Thickness dependence of the switching voltage in all-oxide ferroelectric thin-film capacitors prepared by pulsed laser deposition

Citation for published version (APA):

DOI:
10.1063/1.363961

Document status and date:
Published: 01/01/1997

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain.
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 17. Sep. 2020
Thick Film dependence of the switching voltage in all-oxide ferroelectric thin-film capacitors prepared by pulsed laser deposition

J. F. M. Cillessen, a) M. W. J. Prins, and R. M. Wolf b)
Philips Research Laboratories, Prof. Holstlaan 4 5656 AA Eindhoven, The Netherlands

(Received 3 October 1996; accepted for publication 2 December 1996)

Thin-film ferroelectric capacitors consisting of PbZrTiO3 sandwiched between La0.5Sr0.5CoO3 electrodes have been deposited using pulsed laser deposition. The combination of oxidic perovskite-type materials results in capacitors with a coercive field (Ec) which is comparable with values for bulk ceramics. Textured thin-film capacitors with a columnar microstructure show lower switching voltages than epitaxial films. No thickness dependence of Ec and a good endurance up to 1011 cycles have been observed for epitaxial as well as textured capacitors with oxidic electrodes. In contrast, capacitors with a metallic top electrode show an increase of Ec with decreasing thickness of the ferroelectric layer. We show that charge injection can explain the experimentally observed increase of Ec with decreasing ferroelectric layer thickness. An overview is given of the growth conditions needed for PbZrTiO3 films, because the precise stoichiometry of the utmost importance for the capacitor quality. © 1997 American Institute of Physics.

I. INTRODUCTION

PbTiO3 and its lanthanum and/or zirconium substituted derivatives, forming the [Pb,La][Zr,Ti]O3 system, are the most intensively studied ferroelectric materials. Thin films of these materials are interesting for electronic device applications such as nonvolatile memories, infrared and pressure sensors, and integrated optical switches and modulators.1 In thick ceramic capacitors, the influence of grain size and grain boundaries has been studied in detail.2 In thin-film capacitors, particularly the influence of the electrode-ferroelectric interface is more pronounced. This is demonstrated by an increased switching voltage (Vsw) of ferroelectric thin films compared with extrapolated values of coarse grained ceramics. The integrated application of ferroelectric materials requires films with a submicron thickness to comply with IC voltages of a few volts.3 This calls for a detailed comprehension of ferroelectric thin films and electrodes. Furthermore, ferroelectric capacitors for memory applications should withstand more than 1011 switching cycles.

The beneficial combination of oxidic electrodes and oxidic ferroelectrics was first shown by Pulvari and Srour4 in 1969. In their work, the use of doped SnO2 electrodes as x voltages in textured PbZrX0.53 Ti1–x O3 single-crystal platelets. Several groups reported on switching voltages of a few volts.3 This calls for a detailed comprehension of ferroelectric thin films and electrodes. Furthermore, ferroelectric capacitors for memory applications should withstand more than 1011 switching cycles.

In this article, the influence of the electrode material is studied by analyzing the switching voltage as a function of the PbZrTi1–x O3 thickness. Results are compared for PbZrTi1–x O3 films on oxidic bottom electrodes, with either oxidic or metallic top electrodes. A one-dimensional model is proposed to explain the observed thickness dependence of the switching potential. Second, the influence of the PbZrTi1–x O3 microstructure on the switching characteristic of all-oxide capacitors is investigated by comparing single-crystalline capacitors deposited on (100)MgO with textured layers grown on (100)Si. Additionally, the endurance of our capacitors is studied.

II. EXPERIMENTAL ASPECTS

Thin films in a capacitor geometry are deposited using the pulsed laser deposition (PLD) technique. An ArF excimer laser beam (with a wavelength λ=193 nm, a pulse width of 15 ns, and a repetition rate of 2 Hz) is focused onto a rotating, sintered target. For the deposition of LaxeSr0.5CoO3 (the electrode material) a stoichiometric target is used, whereas for PbZr0.5Ti0.47O3 (a chemical composition with a low ferroelectric switching field11,12) a PbO-enriched target is used. A detailed description of the stoichiometric growth of PbZr0.5Ti0.47O3 and the reason for PbO target enrichment is presented in the Appendix. The fluence of the incident laser beam on the target is 4 J/cm2 and the base pressure of the vacuum chamber is in the 10−7 mbar range. Films are deposited onto a heated substrate in a 0.2 mbar oxygen partial pressure ambient. After the growth, the sample is cooled to room temperature (10 °C/min) in 1 bar of oxygen. The films are analyzed by secondary-ion-mass spectrometry (SIMS), x-ray diffraction (XRD), and x-ray fluorescence spectroscopy (XRF).

a)Electronic mail: cillessn@natlab.research.philips.com
b)Present address: Philips Laboratories, Scarborough Road, Briarcliff Manor, New York.
Three types of samples are prepared as shown in Fig. 1. Samples of type A consist of a MgO(100) substrate with a heteroepitaxial La$_{0.5}$Sr$_{0.5}$CoO$_3$ bottom electrode and a heteroepitaxial PbZr$_{0.53}$Ti$_{0.47}$O$_3$ film. La$_{0.5}$Sr$_{0.5}$CoO$_3$ was chosen since it exhibits a cubic lattice parameter of 0.383 nm$^3$ and a perovskite-type structure, which both match the ferroelectric material. It has been shown that heteroepitaxial growth of PbZr$_{0.53}$Ti$_{0.47}$O$_3$ (0.404 nm) is possible on top of this electrode material. Gold top electrodes are ex situ sputtered in a scanning electron microscope (SEM)-coating unit (20 kV, 20 mA) onto the heterostructure using a contact mask. The B-type samples are similar to the A types, but the top electrodes consist of in situ grown La$_{0.5}$Sr$_{0.5}$CoO$_3$. The C-type samples are the same as the B type, but are grown on Si (including native oxide).

La$_{0.5}$Sr$_{0.5}$CoO$_3$ films are deposited at a substrate temperature of 650 °C (MgO) and 590 °C (Si). The La$_{0.5}$Sr$_{0.5}$CoO$_3$ thickness is 70 nm on MgO and 120 nm on Si. PbZr$_{0.53}$Ti$_{0.47}$O$_3$ films with thicknesses $d$ ranging from 50 to 1000 nm are in situ deposited on top of the La$_{0.5}$Sr$_{0.5}$CoO$_3$ films. The substrate temperature used for PbZr$_{0.53}$Ti$_{0.47}$O$_3$ deposition is 587 ± 2 °C (see Appendix). Subsequently, 70 nm La$_{0.5}$Sr$_{0.5}$CoO$_3$ top electrodes are in situ deposited at 587 °C. In order to ease contacting, top electrodes are silver coated (ex situ sputtered). The La$_{0.5}$Sr$_{0.5}$CoO$_3$-Ag top layers are structured to form electrode dots of varying sizes using photolithographic processing and Ar-ion etching.

The switching voltage $V_{sw}$ and remnant polarization $P_r$ are determined using a Sawyer–Tower circuit. $V_{sw}$ is also determined by $C$–V analyses using a probing ac voltage of 0.05 V at 10 kHz and a voltage sweep at a rate of 0.5 V/s. The endurance of a C-type capacitor: PbZr$_{0.53}$Ti$_{0.47}$O$_3$ thickness 80 nm.

FIG. 1. Three types of samples prepared: all layers were in situ grown by PLD except for the sputtered Au electrode. Thickness $d$ is variable.

III. RESULTS AND DISCUSSION

We reported the growth and microstructure of La$_{0.5}$Sr$_{0.5}$CoO$_3$ films on MgO and Si substrates in an earlier paper. Several other groups also reported on these subjects. Despite the 9.8% lattice mismatch between La$_{0.5}$Sr$_{0.5}$CoO$_3$ and (100)MgO, heteroepitaxial growth is observed in XRD pole-figures and TEM analyses. XRD patterns of La$_{0.5}$Sr$_{0.5}$CoO$_3$ films on MgO(100) showed only sharp (00l) diffraction peaks and a lattice spacing of 0.382 ± 0.002 nm was determined. La$_{0.5}$Sr$_{0.5}$CoO$_3$ films are smooth, shiny, and black in appearance. The resistivity of epitaxial La$_{0.5}$Sr$_{0.5}$CoO$_3$ films is 1.7 ± 0.2×10$^{-4}$ Ω cm, a value which is slightly lower than the reported literature value for bulk ceramics. For the growth of La$_{0.5}$Sr$_{0.5}$CoO$_3$ films on Si substrates (including native oxide), we observed a columnar microstructure with an average column diameter of 40 nm. For films deposited at 587 °C, SIMS analysis indicates only a slight interdiffusion between La$_{0.5}$Sr$_{0.5}$CoO$_3$ and Si. The resistivity of these La$_{0.5}$Sr$_{0.5}$CoO$_3$ films is comparable with our epitaxial films on MgO. Deposition on Si substrates at temperatures above 650 °C results in severe interdiffusion. This is confirmed by the presence of Sr silicates in XRD patterns as well as a strong increase of the La$_{0.5}$Sr$_{0.5}$CoO$_3$ resistivity.

PbZr$_{0.53}$Ti$_{0.47}$O$_3$ films grown on La$_{0.5}$Sr$_{0.5}$CoO$_3$ electrodes on MgO (capacitor types A and B) are heteroepitaxial as indicated by the XRD pattern in Fig. 2(a). A detailed growth study of epitaxial PbTiO$_3$ films on a variety of materials with different lattice parameters was published earlier. For the C-type capacitors, a columnar growth with a preferential (00l) orientation is observed for both La$_{0.5}$Sr$_{0.5}$CoO$_3$ and PbZr$_{0.53}$Ti$_{0.47}$O$_3$ films. This can be described by grain-to-grain epitaxy; each PbZr$_{0.53}$Ti$_{0.47}$O$_3$ grain shows an epitaxial relation with a grain from the bottom electrode and the top electrode. The XRD pattern of such capacitors [Fig. 2(b)] indicates the presence of two distinct La$_{0.5}$Sr$_{0.5}$CoO$_3$ lattice parameters of 0.381 and 0.384 nm, respectively. A

FIG. 2. XRD pattern ($\theta$–2$\theta$ scan, Cu $K\alpha$ radiation) of: (a) B-type capacitor: PbZr$_{0.53}$Ti$_{0.47}$O$_3$ thickness 80 nm, (b) C-type capacitor: PbZr$_{0.53}$Ti$_{0.47}$O$_3$ thickness 80 nm.
shift of the bottom electrode lattice parameters is most probably caused by built-in strain.

Typical hysteresis loops, measured for two different voltage sweeps, for C-type samples are shown in Fig. 3. $P_r$ values are $20 \pm 5 \mu C/cm^2$. For all samples the switching potential ($V_{sw}$) as a function of the PbZr$_{0.53}$Ti$_{0.47}$O$_3$ thickness is shown in Fig. 4. The differential coercive fields $\Delta V_{sw}/\Delta d$, calculated from the slopes for different types of capacitors are $21 \pm 3$ (type A), $23 \pm 4$ (type B), and $12 \pm 4$ kV/cm (type C). It is striking that the slopes for the A- and B-type samples are similar. This shows that the differential coercive field is independent on the type of top electrode and directly refers to the intrinsic properties of the PbZr$_{0.53}$Ti$_{0.47}$O$_3$ film. The C-type samples show a significantly lower coercive field, approaching the value for bulk material. The microstructural difference between the B- and C-type samples indicates that a textured microstructure facilitates ferroelectric switching. From bulk ceramics it is well known that the switching field is related to the microstructure. In our single crystalline samples (B type), ferroelectric domain wall motion is obviously hindered by the lack of grain boundaries, which results in an increase of $V_{sw}$. Studies on [Pb,La](Zr,Ti)O$_3$ capacitors by Ramesh et al. also indicate a lowering of $V_{sw}$ for a textured microstructure.

From Fig. 4, it appears that the extrapolated switching potential to zero film thickness is different for ex situ sputtered gold (A type) and in situ grown La$_{0.5}$Sr$_{0.5}$CoO$_3$ top electrodes (B and C type). For the A-type samples, the intercept is 1 V, whereas for the B- and C-type samples the intercepts are close to zero. As a consequence, $E_c (= V_{sw}/d)$ for the A-type samples is increasing for films below 500 nm. These results suggest that the offset voltage as observed for the A-type samples, is related to an interface effect rather than to a bulk effect. A model to explain the observed thickness dependence of the switching potential is described in Sec. IV.

For applications, the endurance of ferroelectric capacitors is important. The results of Fig. 5 show that C-type samples do not degrade within $10^{11}$ switching cycles. The switching polarization tends to increase slightly with the number of switching cycles. This is attributed to a poling of the capacitor, i.e., a field induced effect which causes an increasing part of the capacitor to switch. Since the ionic displacement in pseudocubic PbZr$_{0.53}$Ti$_{0.47}$O$_3$ is small, the energy involved to reorient domains is relatively small. Since
most of the PbZr$_x$Ti$_{1-x}$O$_3$ compositions are efficient piezoelectric materials, ferroelectric capacitors must be able to withstand mechanical stresses induced by electrical fields. We assume that the good endurance of our capacitors is related to the chemical stability (low interdiffusion) as well as the mechanical strength of oxidic interfaces.

In addition to the experiments described, heteroepitaxial capacitors consisting of PbZr$_{0.53}$Ti$_{0.47}$O$_3$ sandwiched between SrRuO$_3$ electrodes on SrTiO$_3$(100) substrates have also been investigated. The lattice match of SrRuO$_3$ ($a = 0.394$ nm) with the ferroelectric ($a = 0.404$ nm) as well as the substrate ($a = 0.390$ nm) is better than for the above-mentioned samples. However, we did not observe an improved capacitor quality for SrRuO$_3$ electrodes as compared with La$_{0.5}$Sr$_{0.5}$CoO$_3$ in terms of $E$ or endurance.

IV. INJECTION MODEL

Our measurements as well as the experimental results of other publications$^{19,20}$ demonstrate that in ferroelectric thin-film capacitors with at least one non-oxidic electrode, $E_f$ increases with decreasing PbZr$_x$Ti$_{1-x}$O$_3$ thickness. In other words, the switching voltage of thin-film capacitors is larger than expected from extrapolated bulk ferroelectric properties. Although it is clear that the presence of the electrode/ferroelectric interfaces is decisive, the nature of the interfacial disorder and the physical properties of the near-electrode material are still under debate. In this section, we describe a one-dimensional model of a ferroelectric thin-film capacitor, we indicate why charge injection into the near-electrode regions can be of importance, and explain the consequence of charge injection for the switching potential.

In the thin-film capacitor, we define a near-electrode region with an electric polarizability which is different from the polarizability of the ferroelectric material.$^{21}$ This is schematically shown in Fig. 6(a), for the case of a single nonideal near-electrode region.$^{22}$ Region “f” refers to the ferroelectric part of the capacitor, while region “n” corresponds to the nonideal near-electrode layer. $\sigma_f$ is the charge density present on electrode (1), $\sigma_n$ refers to the charge density on electrode (2). It follows from Gauss’ law that $\sigma_f = D_n = \varepsilon_0 E_n + P_n$, where $D_n$ equals the dielectric displacement, $E_n$ is the electric field, and $P_n$ is the electric polarization, all parameters in the $n$ region. In order to estimate the electric field in the $n$ layer, let us assume that the $n$ region shows a dielectric behaviour. In that case $P_n = (\varepsilon_r - 1) E_n$, where $\varepsilon_r$ is the relative permittivity, and the electric field in the $n$ region is given by: $E_n = \sigma_f / \varepsilon_0 \varepsilon_r$. When $\varepsilon_r$ equals 100 or less, and for a charge density of the order of 10 $\mu C/cm^2$ (see Sec. III), we find an electric field in the $n$ region of 1 MV/cm or larger, such that charge injection can realistically take place.

A simple equivalent electrical circuit to describe charge injection is shown in Fig. 6(b). The charge density injected across the $n$ region, into trap states for example, is described by $\sigma_{nj}$ [Fig. 6(a)]. Charge exchange through the $n$ layer across capacitor $C_n$ is allowed by the nonlinear resistor $R_n$. Although the $n$ and $f$ layers are of a different nature, it is clear in that both layers the charge displacement involves the dissipation of energy and gives rise to a hysteresis behavior. The hysteresis of the $f$ layer is due to ferroelectricity, i.e., an ionic displacement within each unit cell, whereas the hysteresis behaviour of the $n$ layer is caused by charge exchange between the electrode and near-electrode trap states. In the $n$ layer, the “coercive field” is determined by the threshold field for charge transport across that layer, i.e., the field needed to inject carriers or to liberate previously injected trapped charge. The total switching potential $V_{sw}$ of the serial arrangement of the $n$ and $f$ layer is the sum of the individual switching potentials,$^{23}$

$$V_{sw} = V_{sw,n} + V_{sw,f} = d_n E_{th,n} + d_f E_{c,f} = d_n (E_{th,n} - E_{c,f}) + d_{tot} E_{c,f}, \quad (1)$$

where $d_{tot} = d_n + d_f$ is the total film thickness, $d_n$ and $d_f$ represent the thickness of layer $n$ and $f$ respectively, $E_{th,n}$ is the threshold field in layer $n$ and $E_{c,f}$ is the coercive field in layer $f$. As long as the threshold electric field $E_{th,n}$ is not reached, no charge is injected into the $n$ layer; then $V_{sw,n} = 0$ and the switching potential of the total capacitor equals to the coercive potential of the ferroelectric layer. In the case that injection into the $n$ layer takes place, the switching potential of the total capacitor is larger than the coercive potential of the single ferroelectric layer. Equation (1) is in good agreement with the experimental results of Fig. 4, showing a linear dependence of the switching potential on the total film thickness, and a nonzero value of the switching potential towards zero film thickness. The increase of the observed switching voltage as shown in Fig. 4 cannot be explained by assuming only a series capacitor as an electrical equivalent for the $n$ layer (and thus neglecting charge injection). In such a case the switching potential is not changed although a higher voltage is required for charge displacement. This is experimentally demonstrated in Fig. 7. In Fig. 4 the differential coercive field $\Delta V_{sw}/\Delta d_{tot}$ equals the true coercive field of the ferroelectric layer $E_{c,f}$. The equivalence of the PbZr$_{0.53}$Ti$_{0.47}$O$_3$ films in the A-type as well as the B-type samples is confirmed by a similar slope for these capacitors. This has already been discussed in Sec. III, where ‘the bulk of the PbZr$_{0.53}$Ti$_{0.47}$O$_3$ film’ refers to $f$ region from this model. From the experimentally determined
The increase of the coercive voltage does not change when the additional capacitor is introduced in the circuit. Only a series capacitor cannot explain the switching field.

From our model, we expect the dependence of the switching field \( \sqrt{d_{\text{tot}}/V_{\text{sw}}} \) on the total film thickness to be reduced if charge injection is absent. Charge injection is avoided by using interfaces which do not affect the polarizability of the near-electrode material. In our experiments, we observe superior characteristics for PbZr\(_{0.53}\)Ti\(_{0.47}\)O\(_3\) capacitors sandwiched between oxidic electrodes (type B and C), when compared to the non-ideal behavior of capacitors with an \( \text{ex situ} \) sputtered Au top electrode (type A). The Au electrodes can affect the polarizability of the near-electrode PbZr\(_{0.53}\)Ti\(_{0.47}\)O\(_3\) material by the formation of point defects or a space-charge layer, or by local compositional variations. The latter might be introduced by preferential sputtering of oxygen or lead from the topmost PbZr\(_{0.53}\)Ti\(_{0.47}\)O\(_3\) layer during deposition of the metallic electrode. The use of \( \text{in situ} \) grown oxidic electrodes prevents such problems.

\[ Y \text{-axis intercept in Fig. 4 (between 0 and 1 V switching potential), and a threshold for charge transport (} E_{\text{th,n}} \text{) of the order of 1 MV/cm (} E_{c,f} \text{ is nearly two orders of magnitude smaller), we estimate the thickness of the } n \text{ layer to be 10 nm or less in our samples.} \]

\[ \text{V. CONCLUSIONS} \]

The switching of capacitors with a metallic (\( \text{ex situ} \) sputtered Au) electrode requires higher voltages than capacitors with \( \text{in situ} \) grown oxidic electrodes. The higher switching voltage can be explained by charge injection into a nanometer-thick layer near the electrode. Second, when using only oxidic electrodes, the switching voltage is lower for textured ferroelectric layers (grown on Si) than for heteroepitaxial layers (on MgO). Finally, all-oxide ferroelectric capacitors can withstand more than 10\(^{11}\) switching cycles. Summarizing, without the need for an epitaxial relation with the substrate, thin-film PbZr\(_{0.53}\)Ti\(_{0.47}\)O\(_3\) capacitors combined with oxidic electrodes are interesting candidates for low-voltage switching applications.

\[ \text{ACKNOWLEDGMENTS} \]

The authors thank P. K. Larsen and G. L. M. Kamp-schoer for ferroelectric analyses. They also acknowledge P. C. Zalm and R. C. M. de Kruijf for SIMS analyses, M. Kraan and W. C. Keur for target preparations, J. B. Giesbers for microstructuring, and M. H. J. Bekkers for XRF analyses. Furthermore, they thank D. M. de Leeuw, P. W. M. Blom, L. F. Feiner, and M. S. de Keijser for stimulating discussions.

\[ \text{APPENDIX: THE GROWTH OF PbZr}_x\text{Ti}_{1-x}\text{O}_3 \text{ FILMS} \]

The preparation of ferroelectric capacitors requires a detailed study on the stoichiometry of the ferroelectric component. In this Appendix we describe the conditions needed for the growth of high quality PbZr\(_x\)Ti\(_{1-x}\)O\(_3\) films and discuss the reactions involved in the formation of this material. From the bulk chemistry it is known that single-phase PbTiO\(_3\) can be prepared at temperatures as low as 160 °C by precipitation from aqueous solutions.\(^{25}\) For vacuum deposited crystalline thin films, temperatures above 350 °C have been reported.\(^{26}\) At higher substrate temperatures, the crystalline quality and density of the film significantly increases due to the enhanced surface mobility of the species deposited. Especially for epitaxial films with a low orientational spread (narrow XRD rocking curve), a substrate temperature around 600 °C or higher is preferred. A second reason for the use of high temperatures, is the possible formation of the nonferroelectric pyrochlore-type phase Pb\(_5\)Ti\(_3\)O\(_9\) below 400 °C. It is difficult to convert this material into the perovskite-type phase by post-deposition annealing due to its high chemical stability. The formation of pyrochlore-type phases will not be discussed in this article. It is a generally known problem for this materials system and is well documented in the literature.\(^{27}\)

During the deposition process, species approaching the substrate may either adsorb to the surface, form PbZr\(_x\)Ti\(_{1-x}\)O\(_3\), and adhere to the substrate, or desorb from the surface before formation of the preferred compound can take place. Despite the presence of a variety of species in the plasma plume, the major components involved in the formation of PbZr\(_x\)Ti\(_{1-x}\)O\(_3\) can be sketched as shown below:

\[
\text{Pb}_g \rightarrow (2) \rightarrow \text{Pb}_{\text{ads}} \\
\text{Pb}_g + \frac{3}{2}\text{O}_2 \rightarrow (3) \rightarrow \text{PbO}_g \rightarrow (4) \rightarrow \text{PbO}_{\text{ads}} \\
\text{Ti}_g + \text{O}_2 \rightarrow (5) \rightarrow \text{TiO}_2 \rightarrow (6) \rightarrow \text{TiO}_2 \text{ atm} \\
\text{Zr}_g + \text{O}_2 \rightarrow (7) \rightarrow \text{ZrO}_2 \rightarrow (8) \rightarrow \text{ZrO}_2 \text{ atm} \\
\text{PbO}_{\text{ads}} + (1-x)\text{TiO}_2 \rightarrow (9) \rightarrow \text{PbZr}_x\text{Ti}_{1-x}\text{O}_3 \text{ atm} \\
\]

According to these equations four species are involved in the formation of PbZr\(_x\)Ti\(_{1-x}\)O\(_3\), namely, TiO\(_2\), ZrO\(_2\), Pb, and PbO. For the following description, a substrate temperature of 600 °C is assumed. The relevant properties of species at the used growth temperature are listed in Table I. Ablation from oxidic targets will produce the oxidized species as represented in bold in Eqs. (2)–(9). Due to the large heat of formation a reduction of TiO\(_2\) or ZrO\(_2\) \([\text{Eqs. (5) and (7)}] \) in the plasma is not expected for oxygen partial pressures higher than \(10^{-9}\) mbar.\(^{28}\) Furthermore, the affinity of TiO\(_2\) and ZrO\(_2\) towards oxidic surfaces and the low vapor pressure of both species imply a sticking probability of one \([\text{Eqs. (6) and (8)}] \). As a consequence TiO\(_2\) and ZrO\(_2\) will be present at the substrate surface in the same ratio as in the target.\(^{29}\) This
TABLE I. Properties of the species of importance for the formation (Ref. 32) of PbZr$_{1-x}$Ti$_x$O$_3$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Delta G_{298}^{\text{sol}}$ (kJ/mol)</th>
<th>Vapor pressure at 600 °C (see Ref. 33) (mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>3.5 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>PbO</td>
<td>-292.7</td>
<td>1.5 x 10^{-4}</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>-1010.0</td>
<td>$&lt;10^{-8}$</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>-1163.7</td>
<td>$&lt;10^{-8}$</td>
</tr>
<tr>
<td>PbTiO$_3$</td>
<td>-1319.8</td>
<td></td>
</tr>
</tbody>
</table>

is different for PbO, which exhibits a much smaller heat of formation at the temperature used. Therefore a reduction towards metallic lead is likely to take place. The tendency of Pb to evaporate is high, because of the high vapor pressure. Moreover, the sticking probability for metallic Pb on oxidic surfaces is expected to be low (Eq. 2). According to Eq. (3), the reduction of PbO can be suppressed by applying a high oxygen pressure during deposition. An additional difficulty which might cause a lead deficiency in the film is the high vapor pressure of PbO. In summary, this means that a competition takes place between the formation of PbZr$_{1-x}$Ti$_x$O$_3$ (which is thermodynamically likely, due to the large $\Delta G_{298}^{\text{sol}}$) and the desorption of PbO [Eq. (4)].

Here, we analyze the precise cation stoichiometry [Pb]/[Ti] for films of PbTiO$_3$, which is the basic compound of the PbZr$_{1-x}$Ti$_x$O$_3$ materials system. The growth of PbTiO$_3$ films at elevated temperature is controlled by three important parameters: the target composition, the oxygen partial pressure, and the substrate temperature during deposition. Experiments are carried out with a fixed target composition using various deposition temperatures and oxygen partial pressures. Targets consist of 70 wt % PbTiO$_3$ and 30 wt % PbO$^{30}$ which corresponds with a molar ratio [Pb]/[Ti] = 1.58. First, the cation stoichiometry as a function of the substrate temperature is investigated. The [Pb]/[Ti] ratio recovered in the film for temperatures below 400 °C is similar to the target composition [Fig. 8(a)]. This confirms that stoichiometry is retained during the transport of material from the target into the gas phase. When the substrate temperature is increased, the elemental composition of the film starts to deviate from the target. The reduced [Pb]/[Ti] ratio in the film is therefore attributed to a reduced sticking probability for lead at high substrate temperatures. Second, the influence of the oxygen partial pressure during deposition on the cation stoichiometry in the film is analyzed. As shown in Fig. 8(b), an oxygen partial pressure higher than 3 x 10^{-2} mbar is necessary to shift the equilibrium of Eq. (3) to the right-hand side. Below the critical pressure of 3 x 10^{-2} mbar a multiphase film with an overall Pb deficiency is formed consisting of PbZr$_{1-x}$Ti$_x$O$_3$, anatase-TiO$_2$ and ZrO$_2$. This is confirmed by XRD patterns and XRF elemental analyses. Similar critical oxygen pressures have been obtained by Tabata et al.$^{26}$

As a conclusion, the observations have serious implications for the growth of epitaxial PbZr$_{1-x}$Ti$_x$O$_3$ films: once a certain target composition (viz. the excess PbO) is chosen, the deposition parameters regarding the oxygen partial pressure as well as the substrate temperature are fixed.

10 Charge injection in ferroelectric thin films has already clearly been identified in field-effect transistors with a ferroelectric gate insulator, see, for example, S.-Y. Wu, IEEE Trans. Electron Devices 21, 499 (1974), and C. H. Seager, D. McIntyre, B. A. Tuttle, and J. Evans, Integr. Ferroelectr. 6, 47 (1995).
11 Generally, bulk ceramic properties of ferroelectrics strongly depend on the preparation route (grainsize, density). This is reflected by scattering of physical parameters of PbZr$_{1-x}$Ti$_x$O$_3$, the remnant polarization $P_r = 40 \ \mu C/cm^2$, the coercive field $E_c = 8 – 13 \ \text{kV/cm}$ and the relative permittivity $\varepsilon_r$ ranges between 800 and 1000.
12 Landolt-Börnstein, 16a, Ferro-electrics and related substances, subvolume on oxides, pp. 119–125 (Ilcda).
13 Rectified value for JCPDS La$_{0.5}$Sr$_{0.5}$CoO$_3$, filenr. 36–1394.
16 Selected area electron diffraction (SAED) analyses on cross-section TEM samples in our previous studies showed a doubling of the lattice parameter in La$_{0.5}$Sr$_{0.5}$CoO$_3$ films (Ref. 7). In our films, this is definitely not the result of the specimen preparation for XTEM as suggested by Ghonge et al. in S. G. Ghonge, E. Goo, R. Ramesh, T. Sands, and V. G. Keramidas, Appl. Phys. Lett. 63, 1628 (1993). Doubling of the lattice parameter is a phenomenon which is often found in perovskite-type materials. It can be observed using neutron or electron diffraction analyses. In contrast to

FIG. 8. Cation stoichiometry of PbTiO$_3$ films, analyzed by XRF: (a) [Pb]/[Ti] ratio as a function of the substrate temperature using an oxygen partial pressure of 0.2 mbar, (b) [Pb]/[Ti] ratio as a function of the oxygen partial pressure at 587 °C. The lines are guides to the eye.
XRD, these techniques are capable of detecting the lattice-parameter doubling, due to a higher sensitivity for the oxygen positions in the unit cell. The unit cell doubling, however, does not change the in-plane lattice relation and therefore epitaxy is not affected. Literature on this subject. Landolt Bornstein III, 7e: PbMg\(_{0.33}\)Nb\(_{0.67}\)O\(_3\), p. 521; H. B. Krause and D. L. Gibbon, Z. Krist, 134, 44 (1971); D. M. de Leeuw, C. A. H. A. Mutsaers, R. A. Steeman, E. Frikkee, and H. W. Zandbergen, Physica C 158, 391 (1989).


22 The addition of a nonideal near-electrode layer (2) does not modify the conclusions of this section.

23 In practice the switching potential of a thin film is not a constant, but weakly depends on the maximum field experienced in a given hysteresis loop. For clarity this effect is neglected in the present analysis.


28 A partial oxygen pressure of 10\(^{-6}\) mbar roughly corresponds to a monolayer occupation per second, which will do for the deposition rates of 0.1–0.3 nm/s used here.

29 Analyses of the Zr and Ti content of our films were carried out by Rutherford backscattering spectroscopy (RBS) and XRF. Zr/Ti ratios were similar to the target composition for all ambients.

30 This specific target composition is derived from preliminary experiments which roughly indicated the excess PbO corresponding with a substrate temperature necessary for epitaxial growth.

31 The sticking probability of ablated species on room temperature substrates is unity.

32 I. Barin and O. Knacke, Thermodynamical Properties of Inorganic Substances (Springer, Berlin, 1973). To our knowledge the thermodynamic data for PbZr, TiO\(_3\) are not available yet, but we assume that those values are comparable with those for PbTiO\(_3\).

33 Inficon Leybold-Heraeus Co.: ‘Material Evaporation Guide’ & EPI. ‘Vapor Pressure charts.’