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Enhancing polarization by electrode-controlled strain relaxation in PbTiO$_3$ heterostructures

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A large remanent polarization close to theoretical value 80 $\mu$C/cm$^2$ of bulk PbTiO$_3$ is achieved in epitaxial heterostructures of (120–600)-nm-thick PbTiO$_3$ films grown by pulsed laser deposition on (001) SrTiO$_3$ substrate using a 100-nm-thick SrRuO$_3$ bottom electrode layer. The heterostructures employing a 50-nm-thick electrode exhibit a significantly smaller polarization of $\leq$60 $\mu$C/cm$^2$. A detailed x-ray diffraction analysis of the crystal structure allows for relating this large polarization to electrode-controlled relaxation of epitaxial strain in PbTiO$_3$. Based on the observed results, we anticipate that the electrode-promoted strain relaxation can be used to enhance polarization in other epitaxial ferroelectric films. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4939790]

Advanced ferroelectric (FE) miniature devices (e.g., piezomotors, pyroelectric detectors, and FE memories) employ FE films between top and bottom electrodes.$^{1,2}$ The optimal performance of the device often requires FE films with a large and/or stable spontaneous polarization in the direction normal to the substrate surface (out-of-plane direction). In particular, the out-of-plane polarization in single-crystal-type epitaxial perovskite oxide FE films is larger than in polycrystalline films and it may be further enhanced by biaxial in-plane compressive strain due to film-substrate mismatch of lattice parameters and thermal expansion coefficients.$^{3,4}$ For example, high polarization values of around 105 $\mu$C/cm$^2$ and 130 $\mu$C/cm$^2$ have been demonstrated in strained (001)-oriented epitaxial films of PbZr$_{0.7}$Ti$_{0.3}$O$_3$ and tetragonal-like BiFeO$_3$, respectively.$^{5,6}$ Although significant polarization enhancements can be achieved in epitaxial coherently strained FE films, an inevitable strain relaxation is encountered above the misfit-dependent critical thickness. This relaxation may proceed through the formation of defects, domains, and surface roughening.$^{7,8}$ and it restricts the usable thickness range of coherently strained films. Moreover, films with thickness below the critical one often possess undesirable scaling effects, such as large leakage currents, strong depolarization fields, and degraded response functions.$^{9-11}$ Importantly, the strain relaxation in tetragonal FEs may give rise to a formation of $a$-domains with in-plane polarization that may be difficult to switch. Although a controlled nano-sized polydomain configurations and related domain wall properties are particularly interesting in future nanoelectronics,$^{12,13}$ such features are generally undesirable in applications requiring large out-of-plane polarization.

In general, polarization appears to be less sensitive to the lattice strain in FEs with intrinsically high polarization (e.g., PbTiO$_3$) compared to other FEs.$^{4,14}$ A large out-of-plane polarization could be principally obtained in PbTiO$_3$ (PTO) and PbZr$_x$Ti$_{1-x}$O$_3$ films if $a$-domain formation is suppressed therein. The formation, characteristic dimensions, and configuration of $a/c$-domain patterns are controlled by FE film thickness, stress state, and material-specific correlation strength.$^{15,15}$ In particular, $a$-domain formation in PTO on SrTiO$_3$ (STO) can be suppressed by growing a sufficiently thin PTO film below or close to the Curie temperature $T_c$ of the film.$^{16}$ However, a wider use

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of this approach is restricted by small thickness of PTO and low temperatures may be insufficient for other growth techniques.

In this letter, we show that a large out-of-plane polarization (close to the bulk crystal value) can be achieved in epitaxial PTO films with thickness up to 600 nm grown on (001) STO substrates at high deposition temperature of \( T_d = 700 \, ^\circ\text{C} \). PTO films with thicknesses of 120–600 nm were deposited by pulsed laser ablation using (50–100)-nm-thick SrRuO\(_3\) (SRO) bottom electrodes. Parallel plate Pt/PTO/SRO capacitors were formed by shadow-mask deposition of 0.2 mm\(^2\) Pt top electrodes. It is demonstrated that increasing thickness of the bottom SRO layer can promote strain relaxation and consequent polarization enhancement in PTO.

The SRO-STO lattice mismatch is small with an in-plane strain of \( s = (a_{\text{STO}}/a_{\text{SRO}} - 1) \times 100\% \approx -0.6\% \) at \( T_d = 700 \, ^\circ\text{C} \), which allows for a coherent cube-on-cube-type growth of SRO on STO.\(^{17}\) A theoretical in-plane strain in PTO on STO is compressive with \( s = (a_{\text{STO}}/a_{\text{PTO}} - 1) \times 100\% \approx -1.4\% \) at \( T_d = 700 \, ^\circ\text{C} \) and its magnitude decreases on cooling. Thus, it is possible to obtain a room-temperature tetragonal \( c \)-PTO film if the misfit strain is not relaxed (i.e., if the film thickness is small enough).\(^{16}\) When assuming a thicker film with fully relaxed misfit strain at the growth temperature, the mismatch between thermal expansion coefficients of PTO and STO will lead to a tensile in-plane strain in PTO above \( T_c \) and a change of strain from \( s \approx 0.14\% \) to 0.4\% at \( T_c \). This tensile strain in PTO increases on cooling below \( T_c \) and can reach \( s \approx 1.5\% \) at room temperature. The resulting relaxation of the misfit and thermal strains, and the magnitude of residual strain can be influenced by the thickness of PTO as well as by the presence and thickness of SRO, and therefore this relaxation on cooling is theoretically difficult to predict.

The room-temperature crystal structure and strain in the grown Pt/PTO/SRO heterostructures were studied by x-ray diffraction (XRD) using Cu K\( _\alpha \) radiation with D8 Discover diffractometer (Bruker Corporation). Figure 1(a) shows \( \theta-2\theta \) XRD pattern for a 120-nm-thick PTO films on a 50-nm-thick SRO bottom electrode (PTO120/SRO50 for brevity). Qualitatively similar \( \theta-2\theta \) patterns were observed for all studied heterostructures. The main diffractions are assigned to parallel \((00l)\)-planes of perovskite PTO, SRO, and STO. A weak diffraction around \( 2\theta = 40^\circ \) is due to the used Pt electrodes. In addition, all PTO films showed a nanocolumnar microstructure with an average column width of around 50–80 nm (inset of Figure 1(a)).

The average out-of-plane lattice parameters \( c \) of the PTO films were determined from the (004) diffractions using a pseudo-Voigt single-peak fitting. The (004) STO substrate diffraction \( (a_{\text{STO}} = 3.905 \, \text{Å}) \) was used as a reference. The extracted parameters are \( c = 4.097 - 4.129 \, \text{Å} \) (Table I). Compared to bulk PTO \( (c = 4.156 \, \text{Å}) \),\(^{18}\) the \( c \)-PTO films experience an out-of-plane compression of approximately \( s_c = -(0.6\% - 1.4\%) \) in agreement with the above-discussed in-plane lattice strain. This observation suggests an efficient relaxation of misfit strain at \( T_d \). Nevertheless, PTO films grow epitaxially in a cube-on-cube-type manner as evidenced by fourfold symmetry of (101)

![FIG. 1. (a) \( \theta-2\theta \) x-ray diffraction pattern and (b) \( \phi \)-scans on STO (101) and PTO (101) crystal planes of Pt/PTO/SRO heterostructures on STO substrates for PTO120/SRO50 structure. Inset of (a): surface morphology of 120-nm-thick PTO film.](http://creativecommons.org/licenses/by/4.0/ Downloaded to IP: 130.231.54.47 On: Tue, 12 Jan 2016 16:13:33)
TABLE I. Structural and ferroelectric characteristics of Pt/PTO/SRO heterostructures.

<table>
<thead>
<tr>
<th>Structure</th>
<th>PTO120/SRO50</th>
<th>PTO200/SRO50</th>
<th>PTO120/SRO100</th>
<th>PTO600/SRO100</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTO thickness, nm</td>
<td>120</td>
<td>200</td>
<td>120</td>
<td>600</td>
</tr>
<tr>
<td>SRO thickness, nm</td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Average $c$, Å</td>
<td>4.097</td>
<td>4.129</td>
<td>4.123</td>
<td>4.119</td>
</tr>
<tr>
<td>$V_c$, %</td>
<td>82</td>
<td>91</td>
<td>100</td>
<td>85</td>
</tr>
<tr>
<td>$2P_{qs}$, $\mu$C/cm$^2$</td>
<td>120</td>
<td>114</td>
<td>160</td>
<td>150</td>
</tr>
<tr>
<td>$2P_{d}$, $\mu$C/cm$^2$ (1 kHz)</td>
<td>120</td>
<td>110</td>
<td>155</td>
<td>108</td>
</tr>
<tr>
<td>$2E_{cap}$, kV/cm</td>
<td>240</td>
<td>200</td>
<td>300</td>
<td>130</td>
</tr>
<tr>
<td>$2E_{cap}$, kV/cm (1 kHz)</td>
<td>500</td>
<td>315</td>
<td>500</td>
<td>230</td>
</tr>
<tr>
<td>$J$, $\mu$A/cm$^2$ (0.5 V)</td>
<td>13</td>
<td>120</td>
<td>50</td>
<td>0.5</td>
</tr>
<tr>
<td>$c_1//c_2$, Å</td>
<td>4.122/4.097</td>
<td>4.129/4.106</td>
<td>4.124/4.120</td>
<td>4.119</td>
</tr>
</tbody>
</table>

diffractions in $\phi$-scans (Figure 1(b)). The epitaxial relationship of $c$-PTO[100](001)||STO[100] (001) is confirmed.

Reciprocal space mapping (RSM) was performed for (103) and (002) diffractions in order to detect possible presence of $a$-domains and to study epitaxy in more detail. The RSM results were plotted by using reciprocal lattice units (r.l.u.) of STO substrate (r.l.u. = $2\pi/a_{STO} \approx 1.609$ Å$^{-1}$). Typical space maps in proximity of (103) STO lattice point are shown in Figures 2(b) and 2(d). Presence of $a$-domains is detected in the PTO films except in PTO120/SRO100. The volume fraction $V_c$ of $c$-domains was estimated from the $\omega$-rocking curves along the PTO (200) and (002) diffraction peaks (see typical curves in Figures 2(a) and 2(c)) by taking into account the fourfold symmetry of PTO (200) domains. A large $c$-domain fraction $V_c = 80\% - 100\%$ (Table I) evidences that the PTO films are predominantly $c$-oriented. The formation of $a/c$-polydomain state in the tetragonal FE phase is accompanied with tilting of domains away from 90°. In PTO, this domain tilting can be significant due to large tetragonality ($\sim 1.06$ in a relaxed bulk PTO). Here, tilted
PTO α-domains (tilting angle of 2.15°–2.4°) with the out-of-plane lattice constant close to that of STO are found (Figures 2(a) and 2(b)). Overall, the XRD analysis shows that the grown PTO films are pure perovskite, highly c-oriented, cube-on-cube-type epitaxial, with a residual in-plane tensile strain.

The leakage currents together with quasi-static and dynamic polarization loops were measured in the PTO capacitors using TF 2000E Analyzer (aixACCT Systems GmbH) and Precision LCII Ferroelectric Tester (Radiant Technologies, Inc.). The leakage current density at 0.5 V (in proximity of typical Schottky barrier) was (0.5–120) μA/cm², which is excellent for ferroelectric thin-film capacitors. All loops are characterized by double polarization $2P = |P(E^+)| + |P(E^-)|$ and coercive field $2E_c = |E^+| + |E^-|$ (Table I). The quasi-static polarization (Figure 3) is the largest and close to the theoretical bulk value in the c-domain PTO120/SRO100 structure. The polarization decreases slightly with increasing PTO thickness to 600 nm, but it drops significantly with smaller thickness of SRO. Compared to the quasi-static hysteresis, the dynamic loops are influenced by switching kinetics. Importantly, a very large dynamic polarization ($2P_d = 160$ μC/cm² at 10 Hz) is achieved in the PTO600/SRO100 structure. It is noticed that the large out-of-plane polarization is not directly related to the large c-domain volume fraction $V_c$. For instance, the quasi-static polarization is $2P_\text{qs} = 150$ μC/cm² for $V_c = 83\%$ (PTO600/SRO100) and $2P_\text{qs} = 114$ μC/cm² for $V_c = 91\%$ (PTO200/SRO50). Also a direct correlation between the polarization and the lattice parameter $c$ is absent. We stress that polarization is larger in heterostructures using 100-nm-thick bottom SRO electrode. A typical thickness of commonly employed SRO electrodes is small ~4–40 nm in contrast to thicker SRO layers of this study. In the following, we show that thick SRO layers can enable efficient strain relaxation in PTO, resulting in polarization enhancement.

A detailed inspection of perovskite (004) PTO and SRO diffractions is shown in Figure 4. The SRO layers on STO are cube-on-cube-type epitaxial with excellent crystal quality indicated by Laue satellites. The extracted SRO out-of-plane lattice parameters of 3.958 Å (50 nm) and 3.956 Å (100 nm) are in good agreement with those previously reported for coherent SRO films on STO.

The (004) PTO diffractions are broad and asymmetric in the films on the 50-nm-thick SRO layer (Figures 4(b) and 4(c)). The obtained good fits by two pseudo-Voigt peaks indicate a coexistence of two c-domain groups in these films: first one with average out-of-plane lattice parameter of $c_1 \approx 4.12 - 4.13$ Å and another with lattice parameter of $c_2 \approx 4.10$ Å. The small lattice parameter $c_2 \approx 4.10$ Å suggests that the $c_2$-domains may be caused by almost complete relaxation of misfit strain at growth temperature and a consequent buildup of tensile strain on cooling. The PTO films on the 100-nm-thick SRO layer contain the $c_1$-domains mainly (Figures 4(e) and 4(f)). Because of many factors influencing formation of $a/c$ domain patterns, a direct correlation between the formation of $c_2$- and $a$-domains is absent. Our observations imply that the $c_1$-domains are responsible for larger polarization, whilst the presence of $c_2$-domains leads to polarization decrease in the PTO films. Although the mechanism of the decrease is unclear, one may speculate that the $c_2$-domains are non-switchable or difficult to switch.
The formation of undesirable tensile-strained $c_2$-domains is suppressed for thicker SRO layers. The smaller tension in PTO on thicker SRO can be qualitatively understood from mechanical equilibrium, which requires equal traction on both sides at the SRO-PTO interface.\textsuperscript{27,28} This elastic coupling distributes the total stress of the stack between SRO and PTO according to their respected thicknesses. For a fixed PTO thickness and by assuming the misfit strain relaxation being independent of SRO during the deposition of PTO, the increasing thickness of SRO may lead to a smaller tensile strain in PTO.\textsuperscript{19} Experimental indications of such elastic coupling have been found in other heterostructures.\textsuperscript{29} Although further investigations are required to clarify the corresponding mechanisms, our experimental results strongly suggest that the electrode-controlled strain relaxation can be employed for the FE polarization enhancement.

In summary, large polarization close to theoretical bulk value is achieved in epitaxial Pt/PTO/SRO heterostructures with (120–600)-nm-thick PTO films grown on (001) STO substrate using a 100-nm-thick SRO bottom electrode layer. The observed large polarization in PTO films is attributed to relaxation of epitaxial strain promoted by relatively thick bottom SRO layer. Our results indicate that electrode-controlled strain relaxation could be used to enhance polarization in epitaxial ferroelectric films.

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\footnotesize
19 See supplementary material at http://dx.doi.org/10.1063/1.4939790 for leakage current results, additional reciprocal space maps, dynamic hysteresis loops, and more detailed discussion on strain relaxation.