichiometric compound, any excess PbO that is deposited is desorbed before it can be incorporated into the film. Thus, only the PbO that actually reacts with the TiO_2 to form $PbTiO_3$ will be incorporated into the film. Although it has not been shown, it is suspected that this self-limiting behavior will not occur for high deposition rates as the PbO will not have sufficient time to desorb before the film begins to grow over it.

(10) de Keijser, M.; Dormans, G. J. M.; Van Veldhoven, P. J.; Larsen, P. K. High Quality Lead Zirconate Titanate Thin Films Prepared by Organometallic Chemical Vapor Deposition. *Proceedings of the 4th ISIF (Monterrey, CA, 1992)* 243−250.

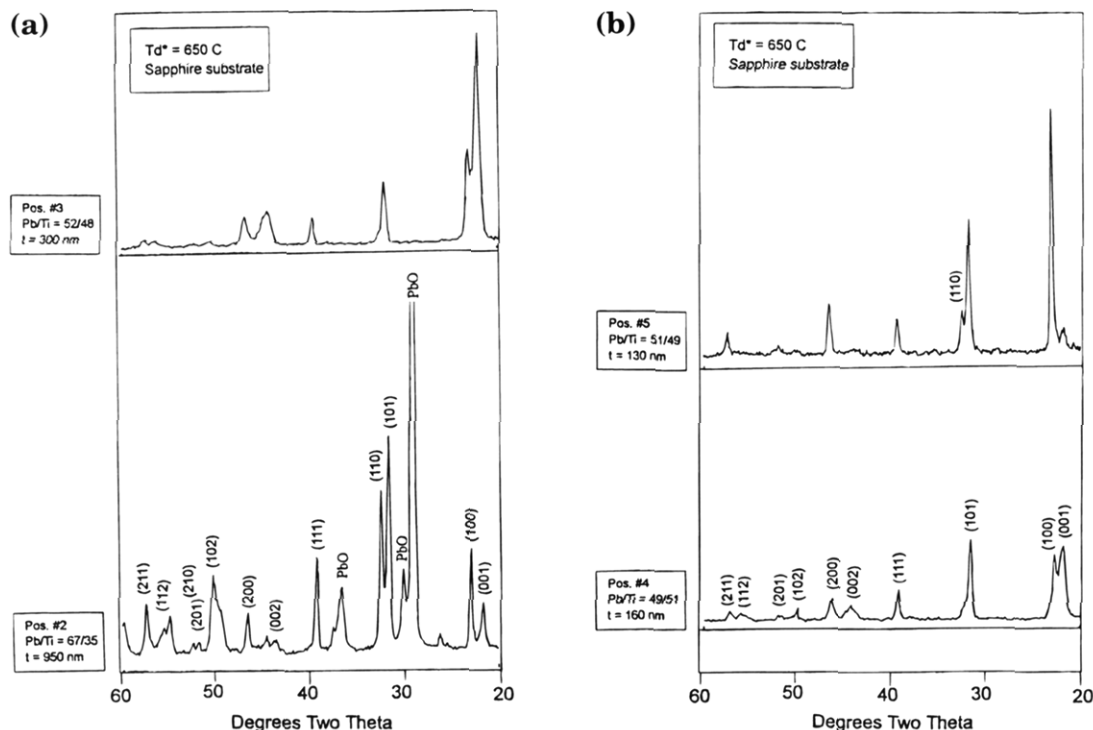


Figure 5. XRD patterns for a typical high-temperature deposition of $PbTiO_3$ on sapphire.

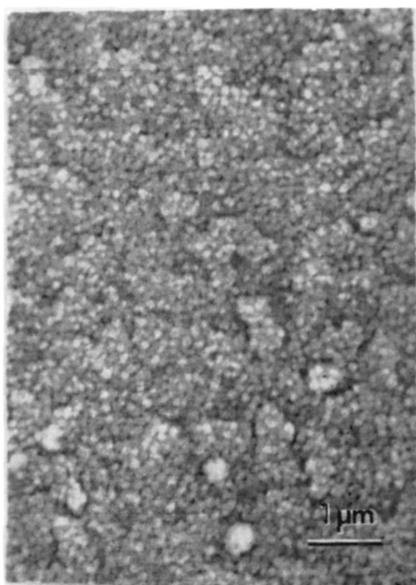
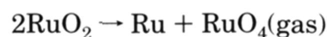


Figure 6. Fine-grained microstructure of $PbTiO_3$ film deposited in the high-temperature regime.

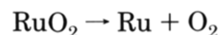
Stability of RuO_2 Substrates in the CVD Process. While successful $PbTiO_3$ films were deposited on ruthenium oxide for temperatures as high as 550 °C, at 650 °C significant problems occurred with the film peeling. For some wafers, peeling was even a problem at low temperatures (550 °C). Several observations were made at this time: (1) the properties of the substrates cut from the same wafer were generally consistent from one run to the next; (2) film peeling was generally found to occur between the RuO_2 layer and the SiO_2 layer which could be confirmed by the metallic luster of the underside of the peeled fragments; (3) the XRD pattern of peeled and partially peeled films showed the existence of either ruthenium metal and no ruthenium oxide or a mixture of ruthenium metal and ruthenium oxide. In no case was ruthenium metal observed for a film that had not peeled or cracked.

On the basis of the XRD patterns, it seems that the cause of the film stress is the chemical reduction of the ruthenium oxide electrode material. However, ruthenium oxide is the stable phase at the temperature and oxygen partial pressures used in the MOCVD system.[11,12] Ruthenium oxide can be transformed to ruthenium metal by two different reactions depending on the environment. In an oxidizing atmosphere, disproportionation is preferred which proceeds as follows:[12]



$$2RuO_2 \rightarrow Ru + RuO_4(\text{gas})$$

In a nonoxidizing atmosphere, reduction is preferred:[12]



$$RuO_2 \rightarrow Ru + O_2$$

It is not clear which reaction is operating in this case, but for both there is a large decrease in volume associated with each and consequently a large tensile stress that would be generated in the ruthenium/ruthenium oxide film. It may be possible to verify the actual mechanism using RBS.

To determine the influence of the CVD process on the reduction reaction, the CVD run was performed with the ruthenium oxide substrates as usual but without sending precursor vapors, and hence no film formation resulted. These substrates were completely untransformed after removing them from the reactor; this suggests that either the presence of the film or the reactive species in the CVD gas stream play a role in

(11) Seddon, E. A.; Seddon, K. R. *Chemistry of Ruthenium*; Elsevier: New York, 1984; pp 113–116.
(12) Tagirov, V. K.; Chizhikov, D. M.; Kazenas, E. K.; Shubochkin, L. K. Thermal Dissociation of Ruthenium Dioxide and Rhodium Susquioxide. *Zh. Neorg. Chim. (Russ. J. Inorg. Chem.)* **1975**, *20*, 1133–34.

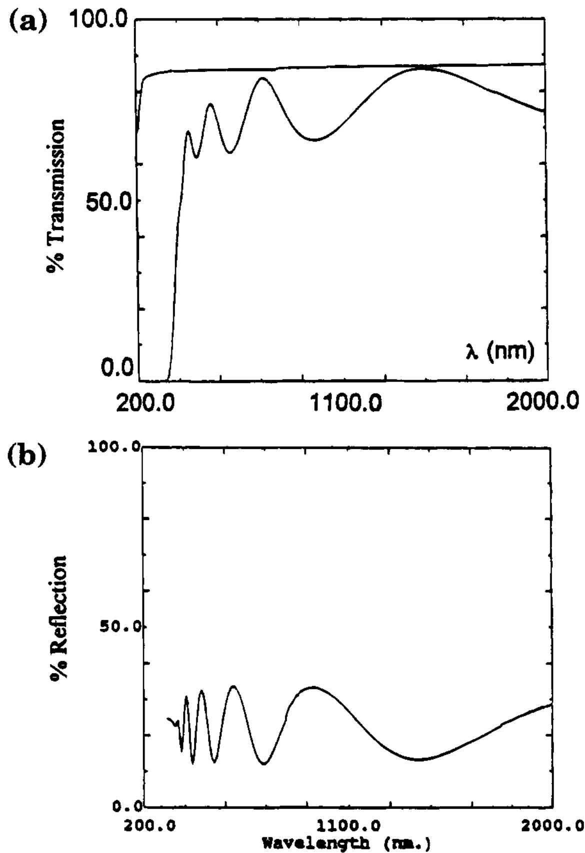


Figure 7. UV–vis–NIR specular reflectance and transmission spectra for MOCVD $PbTiO_3$.

the ruthenium formation reaction. However, using a nitrogen atmosphere of 6 Torr at 550 °C, it was possible to form Ru even in the absence of precursor species or film.

Optical Properties Using UV–vis–NIR Spectrophotometry. Optical properties were obtained from a $PbTiO_3$ sample prepared on sapphire at 550 °C. UV–vis–NIR specular transmittance and specular reflectance spectra appear in Figure 7. The transmission properties of the film revealed a highly specular, nonabsorbing film.

The dispersion relationship for the refractive index, n, and the behavior of the absorption coefficient with photon energy were both determined using the envelope method, as was the film thickness which in this case was found to be 325 nm. The dispersion relationship and absorption behavior are given in Figure 8. Using an effective medium approximation, the film packing density was estimated to be 89%.

Ferroelectric Properties. The electrical properties of most films were generally found to be quite poor owing to very high film conductivities ($\varrho = 10^6$–10^8 Ω cm); however, hysteresis behavior could sometimes be observed as shown in Figure 9 with $P_r = 1.1\ \mu C/cm^2$ and $E_c = 45$ kV/cm. The loop does not appear to be fully saturated, probably due to high conductivity. Lead titanate is notorious in the literature for being very conductive when synthesized in thin-film form, whether the process used is MOCVD or other techniques including sol–gel and sputtering. One likely cause is the large volume change for $PbTiO_3$ that occurs when ever the material passes through the Curie point (490 °C) and transforms between the nonferroelectric cubic phase

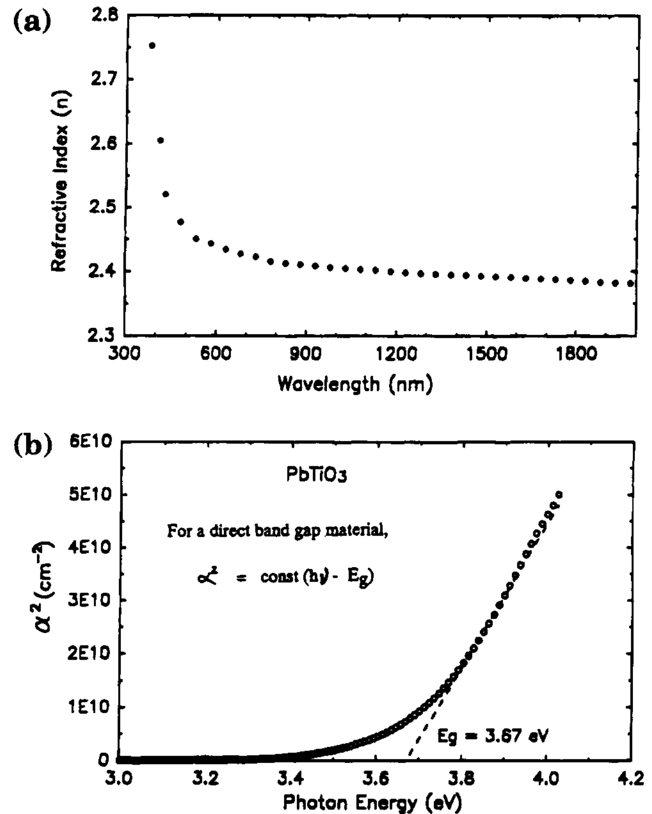


Figure 8. (a) Dispersion relationship and (b) absorption behavior inferred from optical properties in Figure 7.

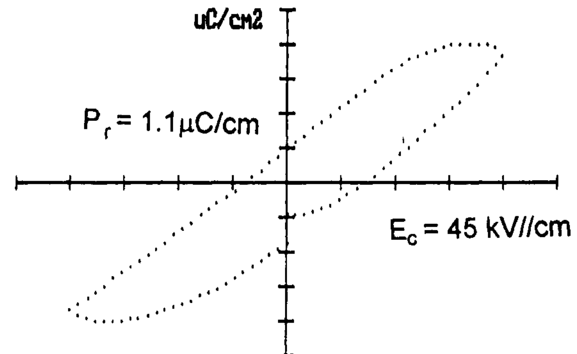


Figure 9. Ferroelectric hysteresis of MOCVD $PbTiO_3$ on Pt substrate; the conventional low-temperature technique was used.

(high temperature) and the ferroelectric tetragonal phase (low temperature).[13] The use of PZT can significantly reduce the volume change and anisotropy, and this is part of the reason for the popularity of PZT.[13]

Summary and Conclusions

Lead titanate was successfully deposited using a hot-walled MOCVD process with lead tetramethylheptadionate $Pb(thd)_2$ and titanium ethoxide $Ti(OEt)_4$. The films were deposited under a variety of conditions; the composition of the films was found to be extremely sensitive to the source gas composition at the low temperatures (550 °C and below), while at the higher temperatures (greater than 600 °C) it was found that the composition was extremely insensitive to experi-

(13) Moulson, A. J. *Electroceramics* Chapman & Hall: New York, 1990; p 253.

mental parameters. The deposition rate was found to vary considerably with reactor position which is commonly the case with hot-wall tube reactors; however, use of these reactors facilitates simple modeling and large-scale batch processing for industry.

XRD was used to study the constituent phases in the material which was found to be dependent on the overall deposition rate as well as the film composition. While good optical properties could be obtained, film conductivity remains a major problem for obtaining ferroelectric properties. Some problems were also encountered regarding the adhesion of the ruthenium oxide substrates in the MOCVD experiment; this problem was found to be caused by the formation of ruthenium metal from the ruthenium oxide and the large tensile stress associated with the transformation.