Enhanced ferroelectric and dielectric properties of (111)-oriented highly cation-ordered PbScO.5Ta0.5O3 thin films

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Cation-ordered (111)-oriented epitaxial PbSc0.5Ta0.5O3 (PST) thin films were deposited by pulsed laser deposition on SrRuO3-electroded SrTiO3 (111) substrates at three different temperatures of 525 °C, 550 °C, and 575 °C. All the films were well crystalline and (111)-oriented at all the three growth temperatures; however, the films deposited at the temperatures other than 550 °C exhibited the presence of a pyrochlore phase. X-ray diffraction analysis and transmission electron microscopy measurements revealed that the films were epitaxial and highly cation-ordered. In comparison to (001)-oriented PST films, (111)-oriented films on SrRuO3/SrTiO3 (111) exhibited enhanced ferroelectric and dielectric properties with a broad size distribution of cation-ordered domains (5–100 nm). At a measurement temperature of 100 K, the remnant polarization of PST (111) films is almost 3 times larger than the remnant polarization observed for (001)-oriented PST films, which is attributed to the (111) orientation of the films, as the spontaneous polarization in PST lies close to the [111] direction. The observed dielectric constant and loss at 1 kHz were around 1145 and 0.11, respectively. The dielectric constant is thus almost three times higher than for previously reported (001)-oriented PST thin films, most probably due to the enhancement in cation-ordering. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4846817]

I. INTRODUCTION

PbSc0.5Ta0.5O3 (PST) is a typical example of a relaxor ferroelectric with perovskite structure, having the general compositional formula of A(B'B'O3)2.1,2 Technologically, there has been considerable interest in PST due to its high pyroelectric figure of merit which makes it a suitable and promising candidate for uncooled infrared (IR) radiation sensors, with respect to a wide range of applications such as fire alarms, intruder detection, and thermal imaging.3,4 Due to the unique combination of charge and size of the Sc3+ and Ta5+ ions on the B-site, PST is close to the border between the ordered and disordered arrangement of B-site cations. The ferroelectric and dielectric properties of PST can be altered by controlling B-site cation ordering, which makes PST a scientifically interesting material.5 In a fully cation-ordered PST, the space group changes from Pm-3 m to Fm-3 m by doubling the unit cell lattice parameter. Depending on the degree of B-site cation-ordering, the Curie temperature for bulk PST lies between 26 °C and 0 °C.6,7 Below the Curie temperature, PST has a rhombohedral structure, whereas above the Curie temperature, it is cubic. In rhombohedral perovskite, the spontaneous polarization lies close to the pseudo-cubic [111] direction. (Throughout this paper, pseudocubic indexing is used.) Thus, in order to explore maximum spontaneous and remanent polarization values for applications, it is desirable to grow PST thin films in (111) orientation. However, epitaxial (111)-oriented PST films have been most rarely investigated and reported so far.

TiO2-terminated and atomically flat SrTiO3 (STO) (001) surfaces with unit-cell high step-terrace structures can be obtained by using standard chemical and appropriate annealing treatments of vicinal (001)-oriented STO substrates.8 However, it is difficult to obtain similar STO substrates with (111) orientation due to the lack of a well-established chemical treatment method and due to the polar nature of the (111) surface.9,10 In this paper, we report on the growth of highly cation-ordered PST (111) thin films with enhanced ferroelectric and dielectric properties on STO (111) substrates.

II. EXPERIMENTAL PROCEDURE

The films were grown by pulsed laser deposition. The PST target used for the growth of the films was self-prepared by a conventional solid state reaction method, achieving a fairly good density (around 80% of the theoretical density). For the PST target preparation, relevant oxide powders PbO (99.9%, Alfa Aesar), Sc2O3 (99.9%, Alfa Aesar), and Ta2O5 (99.95%, Alfa Aesar) were mixed in the appropriate ratio by ball milling in ethanol for 10 h. In order to compensate for Pb losses during sintering and deposition, 10 mol. % excess of PbO was added. The ball-milled mixture was dried and then calcined at 1200 °C for 12 h in air to obtain the intermediate oxide as the precursor material. Then, the precursory material was thoroughly mixed, reground, and pressed into pellets with a size of 35 mm in diameter, and finally targets were sintered at 1200 °C for 12 h in a lead oxide atmosphere. The
structure of the PST target was analyzed by x-ray diffraction (XRD). The phase purity of the sintered target depends on the sintering time, and it was found that the target which was sintered only for 5 h showed additional peaks indicating the presence of a secondary phase. The target which was sintered for 10 h, however, showed a pure perovskite phase and all the peaks were identified assuming pseudocubic indexing as shown in Fig. 1(a).

Using this PST target, epitaxial (111)-oriented PST thin films were deposited on SrRuO$_3$ (SRO)/STO (111) substrates by ablating the target with KrF excimer laser pulses (wavelength of 248 nm, duration 20 ns). Prior to the deposition, STO (111) substrates (CrysTec GmbH, Berlin) were chemically treated and annealed in O$_2$ atmosphere at a temperature of 950 °C as reported by Chang et al. For the electrical measurements, a 90 nm thick epitaxial SRO layer was deposited as a bottom electrode with 5 Hz repetition rate and a fluence of 2 J/cm$^2$. The SRO layer was deposited at electrical measurements, a 90 nm thick epitaxial SRO layer was deposited as a bottom electrode with 5 Hz repetition rate and a fluence of 2 J/cm$^2$. The SRO layer was deposited at optimized growth pressure and temperature of 0.141 milli bars and 700 °C, respectively. In order to investigate the influence of substrate temperature, PST films were deposited at three different temperatures of 525 °C, 550 °C, and 585 °C. More on the PST growth conditions can be found elsewhere. All the films were deposited in-situ and were cooled down to room temperature (RT) with a slow cooling rate of 5 °C min$^{-1}$. For the electrical measurements, Pt top electrodes with 60 × 60 μm$^2$ area were sputtered by radio frequency sputtering at room temperature through a shadow mask.

Crystallographic characterizations were performed using a Philips X’Pert MRD X-ray diffractometer with Cu K$\alpha$ ($\lambda = 0.15418$ nm) radiation. Samples for transmission electron microscopy (TEM) were prepared by mechanical and ion-beam based standard techniques. TEM images were recorded in a Philips CM20T operated at 200kV. Surface morphology and local polarization switching were investigated by a commercial atomic force microscope (AFM) (XE-100, Park Systems), using the piezoresponse force microscopy (PFM). Polarization-voltage ($P$–$V$) hysteresis loop and switching-current-voltage ($I$–$V$) characteristics of the PST films were recorded by means of a ferroelectric tester (AixACCT 2000). Dielectric constants were calculated from the capacitance measured by a Hewlett Packard 4194 A impedance analyzer using a small ac signal of 100 mV.

III. RESULTS AND DISCUSSIONS

XRD patterns obtained for PST thin films deposited at three different growth temperatures are shown in Fig. 1(b). All the films were (111)-oriented as shown in θ-2θ scans. It was found that the films deposited at 550 °C consist of a pure perovskite phase and no pyrochlore phase was observed in these films. The pyrochlore phase in PST films has been known for degrading the ferroelectric properties and thus it is unwanted. The films deposited at 575 °C and 525 °C were found to contain a pyrochlore phase emphasizing that phase-pure PST films are confined to a rather narrow window of growth temperature. The amount of pyrochlore phase (%) for these PST films was calculated by using the following empirical relation:

$$\text{Pyrochlore phase} = \frac{I_{\text{pyro}}}{I_{\text{pyro}} + I_{\text{perov}}} \times 100,$$

where $I_{\text{pyro}}$ and $I_{\text{perov}}$ are major integrated X-ray peak intensities for the (222) reflection of the pyrochlore phase and the (111) reflection of the perovskite phase, respectively. The calculated amount of pyrochlore phase was found to be around 80% and 20% for the PST films deposited at 575 °C and 525 °C, respectively. The out-of-plane (111) interplanar lattice distance calculated from the (111) reflection of PST has been found to be 0.236 nm (±0.01) which is slightly larger than the bulk value [0.234 nm (±0.01)], signifying that our PST films have grown under compressive in-plane stress. The lattice mismatch between STO and PST films is ~4.17%. The epitaxial cube-on-cube growth of each layer on each other and on STO substrates has been established by φ scan measurements performed on the substrate and the thin films for (200) reflections as shown in the inset of Fig. 1. The full width at half maximum (FWHM) values of the (200) reflections calculated from φ scan for STO, SRO, and PST are 0.69°, 0.76°, and 1.11°, respectively, which indicate a good crystallinity of the epitaxial growth of both SRO and PST. However, the FWHM values of SRO and PST on STO (111) are relatively large as compared to the growth of SRO and PST films on STO (001) substrates, possibly due to the polar nature of the STO (111) surface. Nevertheless, the epitaxial relationship between substrate, electrode, and PST film can be given as: (111) PST/(111) SRO/(111) STO. Superstructure reflections of type (1/2 1/2
1/2) obtained at 18.75°C confirm that these PST films are cation-ordered. The degree of cation ordering was measured in the films by calculating the order parameter $S$, which is defined as:

$$S^2 = \frac{I_{(1/2,1/2,1/2)}(\text{observed})}{I_{(1/2,1/2,1/2)}(\text{calculated, } S = 1)},$$

where $I$ is the integrated intensity of the subscripted reflections. The value of the order parameter ($S$) varies from 1 to 0 with translation from a completely ordered to a disordered system. The average degree of cation ordering for the PST has been calculated by using the above empirical formula and found to be ~40%, which is slightly higher than reported for PST(001) films.

The surface morphology of the STO (111) and PST thin films has been analyzed by AFM measurements in tapping mode. The surface morphology of a chemically treated and subsequently annealed STO (111) substrate is shown in Fig. 2(a). An ideal etching on an STO (111) substrate should produce terraces of atomic step height (in this case ~0.25 nm); however, in our experiments, the average step height of STO (111) terraces was found to be ~0.350 nm. It was observed that both step height and terrace width were found to vary from substrate to substrate due to variations of the miscut angle and in some cases different step heights and widths were observed within one substrate. This shows that chemical etching does not reproduce a very clean and single step terraced (111)-oriented STO surface, which is most probably responsible for the large value of FWHM observed for the top layer grown on STO (111) substrates and thus it brings additional difficulties to grow high quality epitaxial (111)-oriented PST thin films. A typical surface morphology of a PST (111) film grown on SRO (111)/STO (111) is shown in Fig. 2(b). The STO (111) substrate used for the thin film growth had a surface roughness of ~0.2 nm over an area of 2 x 2 $\mu$m$^2$. The PST film has a surface roughness ~2.5 nm over an area of 2 x 2 $\mu$m$^2$, which is significantly higher compared to PST (001) thin films as reported earlier.\textsuperscript{11}

The microstructure of the PST films was studied through TEM investigations. Cross-sectional TEM and selected area electron diffraction (SAED) investigations revealed, e.g., the epitaxial growth of a 85 nm thick PST film on a 90 nm thick SRO bottom electrode film as shown in Figs. 3(a) and 3(b). In the SAED patterns, an additional set of reflections (shown in red color in the SAED) were observed, and these reflections were identified as superstructure reflections. Using one of the observed superstructure reflections, a dark field image was recorded as shown in Fig. 3(c). The bright contrast observed in the dark field image of the PST film reveals the presence of cation-ordered clusters distributed in the disordered matrix. In comparison to the earlier reported PST (001) films where the size of cation-ordered domains was rather uniform (5–10 nm), a broad size distribution from ~5 nm to 100 nm is observed in these PST (111) films.

FIG. 2. AFM images of 2 x 2 $\mu$m$^2$ area recorded for (a) an etched and subsequently annealed STO (111) substrate, showing irregular terraces, and (b) a PST thin film, showing island-type of growth.

FIG. 3. (a) A cross-section dark-field image of a PST (111) film on SRO/STO (111) recorded along the [-211] pole; (b) cross-sectional SAED pattern showing superstructure reflections; (c) a cross-sectional dark field image captured using one of the encircled red color superstructure reflections in (b), revealing the broad size distribution of cation-ordered domains in the PST film.
Macroscopic and local ferroelectric properties of the PST films deposited at 525 °C, 550 °C, and 575 °C were investigated at RT. Macroscopic P–V hysteresis and I–V switching currents were measured for the PST thin film sandwiched between top and bottom electrodes at 1 kHz as shown in Figs. 4(a) and 4(b). It was found that the films with pure perovskite phase show better ferroelectric properties compared to the films containing the pyrochlore phase. With increase in pyrochlore phase, a degradation in ferroelectric properties was observed which is certainly a consequence of phase impurity of these films. At room temperature for the phase-pure PST films, the remanent polarization \( P_r \) and coercive voltage \( V_c \) under the application of 4 V were found to be 6.5 \( \mu \)C/cm\(^2\) and 0.50 V, respectively. The remanent polarization value observed in PST (111) films is thus considerably higher as compared to the previously reported values for PST (001) thin films of similar thickness.\(^{11}\) The \( I–V \) measurements show sharp and distinct switching peaks for the phase-pure films revealing that the films can be switched in either direction. For comparison, ferroelectric properties of phase-pure PST (111) and PST (001) films of similar thickness were investigated at 100 K as shown in Figs. 5(a) and 5(b). Ferroelectric and dielectric properties observed at RT and 100 K are tabulated in Table I. The remanent polarization for the PST (111) films was found to be almost \( \sqrt{3} \) times higher as compared to PST (001) films at 100 K. This significant enhancement in ferroelectric properties in the PST (111) films is certainly a consequence of the (111) orientation as the spontaneous polarization lies close to the [111] direction. At 100 K, PST (001) films exhibit well-saturated hysteresis loops under the application of 7 V. However, in case of PST (111) films no saturation was observed until breakdown. This behavior of (001) and (111)-oriented PST thin films can be explained on the basis of a model suggested for rhombohedral Pb(Zr,Ti)O\(_3\) (PZT) thin films.\(^{17–19}\) Below the Curie temperature, PST has a rhombohedral structure with large domain size as reported in the literature.\(^{6}\) In the rhombohedral phase for (001)-oriented thin films, out of eight only four directions are proper polarization directions [Fig. 6(a)] which are at an angle of 54.44° (denoted by i) with respect to the normal (denoted by N) to the (001)-plane. Under the application of an electric field, polarization reversal for all the four polarization directions will take place simultaneously. Thus, (001)-oriented PST thin films exhibit a smaller coercive voltage and show saturated loops at lower applied voltage in comparison to the (111)-oriented films as observed in hysteresis loops recorded at 100 K. For (111)-oriented thin films, there are three polarization directions at 71° (denoted by j) and one at 180°.

![FIG. 4. (a) and (b) Macroscopic polarization-voltage and switching current-voltage hysteresis curves recorded at RT for the PST film grown at three different temperatures.](image)

![FIG. 5. (a) and (b) Macroscopic polarization-voltage and switching current-voltage hysteresis curves recorded at 100 K for the PST (111) and PST (001) thin films.](image)

### Table I. Ferroelectric properties of (001) and (111)-oriented PST thin films at RT and 100 K.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temperature</th>
<th>Remanent polarization ((\mu C/cm^2))</th>
<th>Coercive voltage (V)</th>
<th>Dielectric constant</th>
<th>Ref. No</th>
</tr>
</thead>
<tbody>
<tr>
<td>PST (Bulk)</td>
<td>RT</td>
<td>~1</td>
<td></td>
<td></td>
<td>5000</td>
</tr>
<tr>
<td>PST/SRO/STO (001)</td>
<td>RT</td>
<td>3.4</td>
<td>0.25</td>
<td>467</td>
<td>17</td>
</tr>
<tr>
<td>PST/SRO/STO (001)</td>
<td>100 K</td>
<td>12</td>
<td>1.07</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>PST/SRO/STO (111)</td>
<td>RT</td>
<td>6.54</td>
<td>0.50</td>
<td>1450</td>
<td>This work</td>
</tr>
<tr>
<td>PST/SRO/STO (111)</td>
<td>100 K</td>
<td>22</td>
<td>1.10</td>
<td></td>
<td>This work</td>
</tr>
</tbody>
</table>
(denoted by k) with respect to the (111)-plane as shown in Fig. 6(b). For (111)-oriented PST films with the application of an electric field, polarization reversal takes place first for the 180°/C14 domains and then later for 71°/C14 domains. Thus, a higher field will be required for the complete polarization reversal and for complete saturation of (111)-oriented PST films as observed in hysteresis loops. Butterfly-shaped curves obtained for the field-dependent dielectric constant (e-V) for 100 kHz (Fig. 7) confirm that the films are indeed ferroelectric at RT. The asymmetric shape of the e-V curve is due to the different materials used as top (Pt) and bottom electrodes SRO.20–22

The local ferroelectric switching of the PST films deposited at three different temperatures was investigated by PFM with a modulation voltage of 0.5 Vrms at 25 kHz, as shown in the PFM phase and amplitude images of Figs. 8(a) and 8(c). A 3 × 3 μm² area was poled as downwards by applying a voltage of +4 V. Then, at the center, a smaller area of 1 × 1 μm² was switched as upwards by applying a voltage of −4 V. Films deposited at 550 °C and 525 °C [Figs. 8(a) and 8(c)] showed clear switching by the application of an external voltage. However, clear switching was not observed in the films deposited at 575 °C. This could be due to the large amount of pyrochlore phase (80% in this case) present in the PST films deposited at 575 °C. At a frequency of 1 kHz, the value of the dielectric constant and loss tangent were around 1145 and 0.11, respectively. The measured dielectric constant for PST (111) films is almost three times higher as compared to that of the previously reported PST (001) films on STO substrate (not shown here) which might be a result of the influence of enhanced cation-ordering and presence of large cation-ordered domains.

**IV. CONCLUSIONS**

Summarizing, the aim of this study was to investigate the growth of the PST films along the polar [111] axis and to improve the ferroelectric properties so that films can be useful for future device applications. Epitaxial and highly cation-ordered (111)-oriented PST thin films have been grown on SRO/STO (111) substrates at three different temperatures. It has been demonstrated that the PST films are very sensitive to the growth temperature. Phase-pure PST films exhibited good ferroelectric and dielectric properties. The remnant polarization for the PST (111) films has been found to be 6.54 and 22 μC/cm² at RT and 100 K, respectively. These values are almost 3 times higher than those for the PST (001) thin films. At 1 kHz, the dielectric constant was 1145 which is almost three times higher than that for PST (001) thin films. The large size of cation-order domains

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**FIG. 6.** Schematic of domain configuration of (a) a (001)-oriented rhombohedral PST film and (b) a (111)-oriented rhombohedral PST film. For meanings of the legends and for other details, see the text.

**FIG. 7.** Butterfly shape e-V curves recorded at 100kHz revealing that the PST film is ferroelectric at RT.

**FIG. 8.** PFM phase and amplitude images over an area of 3 × 3 μm² after switching a 1 × 1 μm² area in the middle for (a) a phase-pure PST film and (b) and (c) for PST films containing ~80% and ~20% pyrochlore phase, respectively.
observed in PST (111) films with enhanced dielectric and ferroelectric properties brings us one step closer to the use of epitaxial PST films in future technology.

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