Chemical Vapor Deposition of Electroceramic Thin Films

M. de Keijser and G.J.M. Dormans

Introduction

A nonconventional way of producing nonvolatile memories is to use ferroelectrics, a class of electroceramic materials. These materials have a remanent polarization. The direction of this polarization can be changed by an electric field. Ferroelectric materials possess a "natural memory," so to speak. Ferroelectrics have been known for a long time, and the idea to use them for binary data storage originates in the 1950s. The basic element of this type of memory is formed by a ferroelectric capacitor—a ferroelectric layer sandwiched between electrodes. Early prototypes were unsuccessful because rather high voltages were needed to switch the ferroelectric capacitor (200–300 V) and the memories suffered from crosstalk. (Programming one particular cell influenced neighboring cells.) The revival of ferroelectric memories was driven by the development of thin-film deposition techniques that allowed the formation of capacitors with ferroelectric thin films of submicron thicknesses. These capacitors can be switched with normal intergrated-circuit (IC) voltages. The crosstalk problem is circumvented by isolating each memory cell by a transistor (similar to a dynamic random-access memory [DRAM]). Compared to "standard" nonvolatile memories, ferroelectric memories offer the advantage of very fast access times (both for reading and writing), low-voltage operation, and good write/read endurance. A ferroelectric material that is already being used in commercially available memories is lead zirconate titanate, $PbZr_xTi_{1-x}O_3$. To combine a ferroelectric material with IC technology is a challenge, and many problems have been (and will be) encountered.

In the case of volatile memories (DRAM, static RAM [SRAM]), decreasing lateral dimensions in ICs calls for nonconventional materials to be integrated in these ICs. For example, the available chip area for storage of a given amount of charge on a capacitor is ever decreasing. One approach to maintain the necessary amount of charge on these capacitors is to use materials having higher values for the dielectric constant than the commonly used SiO_2 and Si_3N_4. Electroceramic materials that may be used for such applications are $SrTiO_3$ and $(Ba,Sr)TiO_3$. The dielectric constant of such materials typically is two orders of magnitude higher than that of conventional materials. Consequently the area of the storage capacitor can be proportionally decreased.

For integrated applications of electroceramic materials, obviously it is a prerequisite to synthesize them in the form of thin films. During the last decade, "classic" deposition techniques—for example, sputtering—have been greatly improved and new ones have been developed, such as pulsed laser deposition, spin coating (sol-gel, metalorganic decomposition [MOD]), and organometallic chemical vapor deposition (OMCVD).

(OM)CVD is expected to have some distinct advantages over other deposition techniques when uniform deposition over large areas is desirable. Generally good step coverage can be obtained by this technique. Chemical vapor deposition is compatible with IC technology, and many equipment suppliers are active in the field. The deposition of a number of electroceramic thin films by CVD has now been reported. These include conductors (e.g., RuO_2),[1] ferroelectrics (e.g., $PbZr_xTi_{1-x}O_3$, $Bi_4Ti_3O_{12}$),[2] high T_c superconductors ($YBa_2Cu_3O_{7-\delta}$),[3] dielectrics ($(Ba,Sr)TiO_3$),[4] and several types of buffer layers.[5]

A limitation of the CVD of electroceramic thin films has been, and still is, the availability of suitable precursors. A precursor should have a vapor pressure sufficiently high to enable transportation via the gas phase. Decomposition of the precursor should result in the liberation of compounds (single metals, combinations of metals, or oxides) that form the desired film without incorporation of elements such as carbon or halogens. For some elements, for example barium and strontium, potential precursors have a low vapor pressure (<1 mTorr at 20°C). Such limitations have led to the development of alternative ways of precursor transportation—that is, dissolved in liquids[6] or even as solids.[7]

In this article, the CVD of electroceramic thin films will be described. As an example, the deposition of $PbZr_xTi_{1-x}O_3$

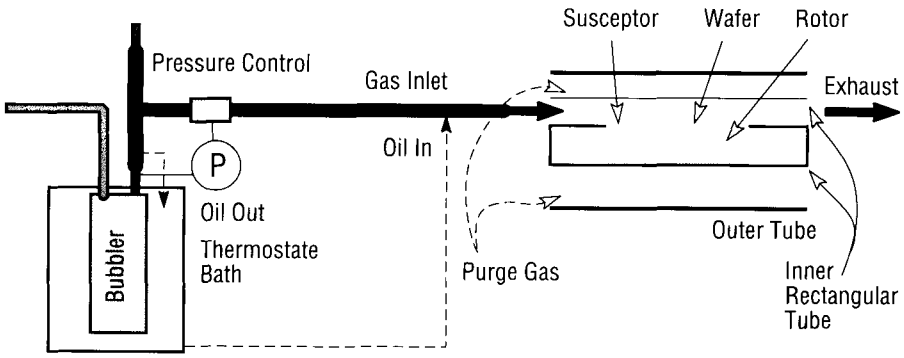

Figure 1. Schematic of an organometallic-chemical-vapor-deposition setup. The gas lines are heated by oil flowing through the outer tube of the coaxial tubing. The setup has a horizontal single-wafer reactor cell.

(PZT) by conventional OMCVD, as first described by Okada in 1988,[8] will be treated. Attention will be given to alternative ways of CVD that have been developed mainly to handle precursors with extremely low vapor pressures.

Chemical Vapor Deposition

On the topic of chemical vapor deposition, useful textbooks are available.[9] If organometallic compounds are used as precursors, the technique is referred to as organometallic chemical vapor deposition (OMCVD). Organometallic compounds tend to have relatively high vapor pressures and decompose readily at elevated temperatures.

Basically an (OM)CVD system consists of three parts: (1) a gas-mixing system (the gas system) connected to (2) the reactor cell and (3) a pumping system with gas exhaust. (See Figure 1.) The main parameters controlling the composition of the deposit and deposition rate are the partial pressures of the precursors in the reactor and the deposition temperature. Therefore accurate control of these parameters is essential. Vapors of the precursors are transported to the reactor by leading an inert carrier gas through or over the precursor.

Since the vapor pressures of precursors for electroceramic thin films generally are low, they must be evaporated at elevated temperatures (typically 50–150°C). In order to prevent the condensation of precursors in the gas system, all parts have to be heated to or above the evaporation temperature. A way to achieve this is by making use of coaxial tubing of the gas system. The inner tube is used for transport of the carrier gas containing the precursors and through the outer tube flows hot oil heating the inner tube. (See Figure 1.) Uniform heating of transport lines is accomplished, and it excludes the occurrence of hot spots where the precursor might, prematurely, decompose. (Hot spots easily occur when the heating is by electrical heater tapes.) When heating of the gas system is not critical, the use of simple electrical heater tapes will do. The occurrence of hot spots may be prevented by using tapes with a negative temperature resistance coefficient. Such an approach would link well with existing commercially available CVD systems.

Alternative ways of precursor transportation are being explored. One way is to dissolve a suitable precursor in an organic liquid. This solution then is transported to the reaction chamber. Accurate control of the solution's flow rate is essential. In a multicomponent system, in

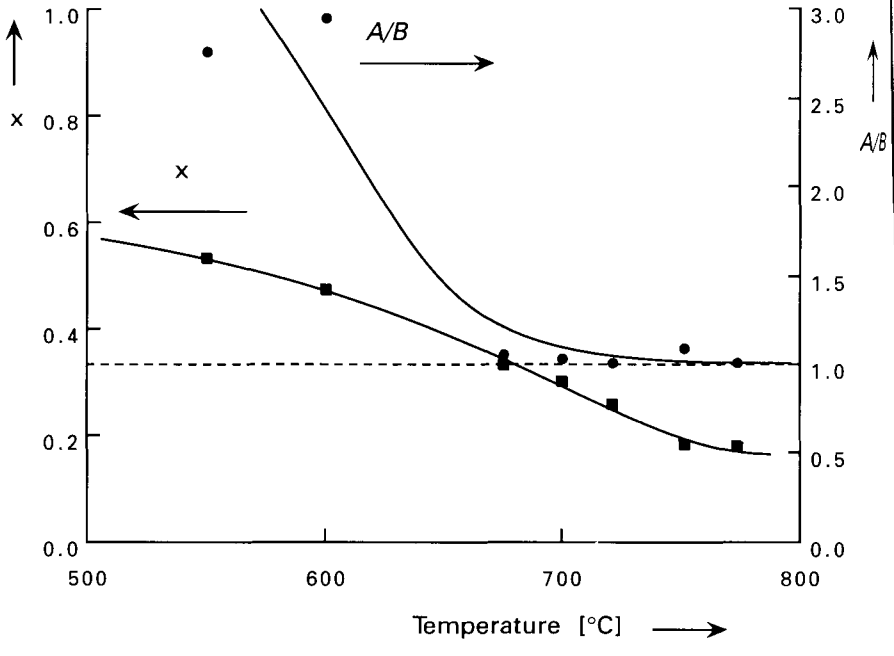

Figure 2. Cation stoichiometry (Pb/(Zr + Ti)) and composition x as a function of the deposition temperature. The fraction of ZTB x_g was 0.5, and $(A/B)_g$ was 1. A leveling-off of A/B at the stoichiometric ratio of unity with increasing deposition temperature is observed. The value of x decreases with increasing deposition temperature.

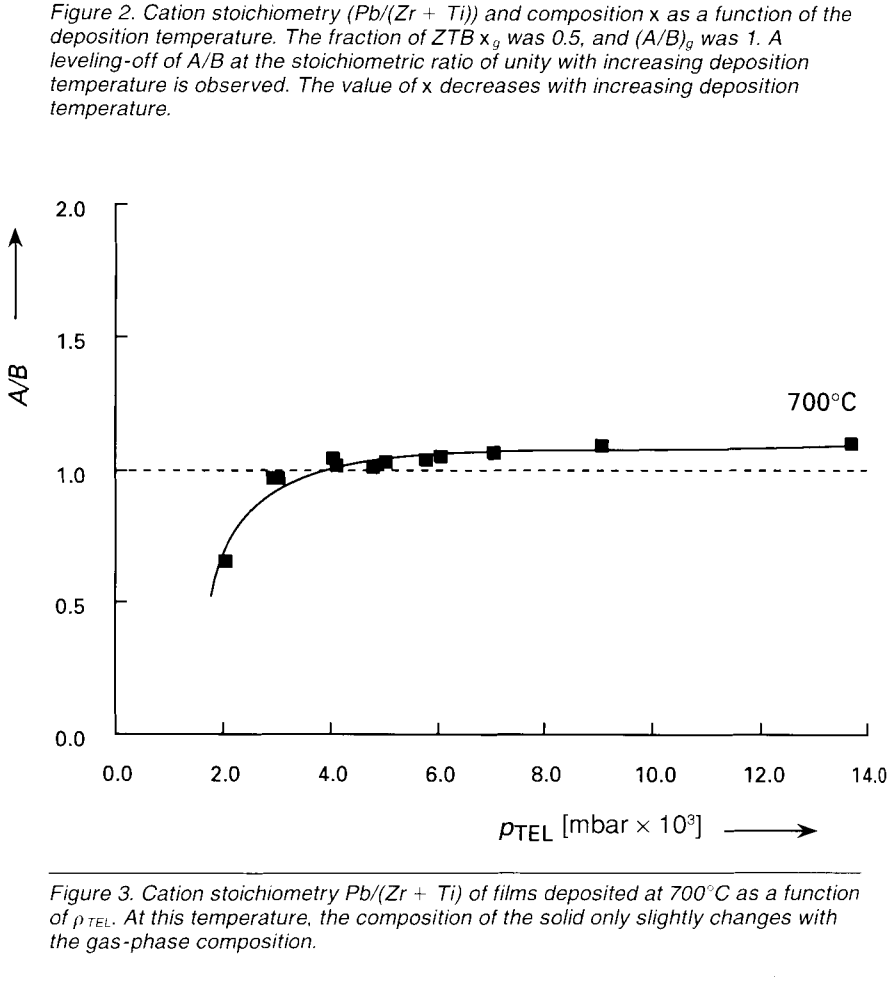

Figure 3. Cation stoichiometry Pb/(Zr + Ti) of films deposited at 700°C as a function of p_{TEL}. At this temperature, the composition of the solid only slightly changes with the gas-phase composition.

principle a separate source per element can be applied. The components may also be mixed into a single solution that is transported to the reactor. At a certain point, the solution is evaporated and the thus formed gas mixture is fed into the reactor. Provided that the solvent is inert, the actual deposition is comparable to that in conventional CVD. Liquid delivery tools, which in principle can be hooked up to standard CVD equipment, are commercially available.[6]

In a second approach,[10] the precursors also are transported as a liquid. This liquid contains precursors of the desired elements in the correct ratio. The mixture then is ultrasonically converted into an aerosol that is carried with an inert gas into the reaction chamber at room temperature. Some decomposition of the precursors takes place by ultraviolet radiation. The desired film is obtained after an anneal. This technique is related to spin-coating methods. The film thickness per deposition is limited, and the technique in principle is a ceramic method.

A third approach makes use of precursors in the solid state.[7] A mixture of metal β-diketonates in the desired ratio is fed into a high-temperature gradient zone. Each constituent vaporizes at its own specific vaporization temperature and is immediately swept to the reactor by a stream of inert carrier gas. Condensation is prevented by maintaining the temperature of the reactor wall at a sufficiently high level. Decomposition of the precursors takes place at the hot substrate. Several materials have been deposited successfully over wafers up to 100 mm in diameter using this technique. The actual deposition of the thin film can be done in a conventional CVD reactor cell.

As far as the reactor cell is concerned, no special features are required for the CVD of electroceramic thin films. In some cases, parts of the cell may require additional heating to prevent condensation of precursors. The susceptor material has to withstand high temperatures in an oxygen ambient or has to be coated with an inert material. In practice, silicon carbide coated graphite susceptors are used. Alternative susceptor materials are, for example, silicon or ceramic materials (e.g., Al_2O_3).

Most modern CVD systems are operated at reduced reactor pressure to minimize the role of heat instabilities due to temperature gradients. Also, since the residence time of the gas mixture is reduced at this increased linear gas velocity, homogeneous gas-phase reactions

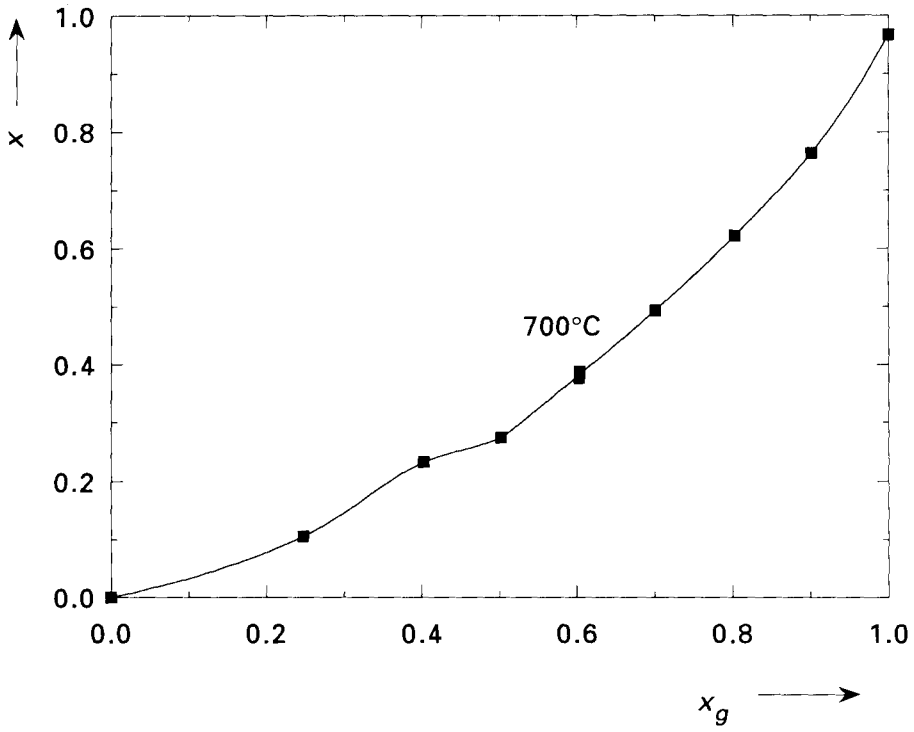

Figure 4. Composition x as a function of x_g for films deposited at 700°C.

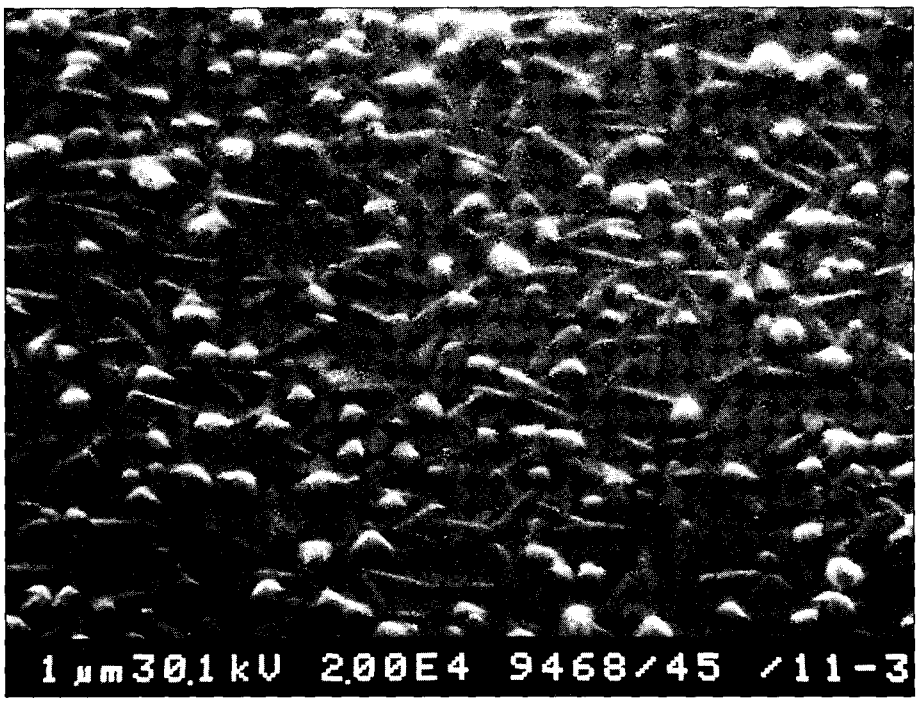

Figure 5. Scanning-electron-microscopy image of the morphology of a film with x = 0.8 and a thickness of 150 nm.

are suppressed. Generally, low-pressure operation improves the uniformity in thickness and composition of the thin film.

The Deposition of Lead Zirconate Titanate

In the following, we present results from our experiments to deposit PZT by conventional OMCVD. A number of typical problems associated with the deposition of electroceramic thin films (control of composition, hardware issues) are encountered in this materials system.

Details of the deposition system built for the deposition of electroceramic thin films are described in Reference 11. In short, it is equipped with a horizontal, rectangular reactor cell containing a rotating silicon-carbide-coated graphite susceptor supporting one 150-mm or 100-mm wafer. Precursors used are tetraethyllead (TEL), zirconiumtetra-*tertiary*butoxide (ZTB), and titaniumtetra*tertiary*butoxide (TTB). Identical alkoxide groups on the zirconium and titanium precursor suppress undesirable effects of the exchange of ligands. Special care has to be taken for handling the TEL since it is rather unhealthy. An advantage of this set of precursors is that it only calls for a moderate heating (<50°C) of the gas system. The substrates were oxidized 100-mm silicon wafers provided with a platinum electrode.

An important issue for CVD of electroceramic thin films is the control of the composition. A useful, nondestructive technique to determine composition is x-ray fluorescence (XRF). To electrically characterize the films, a blanket platinum layer was deposited by sputtering and patterned into electrodes with well-defined areas. Generally it is advantageous to also pattern the $PbZr_xTi_{1-x}O_3$ and the platinum bottom electrode. Ferroelectric properties were measured at a typical frequency of 1 kHz. The capacitor area used for the measurements described here was 10^4 μm^2 in all cases. In future devices such as nonvolatile ferroelectric memories the capacitor areas may be well under 1 μm^2.

Deposition Temperature

The deposition temperature is a major parameter in a (chemical vapor) deposition process. It determines the decomposition rate of the precursors and has a strong influence on the crystallinity and structure of the deposit.

For the deposition of $PbZr_xTi_{1-x}O_3$, the deposition temperature was systematically varied between 550 and 775°C. The partial pressures of the TTB (p_{TTB}) and

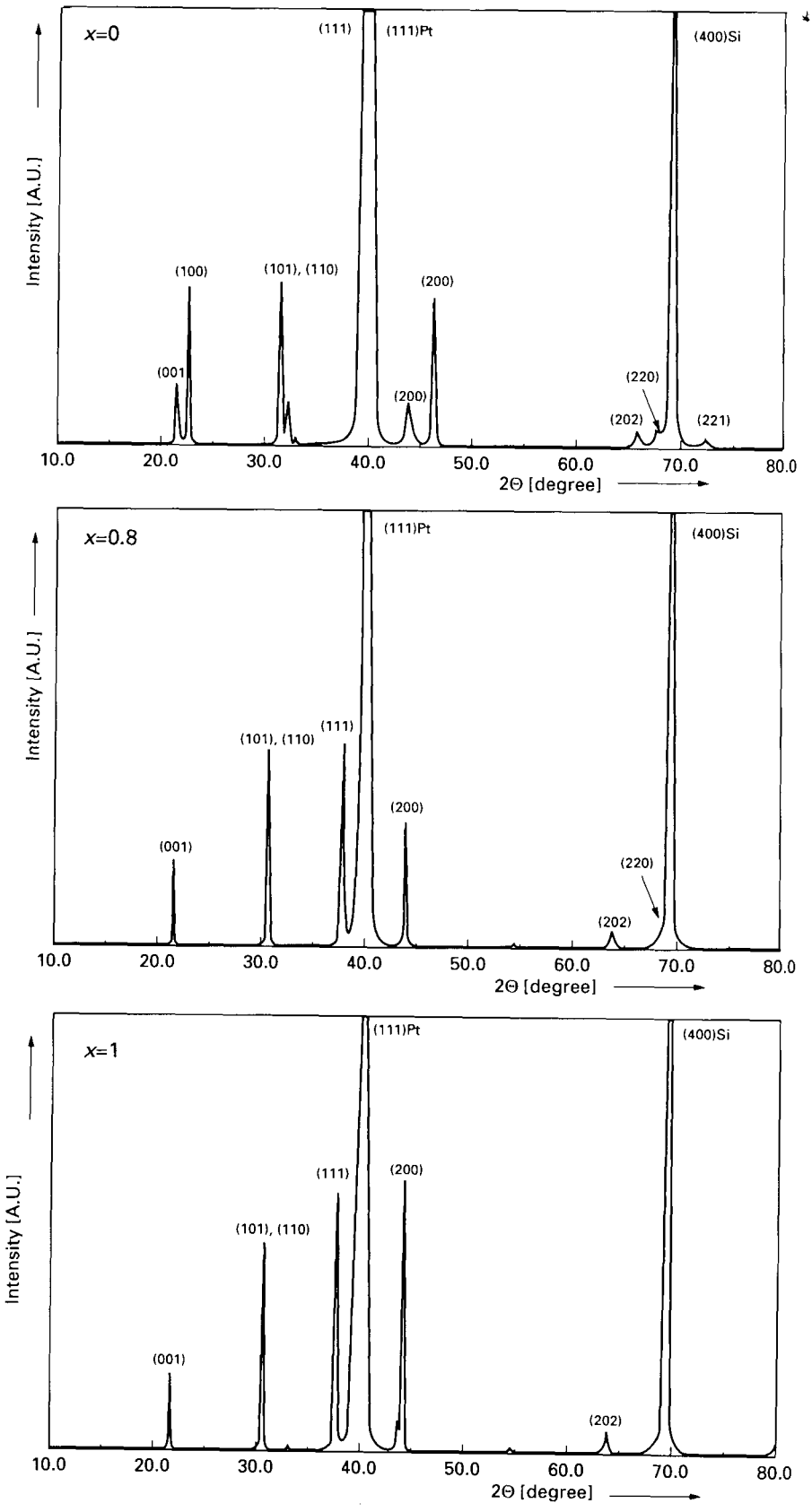

Figure 6. X-ray-diffraction patterns of $PbZr_xTi_{1-x}O_3$ films on $Pt/SiO_2/Si$ with x = 0, 0.8, and 1. Only reflections of Si, Pt, and $PbZr_xTi_{1-x}O_3$ are observed.

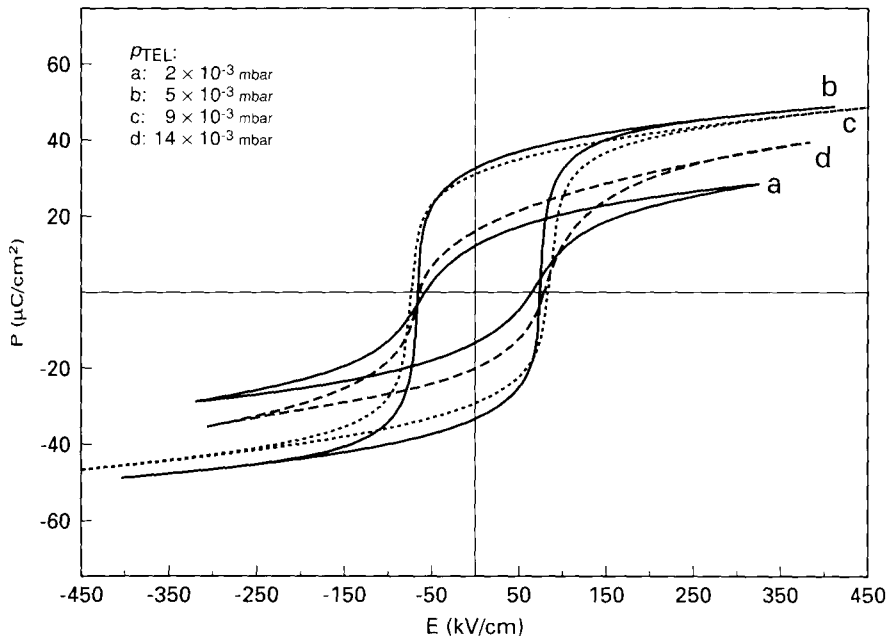

Figure 7. Hysteresis loops of $PbZr_{0.3}Ti_{0.7}O_3$ as a function of the TEL partial pressure.

ZTB (p_{ZTB}) were fixed at 2.5×10^{-3} mbar and that of the TEL (p_{TEL}) at 5×10^{-3} mbar. The cation stoichiometry (A/B = Pb/(Zr + Ti), corresponding ratio of precursors is $(A/B)g$, where g refers to the gas phase) and the composition (x = Zr/(Zr + Ti), corresponding ratio of precursors is x_g) are plotted as a function of the deposition temperature in Figure 2. The effect of a composition-controlled deposition mechanism[12] exhibits a leveling-off in A/B at the stoichiometric ratio of unity with increasing temperature. This result shows that the cation stoichiometry of the films is not very sensitive to temperature variations over the wafer above about 675°C. The occurrence of this process window is the result of the higher vapor pressure of unreacted PbO versus the vapor pressure of the PbO that has reacted with ZrO_2 and TiO_2 to form $PbZr_xTi_{1-x}O_3$. In other words, the excess PbO desorbs. In extreme cases (e.g., a very high temperature), this effect can also lead to Pb deficient films. Also for other materials systems with components having relatively high vapor pressures, for example Bi_2O_3 in $Bi_4Ti_3O_{12}$, and related systems, this effect may occur. In the case of $(Ba,Sr)TiO_3$, the individual oxides have low vapor pressures. The composition-controlled mechanism will thus not occur in this materials system and accurate temperature control is thus required.

The influence of the temperature on the $PbZr_xTi_{1-x}O_3$ depositions reveals a significant decrease in x with increasing temperature. The value for x decreases from about 0.5 to 0.2 in the temperature range of Figure 2. This implies that a spread in temperature of 25°C over the wafer will cause a change in x of about 15%. In order to obtain a good uniformity in x, it is therefore necessary to have a uniform temperature for the wafer.

Partial Pressures

Obviously the partial pressures of the precursors have an influence on the composition and deposition rates of the film. In the following, the influence of the A-site cation precursor and B-site precursors will be described for the deposition of $PbZr_xTi_{1-x}O_3$ films.

The partial pressure of TEL was varied while those of the TTB and ZTB were fixed at 2.5×10^{-3} mbar each. In Figure 3, the cation stoichiometry, Pb/(Zr + Ti), expressed as A/B and obtained for films deposited at 700°C, is plotted versus p_{TEL}. If $p_{TEL} < 4 \times 10^{-3}$ mbar, the films are lead-deficient. Above this partial pressure, a leveling-off at about the stoichiometric ratio of unity is observed. The films tend to become somewhat lead-rich for p_{TEL} higher than 8×10^{-3} mbar. This observation demonstrates that a range of TEL partial pressures can be used where stoichiometric (within experimental error of ±5%) $PbZr_xTi_{1-x}O_3$ forms at this deposition temperature (composition- controlled growth).

The ratio of zirconium to titanium in the films obviously can be varied by changing the ratio of the partial pressures of their precursors. In the following, results will be described for the deposition of $PbZr_xTi_{1-x}O_3$ with a fixed partial pressure of the TEL of 5×10^{-3} mbar. The

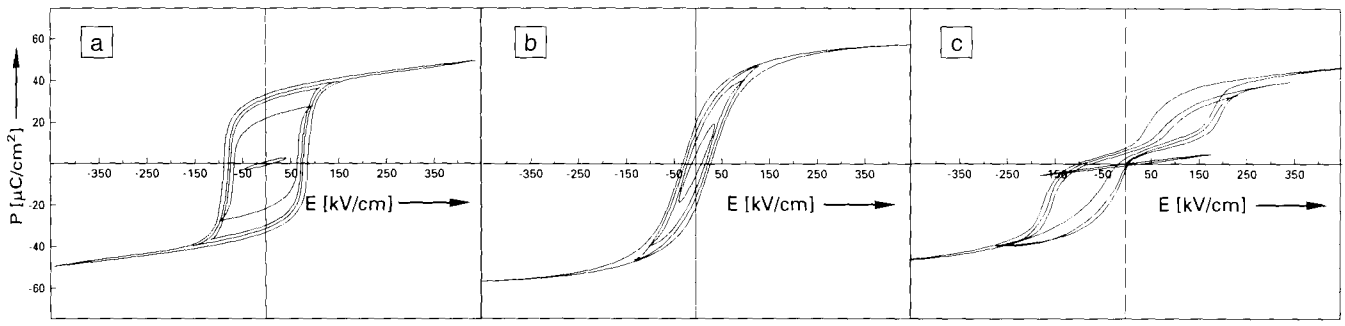

Figure 8. Hysteresis loops measured at several amplitudes of the electric field as a function of the composition x. For x = 0.1, (a) square loops are obtained. For x = 0.8, (b) the loops are much slimmer. In the case of $PbZrO_3$, (c) an antiferroelectric hysteresis loop is observed. In all three cases, the saturation polarization is about the same.

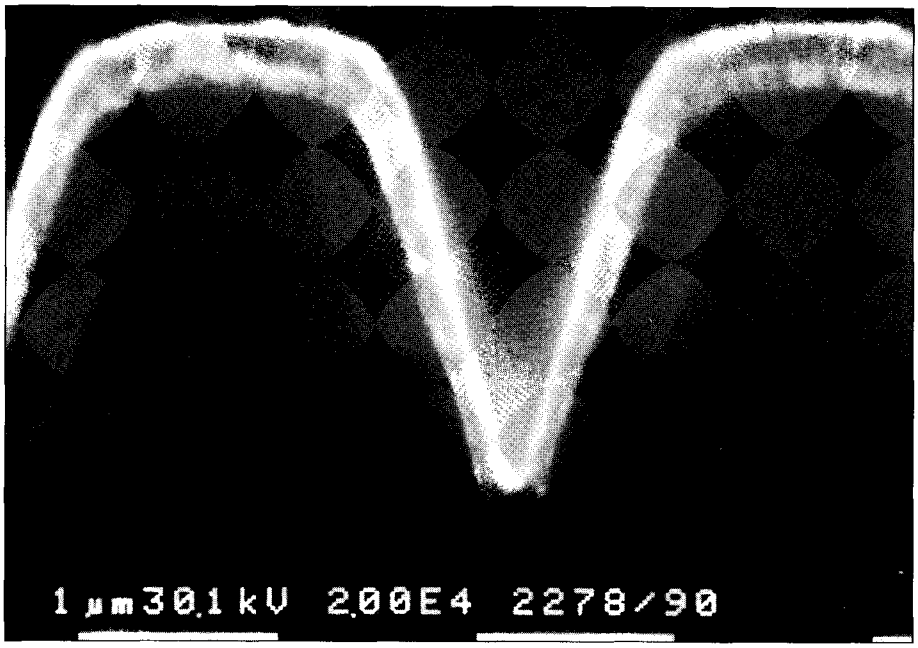

Figure 9. Scanning-electron-microscopy image of a $PbZr_xTi_{1-x}O_3$ film deposited over a trench in a silicon wafer provided with a Pt electrode.

value for $x_g = \rho_{ZTB}/(\rho_{ZTB} + \rho_{TTB})$ was varied by changing both the partial pressures of the ZTB and the TTB. The total of the ρ_{ZTB} and ρ_{TTB} was kept at 5×10^{-3} mbar so $(A/B)_g = 1$. In all cases, the films have the correct cation stoichiometry, $A/B = 1$. In Figure 4, the values for x as measured with XRF for films deposited at 700°C are plotted against x_g. A nonlinear relation between x and x_g is observed.

The surface morphology was examined by scanning electron microscopy (SEM). A representative image of the surface morphology of a film with $x = 0.8$ and a thickness of 150 nm is presented in Figure 5. Individual crystallites of a few tenths of a micrometer are observed. The crystallites seem to be rather densely packed. No large influence of the zirconium to titanium ratio on the surface morphology has been observed. Neither the temperature nor the partial pressure of the TEL, provided the stoichiometry of the films is maintained, have a large influence on the morphology. As a rule, a significant change in the morphology points at an off-stoichiometry of the films.

In Figure 6, representative XRD patterns of films on $Pt/SiO_2/Si$ with $x = 0$, 0.8, and 1.0 are presented. Only reflections due to the $PbZr_xTi_{1-x}O_3$, Pt, and Si are observed. The $PbZr_xTi_{1-x}O_3$ has a (111) preferential orientation. This is attributed to a seeding effect of the (111) Pt-electrode. This preferential orientation is less pronounced for higher values of x. The diffraction pattern can be indexed by a tetragonal structure for $x = 0$. For $x = 0.8$ and 1, the diffraction pattern is indexed by a pseudocubic structure.

Ferroelectric Properties

The hysteresis loops of the films deposited using different values for ρ_{TEL} are presented in Figure 7. The zirconium fraction x was 0.3. The lead-deficient film has a low remanent polarization (see Figure 7a). The off-stoichiometry of this film does not prevent it from being ferroelectric. The ferroelectric performance improves with increasing ρ_{TEL}. The value for remanent polarization P_r increases, and the hysteresis loops saturate at lower field strengths (see Figures 7b and 7c). For the higher values of ρ_{TEL}, the loops have a more rounded shape (see Figure 7d). This shows that the quality of the film drops. Obviously the process window as determined by the ferroelectric properties is somewhat smaller than was found based on the XRF analysis. However, the ferroelectric properties are also invariant to the TEL partial pressure within a certain (smaller) process window. The observation that the films slowly become rich in lead seems to correlate with a degradation of the ferroelectric properties.

Representative hysteresis loops for three values of x are presented in Figure 8. For $x = 0.1$ (see Figure 8a), the loop

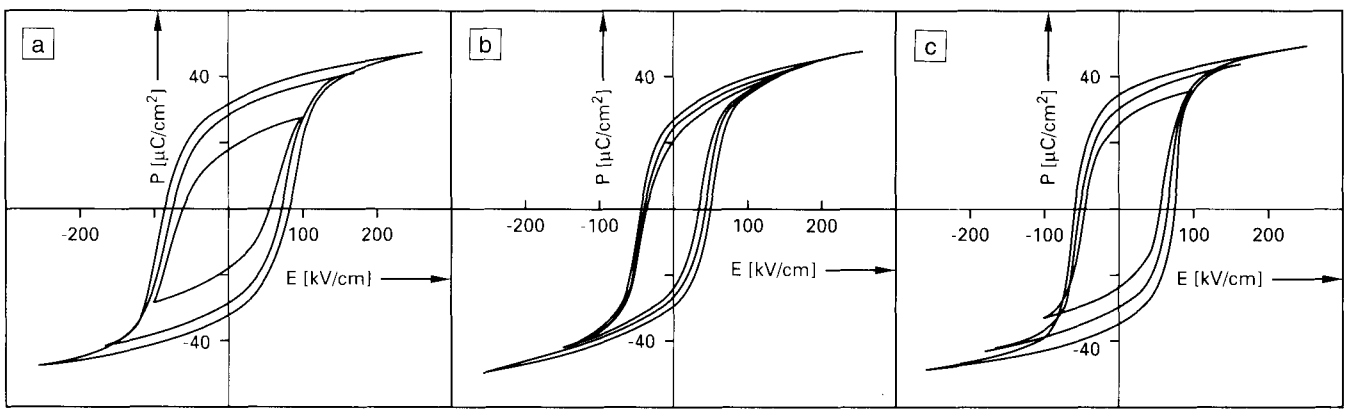

Figure 10. Hysteresis loops of ferroelectric capacitors ($PbZr_{0.5}Ti_{0.5}O_3$ thickness is 300 nm) at three stages of processing. Immediately after structuring (a), after an anneal for 5 minutes at 500°C (b), and after isolation and metallization of the ferroelectric capacitor (c).

is square-shaped and saturates at an applied field of about 300 kV/cm. With increasing x, the coercive field strength decreases, but the saturation field strength remains about the same. For films having the pseudocubic structure, slimmer loops with lower values for the coercive field strength are obtained (see Figure 8b). Also in these cases, the saturation fields are about 300 kV/cm. $PbZrO_3$ is antiferroelectric (see Figure 8c). A double hysteresis loop is observed. The remanent polarization for this material is zero. The saturation polarization is comparable to that of ferroelectric $PbZr_xTi_{1-x}O_3$.

Integration Aspects

One of the attractive features of CVD is that good step coverage can be obtained. This will become increasingly important for future devices. As an example, the deposition of $PbZr_xTi_{1-x}O_3$ over a patterned platinized silicon wafer is shown in Figure 9. The $PbZr_xTi_{1-x}O_3$ film is deposited conformally in the trench. Only at the bottom of the trench does the film thickness appear to be somewhat smaller. This is mainly due to a reduced thickness of the sputtered Pt electrode.

For the use of ferroelectric capacitors in memories, it is essential that during the deposition of the top electrode and subsequent structuring of this electrode and $PbZr_xTi_{1-x}O_3$, no significant degradation of the ferroelectric properties occurs. In Figure 10, hysteresis curves are presented for ferroelectric capacitors with a 300-nm-thick $PbZr_xTi_{1-x}O_3$ layer at three stages of integration. Immediately after the structuring of the ferroelectric capacitors, the loops have an E_c of about 80 kV/cm (see Figure 10a). P_r is about 30 $\mu C/cm^2$. Figure 10b shows that annealing the ferroelectric capacitors leads to a decrease of the coercive field strength to 45 kV/cm. The annealing causes a slight decrease of the remanent polarization. However, the reduction in E_c leads to larger polarizations at lower amplitudes. The annealing of these capacitors was also found to substantially increase the dielectric constant from 750 to 1,130 and to decrease the leakage current (measured at 5 V) from 550 nA/mm^2 to 3 nA/mm^2. The isolation and metallization causes an increase of E_c (to 64 kV/cm) and of P_r (to 33 $\mu C/cm^2$). (See Figure 10c.)

Summary and Conclusions

This article described the use of (OM)CVD for the synthesis of electroceramic thin films with emphasis on the deposition of $PbZr_xTi_{1-x}O_3$. It has been shown that $PbZr_xTi_{1-x}O_3$ films can be deposited using a conventional thermal (OM)CVD process. For many electroceramic materials of interest, the available precursors have relatively low vapor pressures. This substantially complicates the CVD process. This article describes several solutions.

In the case of $PbZr_xTi_{1-x}O_3$ deposition, good results are obtained. Control of the film composition is feasible. The zirconium fraction can be easily varied, leading to films having different ferroelectric properties. $PbZr_xTi_{1-x}O_3$ thin films were successfully integrated in ferroelectric capacitors for memory applications with little or no influence on the ferroelectric performance of capacitors.

Acknowledgment

We would like to acknowledge our colleagues at the Philips Research Laboratories.

References

1. See for example, M.L. Green, M.E. Gross, L.E. Papa, K.J. Schnoes, and D. Brasen, *J. Electrochem. Soc.* **132** (1985) p. 2677.
2. See for example, L.A. Wills, W.A. Feil, B.W. Wessels, L.M. Tonge, and T.J. Marks, *J. Cryst. Growth* **107** (1991) p. 712.
3. For high-T_c superconductors, see for example, *High Temperature Superconductors: Fundamental Properties and Novel Materials Processing*, edited by D. Christen, J. Narayan, and L. Schneemeyer (Mater. Res. Soc. Symp. Proc. **169**, Pittsburgh, 1990).
4. For $(Ba,Sr)TiO_3$, see for example, T. Kawahara, M. Yamamuka, T. Makita, J. Naka, A. Yuuki, N. Mikami, and K. Ono, *Jpn. J. Appl. Phys.* **33** (1994) p. 5129.
5. For $MgAl_2O_4$, see for example, J. Zhang, G.T. Stauf, R. Gardiner, P. Van Buskirk, and J. Steinbeck, *J. Mater. Res.* **9** (1994) p. 1333.
6. P. Kirlin, S. Bilodeau, and P. Van Buskirk, *Integrated Ferroelectrics* 7 (1995) p. 307.
7. R. Hiskes, S.A. DiCarolis, R.D. Jacowitz, Z. Lu, R.S. Feigelson, R.K. Route, and J.L. Young, *J. Cryst. Growth* **128** (1993) p. 781.
8. M. Okada and K. Tomita, U.S. Patent No. 4,792,463 (1988).
9. J.L. Vossen and W. Kern, eds., *Thin Film Processes* (Academic Press, New York, 1978).
10. L.D. McMillan, T.L. Roberts, M.C. Scott, and C.A. Paz de Araujo, in *Proc. 4th Int. Symp. Integrated Ferroelectrics* (Monterey, 1992) p. 666.
11. M. de Keijser, P.J. van Veldhoven, and G.J.M. Dormans, in *Ferroelectric Thin Films III*, edited by E.R. Myers, B.A. Tuttle, S.B. Desu, and P.K. Larsen (Mater. Res. Soc. Symp. Proc. **310**, Pittsburgh, 1993) p. 223.
12. G.J.M. Dormans, P.J. van Veldhoven, and M. de Keijser, *J. Cryst. Growth* **123** (1992) p. 537. □