Growth, microstructure, and ferroelectric properties of Pb(Zr₀.₄Ti₀.₆)O₃/PbZrO₃ superlattices prepared on SrTiO₃ (100) substrates by pulsed laser deposition

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(Received 6 October 2006; accepted 8 January 2007; published online 15 March 2007)

Artificially designed Pb(Zr,Ti)O₃ (PZT)/PbZrO₃ (PZ) superlattices were grown on (100)-oriented SrTiO₃ (STO) substrates with and without SrRuO₃ bottom electrodes by pulsed laser deposition. Their microstructure was characterized using x-ray diffraction and transmission electron microscopy. Different from single PZT films having a c-axis orientation on STO (100) substrates, during growth the PZT and PZ layers in the superlattices turn to an a-axis orientation from the c-axis orientation of the first PZT layer. This growth behavior is explained by minimization of the respective interfacial lattice mismatch. The superlattices have a rather smooth morphology and sharp PZT/PZ interfaces. At the latter, misfit dislocations have been found occasionally. There are indications for the absence of the orthorhombic, antiferroelectric phase in part of the PZ layers, possibly due to strain hindering the phase transition. An elongated, “linearized” shape of the ferroelectric hysteresis loop has been found, with a remanent polarization (Pᵣ) of 17 μC/cm² and a coercive field of about 110 kV/cm, which seems to be the result of a superposition of ferroelectric and antiferroelectric switching. © 2007 American Institute of Physics. [DOI: 10.1063/1.2710285]

I. INTRODUCTION

In recent years, artificial perovskite oxide superlattices composed of combinations between two dielectric layers, ferroelectric layers, ferromagnetic layers, high Tc superconducting layers, etc., have been widely studied, and some unusual physical properties have been reported, such as enhanced dielectric properties and elevated remanent polarization in BaTiO₃/SrTiO₃ (Refs. 1 and 2) and (Pb,Ln)TiO₃/PbTiO₃ (PT) superlattices, antiferroelectric coupling in KTaO₃/KNbO₃ superlattices, enhanced magnetoresistance in Pr₀.₃₅Ca₀.₆₅MnO₃/Ba₁₋ₓSrₓO₁.₅₀₋₀.₁₂TiO₃ superlattices, and artificial ferroelectricity in SrZrO₃/SrTiO₃ superlattices. However, studies of lead-based ferroelectric/antiferroelectric oxide superlattices are still rare because of the difficulty of layer-by-layer growth of Pb-based ferroelectric films due to the high volatility of lead. Kanno et al. prepared PbZrO₃(PZ)/PT superlattices on Pt/MgO substrates by multi-ion-sputtering, and Choi and Lee reported on the preparation of PZT/PT superlattices on La₀.₅Sr₀.₅CoO₃/MgO substrates by pulsed laser deposition (PLD). Obviously, MgO substrates are not an ideal choice for the growth of lead-based ferroelectric oxide superlattices, since MgO is not structurally compatible with lead-based perovskite oxides. In this work, SrTiO₃ (STO) and SrRuO₃ (SRO) were chosen as substrates and bottom electrodes, respectively, for Pb(Zr,Ti)O₃(PZT)/PZ superlattices to improve and study the crystallinity of the latter, since both PZT and PZ have the same perovskite-based structure and similar lattice parameters.

Polycrystalline PZT/PZ multilayered thin films have been prepared on Pt/Ti/SiO₂/Si substrates using a sol-gel process by Jang and Yoon. However, the presence of the antiferroelectric layers resulted in a considerable decrease of the total remanent polarization (although the antiferroelectric layer between the Pt electrode and the ferroelectric layers can act as a barrier to fatigue)

This paper reports on the preparation of PZT/PZ superlattices on (100) STO substrates with and without SRO bottom electrodes by PLD, and their structural and ferroelectric properties.

II. EXPERIMENTAL PROCEDURE

The PZT and PZ layers for the PZT/PZ superlattices were prepared on (100)-oriented STO substrates with and without SRO bottom electrodes by PLD using a KrF excimer laser (λ=248 nm) and ceramic targets of Pb₁₋ₓ(Zr₀.₄Ti₀.₆)O₃ and Pb₁₋ₓZrO₃. The experimental setup is the same as reported before. The substrates were placed parallel to the targets at a distance of 4.5 cm. The substrate temperature and oxygen pressure for the growth of all PZT and PZ layers were kept at 650 °C and 0.2 mbar, respectively. After deposition of all the layers, the samples were cooled down to...
room temperature under an oxygen pressure of 0.2 mbar to prevent loss of lead. The thickness of each PZT and PZ layer was fixed at about 9–10 nm. The superlattices are composed of 21 PZT/PZ alternating layers with PZT as the bottom and top layers. The total thickness of the superlattices was about 200 nm. Note that both PZO and PZT have perovskite structures with lattice spacings of about 4.1 Å, so that each layer has about 23–25 unit cells. For the electrical characterization, some superlattice samples were prepared on SRO-covered STO substrates, and Pt top electrodes were deposited through a stainless steel shadow mask by rf sputtering. The superlattices were characterized by x-ray diffraction (XRD) \( \theta-2\theta \) scans using a Philips X’Pert MRD 4-circle diffractometer with Cu \( K\alpha \) radiation. Transmission electron microscopy (TEM) images and electron diffraction patterns were recorded in a Philips CM20T electron microscope operated at 200 kV. High-resolution TEM (HRTEM) images were taken in a Jeol 4010 electron microscope operated at 400 kV. The polarization versus electric field \((P-E)\) and current-voltage \((C-V)\) properties of the superlattices on (100) SRO/STO substrates were measured by a TF analyzer 2000 ferroelectric tester (AixACCT) at frequencies between 20 Hz and 1 kHz.

III. CRYSTAL STRUCTURES

SrTiO\(_3\) has a cubic perovskite structure (space group \( Pm3m \)), with a lattice parameter \( a_0 = 0.3905 \) nm. SrRuO\(_3\) is an orthorhombic perovskite (space group \( Pbmn \)) with the lattice parameters \( a_0 = 0.557 \) nm, \( b_0 = 0.553 \) nm, and \( c_0 = 0.785 \) nm (Ref. 13) but it is usually treated as pseudocubic, with a lattice parameter \( a_R = 0.3928 \) nm. Pb\((Zr_{0.5}Ti_{0.5})\)O\(_3\) is tetragonal (space group \( P4mm \)) with the lattice parameters \( a_{PZT} = 0.3985 \) nm and \( c_{PZT} = 0.4125 \) nm,\(^{14}\) with a ratio \( c_{PZT}/a_{PZT} = 1.035 \) \((c_{PZT} > a_{PZT})\). PbZrO\(_3\) is orthorhombic (space group \( Pbam \)) with the lattice parameters \( a_{PZ} = 0.388 \) nm, \( b_{PZ} = 1.1787 \) nm, and \( c_{PZ} = 0.8231 \) nm.\(^{15}\) For the purpose of the present paper, it turned out to be convenient and sufficient to use a pseudotetragonal unit cell of PbZrO\(_3\), which had been previously described to have the nominal lattice parameters \( a_{PZ} = 0.4152 \) nm\( = a'_{PZ}/\sqrt{2} \), and \( c_{PZ} = 0.4100 \) nm\( = c'_{PZ}/2 \).\(^{16}\) In view of a proper tetragonal phase of PbZrO\(_3\) existing at around 200 °C which could have been stabilized by strain in our superstructures (see below), we used the lattice parameters of this proper tetragonal PbZrO\(_3\) phase, which only slightly deviate from those of the above mentioned pseudotetragonal unit cell: \( a'_{PZ} = 0.415 \) nm and \( c'_{PZ} = 0.4108 \) nm,\(^{17}\) with a ratio \( a'_{PZ}/c'_{PZ} = 1.012 \) \((c'_{PZ} < a'_{PZ})\).

IV. RESULTS AND DISCUSSIONS

Figure 1 shows XRD \( \theta-2\theta \) scans of a \([\text{PZT}(10 \text{ nm})_{11}/\text{PZ}(10 \text{ nm})_{10}]\) superlattice on a (100)-oriented STO substrate (a) without and (b) with SRO bottom electrode in the range of \( 2\theta \) from 15° to 30° around the (001) substrate reflection at \( 2\theta = 22.78° \). The peak structure is characteristic for a superlattice, involving satellite peaks, which are symmetrically located around the main Bragg reflections. High-order satellite peaks around the (100) main peak can clearly be seen, indicating the formation of a superlattice of good quality. The presence of the high order satellite peaks also indicates that the constituent material layers were indeed epitaxially grown. For the superlattice on the SRO-covered STO substrate, the number of satellite peaks decreased. This indicates that the SRO electrode seems to degrade the superlattice possibly by interdiffusion or interface roughening. At least the SRO bottom electrode changes the nucleation conditions of the first PZT layer, and thus may indirectly influence the subsequent film layers. Atomic force microscopy (AFM) images (Fig. 2) clearly revealed different surface morphologies for the superlattices on STO substrates with and without SRO bottom electrodes: The (100)-oriented upper PZT layer of the superlattice on bare STO substrate shows round-shaped, uniformly distributed grains with an average size of 60 nm, whereas that of the superlattice on a SRO/STO substrate has an irregular grain distribution although the grain sizes are also small.

The stacking periodicity \( \Lambda \) of a superlattice can be calculated from the positions of the satellite peaks by the

![FIG. 1. (Color online) X-ray \( \theta-2\theta \) diffraction patterns of PZT/PZ superlattices on (100)-oriented SrTiO\(_3\) substrates (a) without and (b) with SrRuO\(_3\) bottom electrode. The thickness of all the PZT layers and PZ layers are about 10 nm. The peak labeled \( \square \) is the substrate diffraction peak from STO.](image1)

![FIG. 2. (Color online) AFM images (2×2 \( \mu m^2 \)) of PZT/PZ superlattices on (100)-oriented SrTiO\(_3\) substrates (left) without and (right) with SrRuO\(_3\) bottom electrode. The rms roughnesses are 0.295 and 0.37 nm, respectively.](image2)
Schuller formula $\Lambda = \lambda / \left[ 2(\sin \theta_i - \sin \theta_{i-1}) \right]$,\(^{18}\) where $\lambda$ is the x-ray wavelength in the measurement and $\theta_i$ and $\theta_{i-1}$ are the diffraction angles of the $i$th and $(i-1)$th-order satellite peaks. Calculated in this way, the stacking periodicity $\Lambda = 17.4$ nm is in good agreement with the cross-sectional TEM observations shown below.

Figure 3 shows cross sectional TEM bright- and dark-field overview images of a PZT/PZ superlattice on (100)-oriented STO. (a) Bright field image; (b) dark-field image and diffraction pattern. For the numbers in (a), see the later text.

Figure 4 shows a plan-view diffraction-contrast bright-field TEM image of the same PZT/PZ superlattice as in Fig. 3.

Figure 5 shows two cross-sectional HRTEM images. They display the epitaxial nature of the superlattice and the rather sharp character of the PZT/PZ interface, as well as the vertical columns of about 50–100 nm diameter [see vertical structures in Fig. 5(a)]. As shown in Figs. 5(a) and 5(b), the PZT layers contain many small vertical defects, most probably threading dislocations or subgrain boundaries, whereas the PZ layers are rather perfect. Although the interfaces are more or less abrupt, they are not completely planar. Overall, the crystallography of the multilayer looks fairly perfect on a 50 nm scale [Fig. 5(b)].

Let us enumerate the individual layers, starting from the PZT layer directly on the STO substrate (which becomes
layer 1), so that PZT layers carry an odd number, and PZ layers an even number [cf. Fig. 3(a)]. A detailed evaluation of the relation between the in-plane and out-of-plane lattice parameters of the individual layers has been performed, both in direct space, considering magnified HRTEM images, and in Fourier space, evaluating Fourier transformations taken from small square areas within individual layers. As an example for the latter, Fig. 6 shows Fourier transformations taken from the first six layers. Table I shows the results of these evaluations. It turns out that layer 1 is a (001)-oriented (c-axis oriented) PZT layer, whereas from layer 3 onwards, all PZT layers are (100) oriented (a-axis oriented). All PZ layers, starting from the first layer 2, are (100) oriented (a’-axis oriented). (Note that in PZ, c’_{PZ} < a’_{PZ}, whereas in PZT, c’_{PZT} > a’_{PZT}) However, some of the Fourier transforms of layer 2 contain additional spots that point to the presence of the orthorhombic, antiferroelectric phase in this layer (not shown). Such additional spots were not found in the other PZ layers.

These different crystallographic orientations of the individual layers are obviously due to the minimization of the interfacial lattice mismatch along the different interfaces during growth. Consider the different values of interfacial lattice mismatch in Table II, which were calculated from the nominal lattice parameters of STO, PZT, and tetragonal PZ at room temperature. (Although growth proceeds at 650 °C, we take the lattice parameters at RT, because it can be assumed that the thermal expansion mismatch between PZT and PZ is low.) Assuming that the growth of an individual layer follows the principle of minimizing the lattice mismatch to the underlying layer, and considering the values given in Table II, the orientations of the layers can hypothetically be derived as follows:

Layer 1: Given the underlying in-plane lattice parameter a<sub>STO</sub>, PZT prefers to grow with a<sub>PZT</sub> in plane (f = 2.0%) rather than with c<sub>PZT</sub> in plane (f = 5.5%), i.e., it grows with c<sub>PZT</sub> axis up.

Layer 2: Given the underlying in-plane lattice parameter a<sub>PZT</sub>, PZ prefers to grow with c<sub>PZ</sub> in plane (f = 3.0%) rather than a<sub>PZ</sub> in-plane (f = 4.25%), i.e., it grows with a<sub>PZ</sub> axis up.

Layer 3: Given the underlying in-plane lattice parameter c<sub>PZ</sub>, PZT now prefers to grow with c<sub>PZT</sub> in plane (f = 0.41%) rather than a<sub>PZT</sub> in plane (f = 3.0%), i.e., it grows with a<sub>PZT</sub> axis up.

Layer 4: Given the underlying in-plane lattice parameter c<sub>PZT</sub>, PZ prefers to grow with c<sub>PZ</sub> in plane (f = 0.41%) rather than a<sub>PZ</sub> in plane (f = 0.8%), i.e., it grows with a<sub>PZ</sub> axis up.

Layer 5: like layer 3, etc.

Comparing these conclusions with the experimental results presented in Table I, it is obvious that the latter are very well explained by the hypothesis.

With the exception of layer 2, the microstructure of the PZ layers in the superstructure do not show indications of the orthorhombic, antiferroelectric phase. Consider that at the growth temperature (650 °C), both PZT and PZ grow in the paraelectric, cubic phase with a lattice parameter close to 4.15 Å. When the sample cools down after growth, PZT undergoes the cubic-to-tetragonal phase transition first (at 450 °C), PZ remaining cubic. However, due to the influence of the tetragonal PZT, the thin PZ layers may already now suffer from a tetragonal strain. When the sample, cooling further down, reaches the phase transition temperature of PZ (230 °C), part of the PZ layers may be prevented from assuming the orthorhombic phase due to the stress they are feeling from the upper and lower PZT layers, and due to the rather low temperature of the phase transition which certainly hinders plastic deformation. This may end up in the tetragonal phase of PZ, which is normally stable only at around 200 °C but may be stabilized by strain in our superstructures at RT. However, for the first PZ layer 2, the strain conditions are different from all other PZ layers, due to the underlying c<sub>PZ</sub>-axis oriented PZT layer. This may permit layer 2 to transform into the orthorhombic, antiferroelectric phase.

Figure 7 shows a HRTEM image and a magnified section, both revealing the presence of a misfit dislocation at a

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**TABLE I.** Identity, crystallographic orientation, and nominal in-plane lattice parameter of the first six layers, as determined from Fourier transforms such as the ones given in Fig. 6. R<sub>c</sub>, average radius of the horizontal (in-plane) Fourier reflections; R<sub>v</sub>, average radius of the vertical (out-of-plane) Fourier reflections.

<table>
<thead>
<tr>
<th>Layer No.</th>
<th>Identity</th>
<th>R&lt;sub&gt;c&lt;/sub&gt;/R&lt;sub&gt;v&lt;/sub&gt;</th>
<th>Orientation</th>
<th>Nominal in-plane parameter</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>PZT</td>
<td>1.02</td>
<td>c&lt;sub&gt;PZT&lt;/sub&gt; axis up</td>
<td>a&lt;sub&gt;PZT&lt;/sub&gt;=3.985 Å</td>
</tr>
<tr>
<td>2</td>
<td>PZ</td>
<td>1.02</td>
<td>a’&lt;sub&gt;PZ&lt;/sub&gt; axis up</td>
<td>c&lt;sub&gt;PZ&lt;/sub&gt;=4.105 Å</td>
</tr>
<tr>
<td>3</td>
<td>PZT</td>
<td>0.995</td>
<td>a&lt;sub&gt;PZT&lt;/sub&gt; axis up</td>
<td>c&lt;sub&gt;PZT&lt;/sub&gt;=4.125 Å</td>
</tr>
<tr>
<td>4</td>
<td>PZ</td>
<td>1.01</td>
<td>a’&lt;sub&gt;PZ&lt;/sub&gt; axis up</td>
<td>c&lt;sub&gt;PZ&lt;/sub&gt;=4.105 Å</td>
</tr>
<tr>
<td>5</td>
<td>PZT</td>
<td>0.985</td>
<td>a&lt;sub&gt;PZT&lt;/sub&gt; axis up</td>
<td>c&lt;sub&gt;PZT&lt;/sub&gt;=4.125 Å</td>
</tr>
<tr>
<td>6</td>
<td>PZ</td>
<td>1.02</td>
<td>a’&lt;sub&gt;PZ&lt;/sub&gt; axis up</td>
<td>c&lt;sub&gt;PZ&lt;/sub&gt;=4.105 Å</td>
</tr>
</tbody>
</table>

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**TABLE II.** Nominal in-plane lattice misfit between PZT layers of different (hypothetical) orientation and differently oriented PZ layers, and with the STO substrate, respectively. The table shows that lattice-misfit values are lowest for PZT layers having the c<sub>PZT</sub> parameter in-plane, i.e., for a<sub>PZT</sub>-axis oriented PZT layers, and that the absolute minimum of the misfit value is attained for the in-plane combination of c<sub>PZ</sub> and c’<sub>PZ</sub>, i.e., for a<sub>PZT</sub>-axis oriented PZT layers and a’<sub>PZ</sub>-oriented PZ layers.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PZT</th>
<th>PZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>a&lt;sub&gt;STO&lt;/sub&gt;</td>
<td>2%</td>
<td>5.5%</td>
</tr>
<tr>
<td>a’&lt;sub&gt;PZ&lt;/sub&gt;</td>
<td>4.25%</td>
<td>0.8%</td>
</tr>
<tr>
<td>c&lt;sub&gt;PZ&lt;/sub&gt;</td>
<td>3.0%</td>
<td>0.41%</td>
</tr>
</tbody>
</table>
PT/PZ superlattices on Pt/MgO substrates were studied by XRD patterns, that both PbTiO$_3$ and Pb(Zr$_{0.5}$Ti$_{0.5}$O$_3$) (PZT) used to have vertical defects in quite high density, including them as being intrinsic defects of PZT. Single PZT layers have their origin in misfit dislocations. This rather points to being so rare, the vertical defects in the PZT layers cannot relax. The coercive field can, in fact, not be estimated. Misfit dislocations are rather rarely found in any case, so that the degree of strain relaxation can be estimated to be $f = 0.4\%$, the period of misfit dislocations would be difficult to find in any case, so that the degree of strain relaxation can, in fact, not be estimated. Misfit dislocations being so rare, the vertical defects in the PZT layers cannot have their origin in misfit dislocations. This rather points to them as being intrinsic defects of PZT. Single PZT layers used to have vertical defects in quite high density, including threading dislocations, low-angle grain boundaries, and antiphase boundaries [cf. (Ref. 19 and 20)].

Concerning the crystallographic orientation of multilayers involving PZ, already Kanno et al. had found, by modeling XRD patterns, that both PbTiO$_3$ (PT) and PZ layers in PT/PZ superlattices on Pt/MgO substrates were $a$-axis oriented due to the small lattice mismatch between the in-plane lattice parameters of PT and PZ. Note that a single PZ film was also $a$-axis oriented on a Pt/MgO substrate. In ferroelectric PbTiO$_3$/BaTiO$_3$ superlattices on STO-buffered MgO substrates and Pb(Mg$_{0.35}$Nb$_{0.65}$)O$_3$/PbTiO$_3$ superlattices on La$_{0.5}$Sr$_{0.5}$CoO$_3$-covered MgO substrates, modeling the XRD patterns also indicated that the PT layers were oriented with the $a$ axis along the growth direction, whereas the BaTiO$_3$ and Pb(Mg$_{0.35}$Nb$_{0.65}$)O$_3$ layers were c-axis oriented.

Figure 8 shows the electrical characterization of a PZT/PZ superlattice on (100)SrRuO$_3$/SrTiO$_3$ with Pt top electrodes. Remarkably, no obvious antiferroelectric hysteresis behavior has been observed. The hysteresis loops have an unusual elongated, slim, and “linearized” shape. Nevertheless, the recorded switching current [Figs. 8(a) and 8(b)] shows a series of peaks that most probably can be attributed to both ferroelectric and antiferroelectric switching which might happen at different characteristic coercive voltages. The superposition of these switching peaks with a certain leakage current results, by integration, in the unusual shape of the hysteresis loop. Remarkably, the hysteresis loops do not severely change, if different measuring frequencies ranging from 20 Hz to 1 kHz are applied, as shown in Fig. 8(c). The positive-up-negative-down (PUND) test [Fig. 8(d)] shows a relatively high relaxation of the remanent polarization which might be associated to a high level of back switching. The in-field remanent polarization $2P_r$ and the coercive field were estimated to about 17 $\mu$C/cm$^2$ and 110 kV/cm, respectively, the coercive field slightly depending on frequency. The (100)-oriented growth of the PZT and PZ layers in the superlattice is certainly responsible for the rather low polarization value, although the remanent polarization value of the superlattice is comparable to that reported before for PZ/PT superlattices on Pt/MgO substrates.

The elongated, slim shape of the hysteresis loop with large saturation polarization is different from the shape of usual ferroelectric hysteresis loops. Paik and Komarneni reported that an alternatively deposited PZ/PT film made by the sol-gel technique showed neither ferroelectric nor antiferroelectric behavior, but behaved like a linear capacitor. In addition, it has been reported that antiferroelectric layers in sol-gel-derived polycrystalline PZT/PZ multilayered thin films largely decreased the total remanent polarization. Probably these results are related to the presence of the thin PZ layers. Kanno et al. reported that a 87 nm thin PZ film on Pt/MgO did not show antiferroelectric properties, but rather showed a weak ferroelectric characteristic. Ayyub et al. also confirmed that antiferroelectric thin films showed a weak ferroelectric behavior when the film thickness was less than 100 nm. Therefore, it can be assumed that layers of an antiferroelectric material in ferroelectric/antiferroelectric superlattices, which fail to be antiferroelectric, may weaken the total ferroelectric properties of the superlattice. However, a detailed discussion of this phenomenon requires further studies.

It has also been reported that large strain can induce artificial ferroelectricity in some dielectric superlattices, but the thickness of each constituting material layer must be below several unit cells. We expect that the ferroelectric properties of the PZT/PZ superlattices can be improved by further decreasing the layer thickness.
investigations in turn show that partially a nonantiferroelectric switching with some leakage. The microstructural characterization of a PZT/PZ superlattice grown on a (100) SrRuO$_3$/SrTiO$_3$ substrate. [a] and [b] P-E hysteresis curve and switching current at 1 kHz and at an amplitude of (a) 20 V and (b) 15 V; (c) P-E hysteresis curve recorded at different frequencies, viz. 20 and 100 Hz, and 1 kHz; (d) PUND hysteresis loop recorded at 1 kHz showing the switchable polarization.

V. CONCLUSIONS

Artificial PZT/PZ superlattices were grown on (100)-oriented SrTiO$_3$ substrates with and without SrRuO$_3$ (SRO) bottom electrodes by pulsed laser deposition. The superlattices have rather smooth morphology and sharp PZT/PZ interfaces as well as very few misfit dislocations. Different from single PZT films having a c-axis orientation on STO (100), the PZT and PZ layers in the superlattices turn to a-axis orientation from the c-axis orientation of the first PZT layer. A superlattice on a SRO/STO substrate showed an elongated, slim ferroelectric hysteresis loop with a remanent polarization $2P_r$ and a coercive field of 17 $\mu$C/cm$^2$ and about 110 kV/cm, respectively. The shape of the hysteresis loop indicates a superposition of ferroelectric and antiferroelectric switching with some leakage. The microstructural investigations in turn show that partially a nonantiferroelectric (possibly ferroelectric) tetragonal PbZrO$_3$ phase can be stabilized by strain.

ACKNOWLEDGMENTS

This work was financially supported by DFG via the Group of Researches FOR 404 at Martin-Luther-Universität Halle-Wittenberg. One of the authors (D.H.B.) gratefully acknowledges support from the Alexander von Humboldt Foundation, Germany, and also support from NSFC (Grant Nos. U0634006 and 10574164) and FANEDD (Grant No. 200441).

17Joint Committee on Powder Diffraction Standards, File No. JCPDS 03-0655.
21F. Le Marec, R. Farhi, M. El Marsi, J. L. Delli, M. G. Karkut, and D.


26Remember that PZ is considered to be tetragonal.