Crystal defects and cation ordering domains in epitaxial PbSc$_{0.5}$Ta$_{0.5}$O$_3$ relaxor ferroelectric thin films investigated by high-resolution transmission electron microscopy

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Abstract

Epitaxial thin films of the relaxor ferroelectric PbSc$_{0.5}$Ta$_{0.5}$O$_3$ (PST) were grown by pulsed laser deposition on an SrTiO$_3$ substrate with an SrRuO$_3$ buffer layer and investigated by diffraction contrast imaging and high-resolution transmission electron microscopy (TEM) in cross-section and plan-view. Crystal defects, viz. misfit dislocations, π stacking faults and cation ordering domains, have been characterized and the mechanism of their formation is discussed. The state of the structural disorder in PST relaxor thin films is characterized by the high density of π stacking faults and the rather small size (<10 nm) of the cation ordering domains, and is therefore markedly distinct from the state of the disorder in bulk relaxor PST. Polar nanoregions, supposed to be essential for explaining the relaxor properties, could not be detected using TEM, possibly due to their high fluctuation frequency. The dielectric constant of the relaxor PST thin films is about an order of magnitude smaller than that of bulk relaxor PST, which is attributed to the large density of π stacking faults in the thin films.

Keywords: Thin films; Transmission electron microscopy (TEM); Relaxor; Cation-ordered; π stacking faults

1. Introduction

PbSc$_{0.5}$Ta$_{0.5}$O$_3$ (PST), a relaxor ferroelectric, is a promising material for pyroelectric sensors because of its high figure of merit [1]. In comparison to that of bulk PST, thin films exhibit a significantly lower dielectric loss factor near room temperature and therefore higher figure of merit [2]. PST has a perovskite structure, with Pb$^{2+}$ cations occupying the corner positions of the cubic unit cell, Sc$^{3+}$ and Ta$^{5+}$ cations occupying the body-centered position, and O$^{2-}$ anions occupying the face-centered positions. Alternatively, the perovskite structure can be considered as a close-packed cubic arrangement of PbO$_3$ planes, with Sc$^{3+}$ and Ta$^{5+}$ ions occupying the octahedral interstitials between the planes [3,4]. In the case of ordered PST, Sc$^{3+}$ and Ta$^{5+}$ ions are separately confined to alternate (1 1 1) planes, leading to a superlattice structure with a doubled unit cell.

Due to the unique combination of charge and size of the Sc$^{3+}$ and Ta$^{5+}$ ions, as well as the size of the Pb$^{2+}$ cations, PST is on the boundary between the ordered and disordered arrangement of Sc$^{3+}$ and Ta$^{5+}$ cations [5]. PST ceramics with controlled degree of ordering could thus be prepared by suitable thermal treatment, without having to change the chemical composition. The temperature as well as the nature of the ferroelectric to paraelectric transition in bulk PST is known to depend on the degree of ordering. Perfectly ordered PST shows a classical sharp transition at 32 °C. On the other hand, disordered PST shows a relaxor-type diffuse phase transition between −6
and 13 °C, with an enhanced value of the maximum of the dielectric constant in comparison to ordered PST [6]. The dielectric constant of PST thin films is about an order of magnitude lower than that of bulk PST, the reasons for which are not well understood [7,8]. Like in bulk PST, the formation of polar nanoregions at temperatures above the dielectric maximum was observed also in PST thin films [9]. Thus the intrinsic mechanism of relaxor properties in bulk and thin films of PST appears to be the same. Extrinsic factors, like interfacial capacitance layers [10] and substrate-induced strain Refs. [11,12], have also not been able to explain the lower dielectric constant of PST thin films. Brinkman et al. [7] proposed that the low processing temperatures employed in the fabrication of PST thin films yield an incomplete disordering in the form of clustering of Ta and Sc cations compensated by Pb and O vacancies due to diffusion limitation. The impact of these defects and the reduction in the fraction of the true relaxor region were postulated to be responsible for the low dielectric constant in PST thin films.

The microstructure of bulk PST with differing degrees of structural ordering has been investigated by several groups [13–19]. However, a detailed microstructure investigation of epitaxial PST thin films using transmission electron microscopy (TEM) is lacking, and is therefore carried out in this work using diffraction contrast and high-resolution imaging in plan-view and cross-section. The formation of cation ordering domains and π stacking faults in the PST film, and misfit dislocations at the PST–SrRuO 3 (SRO) interface, as well as the influence of these defects on the dielectric properties, are discussed.

2. Experimental

Epitaxial thin films of PST with a thickness of 60–80 nm were grown on (1 0 0)-oriented vicinal SrTiO 3 (STO) substrates, covered with a 45–85 nm thick conducting bottom electrode layer of SRO, using pulsed laser deposition (PLD) in an oxygen atmosphere at elevated temperatures. A KrF excimer laser with a wavelength of 248 nm and pulse duration of 20 ns was used. The deposition parameters for the epitaxial SRO electrode were: laser fluence of 2 J cm⁻², repetition rate of 5 Hz, oxygen pressure of 0.14 mbar and substrate temperature of 700 °C. Those for the epitaxial PST thin films were: laser fluence of 1.5 J cm⁻², repetition rate of 5 Hz, oxygen pressure of 0.27 mbar and substrate temperature of 550 °C. Further details of the preparation of vicinal STO substrate surfaces and the PST target can be found in Ref. [20]. For electrical measurements, Pt top electrodes were deposited through a metal shadow mask (electrode size of approximately 60 x 60 μm²) by radiofrequency sputtering at room temperature. Details of the polarization and dielectric constant measurements can be found in Ref. [20].

The structure and orientation of the films was investigated by X-ray diffraction (XRD) using a Philips X’pert MRD diffractometer with Cu Kα radiation. TEM diffraction contrast imaging was performed using a CM20T transmission electron microscope operated at 200 kV, and high-resolution (HR) TEM was carried out using a Jeol 4010 operated at 400 kV. TEM samples were thinned to a thickness of about 20 μm by mechanical grinding and polishing using SiC and diamond foils followed by dimpling using a Gatan dimpler. This was followed by Ar+ ion milling using a Gatan PIPS at an accelerating voltage of 5 kV and an incident angle of 4°. Plan-view TEM samples were thinned and ion-milled only from the substrate side. The (0 1 0) and (1 1 0) cross-section TEM samples were prepared by cutting the PST–SRO–STO sample along the (1 0 0) and (1 1 0) planes, respectively, and gluing face-to-face by joining the PST surfaces.

3. Results

3.1. Cross-sectional analysis using HRTEM

Fig. 1a and b show diffraction patterns in the [0 1 0] and [1 1 0] poles, respectively, from regions in a cross-section TEM sample containing the STO substrate as well as the SRO and PST thin films. The diffraction patterns were indexed by assuming a pseudo-cubic structure for PST and SRO. These diffraction patterns show epitaxial growth of PST on SRO/STO. STO was used as an internal reference to determine the d-spacings of the PST thin film.
The $c$ and $a$ lattice parameters of the PST film were observed to both be 0.406 nm. Thus we can state that the strain in the PST film has completely relaxed, although these lattice parameter values are smaller than the cubic lattice parameter of bulk PST (0.407 ± 0.0003) nm measured by XRD at room temperature [21]. \{½ ½ ½\} F-type superstructure reflections [16] are observed in Fig. 1b. The reflections in Fig. 1a on seeming \{½ 0 0\} positions fit with the lattice parameters of SRO and can be attributed to the orthorhombic crystal structure of SRO.

Two-beam dark-field images of a (0 1 0)-cut cross-section sample using different reflections of the [0 1 0] pole are shown in Fig. 2a–d, whereas those using different reflections of the [1 1 0] pole are shown in Fig. 2e and f. The average thickness of the PST and SRO films is observed to be about 78 and 85 nm, respectively. Threading defects passing through the entire film, as well as such ones extending only up to part of the film thickness, are observed. All the threading defects originate at the PST–SRO interface. Most of these threading defects extend only up to

Fig. 2. (a–d) Dark-field images of the same area of a (0 1 0)-cut cross-section TEM sample under two-beam conditions with (a) (2 0 0), (b) (0 0 2), (c) (1 0 1) and (d) (1 0 1) reflections of the [0 1 0] pole. (e and f) Dark-field images of the same area of a (1 1 0)-cut cross-section TEM sample under two-beam conditions with (e) (1 1 0) and (f) (1 1 1) reflections of the [1 1 0] pole. (g and h) Dark-field images of two different regions of a (1 1 0)-cut cross-section sample close to the [1 1 0] pole.
three-quarters of the film thickness and possibly annihilate each other close to the surface of the film. Periodic patterns consisting of short lines are seen at the SRO–PST interface, as in Fig. 2a, e, c and d, recorded using (2 0 0), (T 1 0), (1 0 T) and (1 0 1) reflections, respectively, while they are out of contrast in Fig. 2b, acquired using the (0 0 2) reflection. It is not easy to decide whether these patterns are due to misfit dislocations or rather represent Moiré patterns. Considering, however, the HRTEM observations of misfit dislocations described below, looking at the edge-on-type interfacial dot contrasts in Fig. 2g and h and noting that some of the lines of the pattern are seen to extend into the PST film as threading dislocations, we may assume that these patterns in fact represent misfit dislocations. The average spacing between them when viewed along [0 1 0] (Fig. 2a) and along [1 1 0] (Fig. 2e) is different, at 8 and 12 nm, respectively.

Dark-field images using (1 1 0) reflections of the [1 1 0] pole from two different regions of the (1 1 0)-cut cross-section sample are shown in Fig. 2g and h. In Fig. 2g, the surface of the film is undulatory, consisting of hills and valleys. Threading defects which pass through the entire film are observed in the valleys. Obviously the film exhibited a three-dimensional island growth mode, in which it begins to grow in the form of individual islands which expand and give rise to threading defects when two or more islands meet each other. Some of these islands in Fig. 2g show strikingly different contrast than their neighbors, indicating that the islands are slightly tilted with respect to each other. In comparison, in Fig. 2h the surface of the film is flatter and most of the threading defects extend only up to part of the PST film and then possibly annihilate each other.

An HRTEM cross-section image of the SRO–PST interface along the [0 1 0] direction is given in Fig. 3a. An inverse Fourier transform (IFT) image using first-order reflections ({1 0 0}, {0 0 1}, {1 0 1}) of the HRTEM image close to that in Fig. 3a is shown in Fig. 3b. Masks with a diameter of

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**Fig. 3.** (a) HRTEM cross-section image of the SRO–PST interface acquired along the [0 1 0] direction; (b) IFT image using main diffraction vectors of the HRTEM image at a region close to that of (a).
0.8 nm and smoothed edges were used. Fourier filtering helped reduce the noise in the HRTEM image, thereby enabling the analysis of the defects. The defects in Fig. 3 are numbered. Defects Nos. 1, 4, 7 and 12 are threading defects, while others are misfit dislocations. Threading defect No. 1, lying on the (1 0 0) plane, extends through the entire film and gives rise to clear shifts in the (1 0 1) and (1 0 1) lattice fringes, by \(a/4 [1 0 1]\) and \(a/4 [1 0 1]\), respectively. (This can easily be seen looking on the micrograph along the lattice planes under a small glancing angle.)

Therefore the projected displacement vector at the defect No. 1 is \(a/2 [1 0 0]\). Threading defects Nos. 4, 7 and 12 extend only up to the region marked as 4b, 7c and 12b, respectively. Most of the threading defects are extended and do not appear to be edge-on in this orientation. For defects Nos. 4 and 7, a shift of the fringes is not discernible but a displacement vector of \(a [T 0 0]\) is observed in the region around 4b and 7c while no displacement vector is observed around 4a and 7a close to the interface. For defect No. 12, a shift of fringes similar to that for defect No. 1 is discernible close to No. 12b, where it lies on the (\(\bar{1} 0 1\)) plane, but not close to No. 12a, where it lies on the (1 0 0) plane, and a partial misfit dislocation with a Burgers vector \(b\) of \(a/2 \bar{T} 0 T\) is observed. Defects similar to defect No. 12 were also observed by Qin et al. [22] and interpreted as stacking faults that extend into the film. The defects Nos. 2, 3, 10 and 11 are misfit dislocations with a Burgers vector \(a[T 0 0]\). Defects Nos. 5 and 6 are partial misfit dislocations with a Burgers vector \(a/2 [0 0 1]\) and \(a/2 [1 0 1]\), respectively, and appear to be connected by a stacking fault. Defects Nos. 8 and 9 are similar to defects Nos. 5 and 6, respectively.

An HRTEM cross-section image of the SRO–PST interface along the [1 1 0] direction is given in Fig. 4. A long threading defect which originates at the interface and extends all the way through the PST film is seen. It appears edge-on and lies approximately in the (1 1 0) plane. Both the (0 0 1) and (1 1 0) fringes appear to shift at this defect by \(a/2 [0 0 1]\) and \(a/2 [1 1 0]\) respectively. The displacement vector of this defect is therefore \(a/2 [T 1 0]\) (or \(a/2 [0 0 1]\) if a partial dislocation with a Burgers vector of \(a/2 [T 1 0]\) is imagined at the bottom of this defect). Threading defects which extended into only part of the film and which did not give rise to shift in the lattice fringes were also observed. Misfit dislocations with a Burgers vector \(a/2 [T 1 0]\) were observed at the PST–SRO interface. No other Burgers vectors were observed for the misfit dislocations in this orientation.

![Fig. 4. HRTEM cross-section image of the SRO–PST interface acquired along the [1 1 0] direction. Misfit dislocations are marked by Burgers circuits. A long threading defect is seen in the middle of the image.](image-url)

![Fig. 5. (a) HRTEM image acquired along the [1 1 0] direction at a very thin region. The Fourier transform of the HRTEM image is given in the inset. (b) Corresponding IFT image using superstructure reflections indicated by black circle in the inset of (a).](image-url)
An IFT image of the HRTEM image acquired along the [1 1 0] direction at a very thin region is given in Fig. 5. The IFT image was formed using $\{\frac{1}{2} \frac{1}{2} \frac{1}{2}\}$-type superstructure reflections in the power spectrum (shown in the inset of Fig. 5) of the HRTEM image. Bright regions with a size of about 5 nm are observed.

3.2. Plan-view analysis using HRTEM

Fig. 6a and b are diffraction patterns in [0 0 1] and [1 0 1] poles, respectively, from plan-view TEM samples. The [0 0 1] diffraction pattern exhibits streaking along the [1 1 0] and $[\overline{1} \overline{1} 0]$ directions. The [1 0 1] pole exhibits $\{\frac{1}{2} \frac{1}{2} \frac{1}{2}\}$-type superstructure reflections due to the ordering of $\text{Sc}^{3+}$ and $\text{Ta}^{5+}$ ions.

Nearly two-beam bright-field images using $\{\frac{1}{2} \frac{1}{2} \frac{1}{2}\}$ superstructure reflections acquired from two different PST thin film samples are shown in Fig. 7a and c. These exhibit defect segments with bright contrast which are preferentially aligned along the [1 1 1] and [1 1 1] directions. The corresponding dark-field images in Fig. 7b and d show distinct bright regions with a size of about 10 and 5 nm, respectively. These bright regions are interpreted as ordering domains arising from the ordering of

Fig. 6. TEM–SAED patterns of (a) [0 0 1] and (b) [1 0 1] poles of plan-view samples.

Fig. 7. (a and c) Two-beam bright-field images and (b and d) the corresponding dark-field images using $\{\frac{1}{2} \frac{1}{2} \frac{1}{2}\}$-type reflections, from two different PST samples.
Sc$^{3+}$ and Ta$^{5+}$ ions [16]. The size of the ordering domains in Fig. 7d is comparable to that revealed by HRTEM in Fig. 5 for this sample. The bright defect segments seen in the bright-field images are not explicitly visible in the dark-field images. Considering the results presented below, and Section 4.3, they may be assumed to be planar defects of $\pi$ type.

Two-beam bright-field images using (2 0 0), (0 2 0) and (1 1 0) reflections of the [0 0 1] pole are shown in Fig. 8. Defect segments with a faint contrast and edge-on dislocation-like defects at their ends are seen in all the images. At thick regions and for large (>30$^\circ$) tilts away from the [0 0 1] direction, defect segments exhibited fringes in images with (T T 0)-type reflections (Fig. 8c, inset). These defects lie in the (1 T 0) plane, which is inclined to the beam under this particular two-beam condition.

Two-beam bright-field images using (1 0 T) and (T 0 1) reflections of the [1 0 1] pole of a plan-view sample are given in Fig. 9a and c, respectively. The corresponding dark-field images using different reflections are shown in Fig. 9b, d, e and f. In the bright-field images using (1 0 1)-type reflections, the defect segments exhibit a fringe pattern which is dark–bright–dark. In the dark-field images the fringe pattern is bright–dark–bright or bright–dark–bright–dark–bright, depending on the excitation error in the two-beam diffraction condition. The bright- and dark-field images (Fig. 9e and f) using other reflections, like (T T 1) and (0 2 0), exhibit only residual contrast.

Two-beam bright-field images using (1 0 T) reflections acquired at increasing specimen thicknesses and the corresponding dark-field images are shown in Fig. 10. At very thin regions the dark-field images show only single dark fringes. With increasing thickness the fringe pattern changes to bright–dark–bright and then to bright–dark–bright–bright–dark. This thickness effect clearly confirms that the defect segments are indeed planar defects.

Plan-view HRTEM images of individual defect segments are shown in Figs. 11 and 12c. The defect in Fig. 11a mainly lies on the (1 1 0) plane except in the top part of the image, where it bends to lie on the (0 1 0) plane. In the lower part of Fig. 11a, the (1 1 0) and (1 T 0) fringes clearly shift by $a/4$ [1 1 0] and $a/4$ [1 T 0] respectively, therefore the projected displacement vector at the defect segment is $a/2$ [1 0 0]. No such shift, however, is discernible across defects in Figs. 11b and 12c, and they lie primarily on the (0 1 0) plane. It was also observed that the $a/2$ [1 T 0] partial dislocations are usually associated with the planar defects that did not show any shift in the lattice fringes, which indicates that their displacement vector is $a/2$ [1 T 0] (Fig. 12c).

HRTEM images of the threading dislocations with Burgers vector of the type $a$[0 1 0], $a$[1 1 0] and $a/2$[1 T 0], which were found in this sample, are shown in Fig. 12a-c respectively. The $a$[0 T 0] dislocation in Fig. 12a and the $a$[1 T 0] dislocation in Fig. 12b appear to be smeared out over a wider region. An $a$[1 T 0] dislocation dissociated over a length of 30 nm was also observed. On the other hand, the $a/2$[1 T 0] partial dislocation in the bottom right of Fig. 12c shows a sharp core. The density of the threading dislocations was estimated to be $2 \times 10^{10}$ cm$^{-2}$, and about half of them were observed to be partial dislocations. This density is only about half of that estimated from the diffraction contrast images in Fig. 8. Thus the remaining half of the edge-on dislocation-like defects in diffraction contrast images are actually the regions where two or more planar defects meet.
4. Discussion

The epitaxial growth mechanism, the microstructure features namely misfit dislocations, π staking faults, cation ordering domains, polar nanoregions and the correlation of the microstructure with the dielectric properties will be discussed in the following sections.

4.1. Epitaxial growth mechanism

The diffraction patterns in Fig. 1 clearly show the epitaxial growth of PST and SRO. Fig. 2 shows that, while SRO obviously grows by the layer-by-layer mode, PST most probably grows by three-dimensional (3-D) island growth mode. This growth mode plays a significant role in the
formation of the defect structure in the PST film. Hong et al. [23] explained the experimental and theoretical factors responsible for different growth regimes on the example of SRO. In spite of the extensive optimization of experimental parameters, viz. substrate temperature, oxygen pressure and deposition flux, it was not possible to obtain the layer-by-layer growth for PST. The 3-D island growth mode is expected to occur when the surface energy of the substrate–vapor interface is smaller than the sum of the deposit–vapor interface and deposit–substrate interface [24], which might be the case for the PST–SRO–STO system. The driving force for the 3-D island growth mode might be the large misfit of 4% between PST and STO. A detailed microstructural analysis of epitaxial PST films grown by PLD has not so far been reported in the literature. However, Lu et al. [25] reported a 3-D island growth mode in Ba0.3Sr0.7TiO3/LaAlO3 (0 0 1) which has a misfit of about 3.5%.

4.2. Misfit dislocations

Fig. 3 shows a [T 0 0]-, a/2 [T 0 1]- and a/2 [T 0 T]-type misfit dislocations (MDs) at the SRO–PST interface. The density of partial MDs was approximately equal to that of the perfect MDs. When g = (2 0 0), g·b > 0 for all the above MDs and they are therefore visible in Fig. 2a. Thus the average spacing between the perfect [T 0 0] MDs is estimated to be 15.8 nm. In the (1 1 0) cut sample only partial MDs of type a/2 [T 1 0] are observed at the interface (Fig. 4) and have a spacing of about 11.7 nm (Fig. 2e), which is about 2 times smaller than the distance between the perfect a [T 0 0] MDs. These a/2 [T 1 0] partial MDs can be interpreted as the [T 1 0] components of the a [T 0 0] and a [0 1 0] perfect MDs, according to the O-lattice model [22,26,27].

The average spacing between the effective (perfect as well as dissociated) a [T 0 0] MDs is estimated to be 10.5 nm, which corresponds to a strain relaxation equivalent to a misfit of 3.7%. Thus about 90% of the entire misfit strain is accommodated by the a (1 0 0)- and a/2 (101)-type MDs. Introduction of a (1 0 0)-type perfect MDs has been observed to be the common mechanism of relaxing the misfit strain in perovskite films grown on perovskite substrates [22,27–30]. a/2 (1 0 1)-type partial MDs in BaTiO3 films grown on STO and in STO films grown on LaAlO3 have also been observed by Suzuki et al. [30] and Qin et al. [22], respectively, but their density appears to be significantly lower than in the PST films studied in this work. Matthews [31] suggested that partial MDs may be formed when the stacking fault energy is low and the misfit strain is >1%. Considering the high density of planar defects in our films, the stacking fault energy of PST does indeed appear to be low.

In semiconductor epitaxial deposits, (i) the coalescence of islands and (ii) the nucleation and expansion of dislocation loops are used to explain the generation of MDs, TDs and planar defects [24,31,32]. The PST film showed 3-D island growth mode and a [H 100]- MDs (which have lower β2 in comparison to a [1 10]- MDs), which are expected to form at the edges of the growing islands to relax the misfit strain. Recently Misirlioglu et al. [33] have proposed this mechanism for the introduction of a (1 0 0)- MDs in PbZr0.2Ti0.8O3 and Ba0.6Sr0.4TiO3 [34] epitaxial films grown on perovskite substrates. For perovskite epitaxial...
films grown in layer-by-layer mode, the island coalescence model is obviously not applicable and the introduction of MDs has been explained by glide or climb of dislocation half loops by Suzuki et al. [30] and Qin et al. [22]. According to their model, \( a \{1 1 0 \} \) dislocation loops glide on the \( \{1 0 1 \} \) planes and dissociate at the interface to yield MDs of type \( a \{1 0 0 \} \) and edge dislocations of type \( a \{0 0 1 \} \), where the latter are supposed to be eliminated by mutual annihilation. Two different mechanisms for the introduction of partial misfit dislocations in perovskite epitaxial films have been observed. Suzuki et al. [30], in their BaTiO\(_3\) films on STO, observed the dissociation of MDs with \( b = a \{1 0 0 \} \) into two \( a/2 \{1 0 1 \} \) partial MDs, while Qin et al. [22] observed the dissociation of MDs with \( b = a \{1 1 0 \} \) into two \( a/2 \{1 1 0 \} \) partial MDs. In Fig. 3, the pairs of partial dislocations Nos. 5–6 and Nos. 8–9 appear to be dissociated \( \{1 0 0 \} \) MDs, i.e. they are in agreement with the observations of Suzuki et al. [30]. Moreover, partial MDs Nos. 5–6 appear to be connected by a half loop. One possibility is that the partial MDs Nos. 5–6, like partial MDs Nos. 8–9, were close, but spread out with time due to the mutual repulsion between interfacial components of their Burgers vectors. The second possibility is that the partial dislocation half loop was initially nucleated slightly above the interface at a region of high stress between the agglomerating islands and then expanded by glide or climb to reach the interface. From this viewpoint, we speculate that, even in perovskite thin films grown in 3-D island mode, MDs can be introduced by the dislocation half loop mechanism, especially after the coalescence of individual islands.

The peculiar defects Nos. 4 and 7 observed in Fig. 3, where the MDs appear a few tens of nanometers above the interface, can be explained using the phenomena of “bowing” and “fusing” of threading dislocations as described by Suzuki et al. [30]. Defect No. 4 can be interpreted as having formed from the gradual mutual annihilation of two threading dislocations in the \( \{1 0 0 \} \) plane with a Burgers vector of \( a \{1 0 0 \} \), leading to the formation of a “bow” which, at No. 4b, appears like an MD segment with a Burgers vector \( a \{0 0 1 \} \). Defect No. 7 appears to be formed from the fusing of a \( a \{0 1 0 \} \) MD and the accompanying TD in the \( 0 \{1 0 0 \} \) plane with an \( a \{1 0 0 \} \) MD and the accompanying TD in the \( 0 \{1 0 0 \} \) plane to yield a \( a \{1 0 0 \} \) TD which extends out of the \( 0 \{1 0 0 \} \) plane at No. 7c. As expected, the Burgers circuit around \( 7c \) exhibits a projected Burgers vector of \( a \{1 0 0 \} \).

4.3. \( \pi \) stacking faults

The thickness dependent fringe contrast in Figs. 8c, 9 and 10 indicates that the predominant threading defect structure consists of planar defects lying mainly on the \( \{1 0 0 \} \) and \( \{1 1 0 \} \) planes. Indeed, Fig. 8c shows that the planar defects lie in the \( \{1 1 0 \} \) plane. They exhibit antiphase boundary (APB)-like contrast features [35]: (i) the bright-field and dark-field images at \( s = 0 \) show complementary fringe contrast unlike that for \( 2\pi/3 \) stacking faults; and (ii) the outer fringes in the bright- and dark-field images are either both bright or both dark. However, unlike APBs in metal alloys, which are visible only using superstructure reflections, these planar defects in complex oxides are visible using structure reflections, viz. the \( \{1 1 0 \} \) and \( \{1 0 1 \} \) reflections. Such contrast features have been previously reported for the so-called \( \pi \) stacking faults (sometimes also called “cation antiphase boundaries”) observed in AlN [36], rutile [37], Pb(Zr,Ti)O\(_3\) (PZT) [38] and BaTiO\(_3\) [39]. Therefore, here the term “\( \pi \) stacking faults” will be used for these planar defects.

A detailed investigation of the habit planes, displacement vectors and contrast of planar defects in \( (\text{Ba,} \text{Sr})\text{TiO}_3 \) (BST) films deposited on \( \text{LaAlO}_3 \) (LAO) substrates was carried out by Lu et al. [25]. Their findings will be used to interpret the cross-sectional (Figs. 3 and 4) and plan-view (Figs. 11 and 12) HRTEM images. One of their recurring findings was that the stacking faults (SFs) exhibited strong HRTEM contrast and shift in lattice fringes only when the displacement vector had a non-zero component along the beam direction. Fig. 3a shows the planar defect No. 1 lying on the \( \{1 0 0 \} \) plane, revealing a strong contrast and shift in the lattice fringes with a projected displacement vector of \( a/2 \{1 0 0 \} \). Such a displacement vector is expected to be unstable because of the low packing density and ionic separation [25]. Therefore the displacement vector must be of the type \( a/2 \{1 1 0 \} \), the vector \( a/2 \{1 0 0 \} \) being its component perpendicular to the beam direction \( \{0 1 0 \} \). Fig. 4 exhibits a planar defect with a strong contrast lying on the \( \{1 1 0 \} \) plane with a displacement vector of \( a/2 \{0 0 1 \} \) or \( a/2 \{1 1 0 \} \). Both of these displacement vectors are reported to be stable for planar defects on the \( \{1 1 0 \} \) plane [40]. The plan-view HRTEM image in Fig. 11a exhibits a planar defect lying mainly on the \( \{1 1 0 \} \) plane with a projected displacement vector of \( a/2 \{1 0 0 \} \). Since this defect exhibits strong contrast and shift in the lattice fringes, its displacement vector must have a component along the beam direction \( \{0 0 1 \} \). Therefore the displacement vector of this defect is likely to be \( a/2 \{1 0 1 \} \). The displacement vectors in Figs. 11b and 12c can be determined as being of the type \( a/2 \{1 1 0 \} \) only from the Burgers vectors of the partial dislocations at their ends. Since the displacement vector does not have a component along the beam direction \( \{0 0 1 \} \), weak contrast and no shift of lattice fringes is observed in Figs. 11b and 12c. Thus the possible displacement vectors of the planar defects observed in this study are of the types \( a/2 \{1 1 0 \}, a/2 \{1 0 1 \}, a/2 \{0 0 1 \} \) and \( a/2 \{1 1 1 \} \).

The phases introduced by these planar defects in different diffracted beams are summarized in Table 1. It shows that a phase factor (i.e. \( 2\pi \mathbf{R} \cdot \mathbf{g} \)) of \( \pi \) is obtained for \( \mathbf{R} = a/2 \{1 0 0 \} \) and \( \mathbf{g} = (1 1 0) \) or \( (1 0 1) \). Since these are precisely the \( \mathbf{g} \) vectors which exhibited distinct fringe contrast in Figs. 8–10, we conclude that the majority of the threading defects observed in these PST films are planar defects with a phase of \( \pi \). In comparison to Fig. 8c,
acquired with a (½ 1 1 0) reflection. Figs. 9a–d and 10a–f, acquired using a (1 0 1 0) or (½ 1 1 0) reflection, show a much higher density of π-planar defects. This indicates that the density of π-planar defects with in-plane displacement vector of the type a/2 [1 1 0] or a/2 [1 1 0] is higher than those with out-of-plane displacement vectors of the type a/2 [1 0 1] or a/2 [0 1 1] (see Table 1).

Although the streaking in the diffraction patterns indicates that the planar defects lie predominantly on the {1 1 0} planes, the plan-view diffraction contrast and HRTEM images reveal that the planar defects do not strictly adhere to any set of crystallographic planes. They appear to gradually change their habit plane from type (1 1 0) to (2 1 0) to (1 0 0) to (2 0 0) and (2 1 0), are supposed to be formed by different combinations of {1 0 0} and {1 1 0} π-planar defects.

The compressive strain on the PST films grown on STO might also facilitate the formation of a/2 (1 1 0) planar defects, as suggested by Lu et al. [25] for BST films grown on LAO. The a/2 (1 1 0) planar defects involve the removal of PbO (1 0 0) planes, which is favorable for the relaxation of the compressive strain. In the PST films the contribution of planar defects to strain relaxation is expected to be significant (viz. 33%) since about half of the misfit dislocations were observed to be partials of the a/2 (1 0 1) type.

The high density of planar defects and the associated partial and threading dislocations indicate that the microstructure in the PST films is far from the one expected in thermal equilibrium. However, these PST films were grown at a relatively low deposition temperature (550 °C) using PLD, which is known to be a non-equilibrium growth technique.

4.4. Cation ordering domains

Dark-field images in Fig. 7 and the IFT of the HRTEM image in Fig. 5 reveal cation ordering domains with a size smaller than 10 nm in a disordered matrix yielding a 0–3 connectivity for the ordered domains and disordered matrix, respectively. This is in agreement with the XRD analysis, which estimated the volume fraction of ordered domains to be 35% in these films [20]. Such a 0–3 connectivity for the ordered nanodomains and disordered matrix is also the reason why antiphase boundaries expected at the interface between ordering domains in highly ordered samples are generally absent in these mostly disordered films [42,43].

The size of the ordering domains in Fig. 7b and d obtained from two different thin films is slightly different. This indicates that it might be possible to control the size of the ordering domains by optimizing the synthesis parameters. The size of the ordering domains in ordered PST thin films is, however, significantly smaller than in the similarly ordered PST single crystals and ceramics [16,43]. As was observed in single crystals [16], the smaller size of the ordering domains in PST thin films could be related to the lead deficiency. Indeed, Brinkman et al. [11] observed Pb deficiency close to the surface in their ~450 nm thick chemical solution-deposited PST films and close to the interface with the substrate.

The kinetics of the ordering domains in bulk PST has been discussed by Stenger and Burggraaf [44]. That the superstructure reflections in the XRD patterns are broadened and that two distinct heat effects are observed in differential scanning calorimetry experiments prompted those authors to infer that ordering occurs by nucleation and growth, resulting in the coexistence of ordered and disordered regions side by side. The observation of ordered domains in a disordered matrix (Figs. 5 and 7) therefore implies that the ordering in the PST thin films also occurred by a nucleation and growth mechanism. The
appearance of sharp superstructure reflections in Figs. 1b and 6b indicates a long-range order, albeit with a short coherence length of about 10 nm, corresponding to the size of the ordering domains [43]. Such a configuration of ordered domains in a disordered matrix is described as inhomogeneous ordering where the equilibrium situation is still not reached. Considering that the PST thin films under study are processed at the lower temperature of 550 °C, it is expected that an equilibrium is indeed not reached. This inhomogeneous ordering is, however, different from the inhomogeneity in the case of ordered domains in PST single crystals observed by Randall et al. [16]. They observed that Pb-deficient regions of the PST single crystal showed about 100 nm sized ordering domains while the Pb excess regions showed about 100 times larger ordering domains. The ordering domains in the PST thin films were, however, always smaller than 10 nm, indicating that chemical composition is homogeneous on a length scale larger than the distance between the π stacking faults (a few tens of nanometers).

4.5. Dielectric properties and microstructure

The recent and most agreed mechanism for the relaxor behavior of ferroelectrics is through the formation of polar nanoregions (PNRs) [45]. The dynamics of these PNRs is supposed to give rise to large dielectric constant and dielectric relaxation [7]. The PNRs grow in size with decreasing temperature, but in the case of relaxors do not become large enough to result in a cooperative ferroelectric transition, leading to an isotropic relaxor state with random orientation of the polar nanodomains.

Recently evidence for the formation of PNRs in PST thin films has been obtained by means of far infrared spectroscopy [9], indicating that the above-mentioned mechanism of relaxor behavior holds for the PST thin films as well. The relaxor behavior in PST ceramics is observed to increase with decrease in cation ordering [46]. However, a direct one-to-one correspondence between the 5–10 nm large cation ordering domains observed in Figs. 5 and 7 and the polar nanodomains could not be established as the TEM diffraction contrast images (Figs. 2 and 8–10) did not reveal stable polar nanodomains at room temperature. This indicates that the PNRs are rapidly fluctuating and/or the spontaneous distortions of the dipoles are too small [47]. It is possible that Pb and O vacancies, as inferred from the presence of large density of planar defects and dislocations, inhibit the growth of PNRs. The ordering domains could therefore consist of many small randomly fluctuating PNRs, as in the case of PST ceramics [18], the small size of the PNRs resulting in the high fluctuation frequency [48]. It should be noted that no polar nanodomains could be detected by TEM in Pb(Mg_{1/3}Nb_{2/3})O_{3} [47] or in Pb- and O-deficient PST [18] relaxers, which was attributed to the high fluctuation frequency of the PNRs.

There are two peculiar aspects of PST thin films which require an explanation. First is that the dielectric constant of these films is an order of magnitude smaller than the ceramics. Secondly, unlike in ceramics, the dielectric constant of PST thin films increases with increasing order [7]. The reduced dielectric constant of PST thin films could not be explained by external factors like interfacial capacitance layers [10] and substrate induced strain [11,12]. It is likely that the explanation lies in the differences in the microstructure of PST thin films and PST ceramics [7,10].

The microstructure of bulk PST with differing degrees of cation ordering has been investigated previously [13–19]. In PST ceramics with low degree of ordering, cation ordering domains in a matrix of disordered PST were observed. In highly ordered PST, ordering domains separated by APBs were found. A number of different dislocation configurations were also observed [18]. In PST thin films the dominant microstructural feature is observed to be the large density of π stacking faults. We propose that these π stacking faults are the ones responsible for the reduced dielectric constant of PST thin films. Although a detailed characterization of the microstructure of PST thin films has not been carried out previously, Brinkmann et al. [7] did postulate that the state of disorder in disordered PST thin films processed at low temperatures might include vacancy and atomic concentration variations on a length scale longer than two lattice constants, thus departing considerably from the entropy-driven atomic lever disorder found in disordered ceramics annealed near 1500 °C. Therefore Brinkmann et al. [7] further postulated that the true relaxor phase in thin films might be reduced to the small areas between the non-stoichiometric regions, thereby resulting in a reduced dielectric constant in comparison to ceramics. The electron microscopy results in this work make it highly probable that the non-stoichiometric non-relaxor regions are the π stacking faults and the regions in their proximity.

5. Conclusions

Epitaxial thin films of relaxor PST were grown by pulsed laser deposition on an SrTiO$_3$ substrate with an SrRuO$_3$ buffer layer and investigated by diffraction contrast imaging and high-resolution transmission electron microscopy in cross-section and plan-view. The PST films grew by 3-D island growth due to the −4% lattice mismatch with the substrate. Prominent microstructural features are misfit dislocations, π stacking faults and cation ordering domains.

As expected for perovskite thin films on perovskite substrate, $a$ $\langle 100 \rangle$ and $a/2$ $\langle 101 \rangle$ misfit dislocations were observed and could account for the accommodation of about 90% of the entire misfit strain. The large density of partial misfit dislocations and the corresponding stacking faults indicate a low stacking fault energy. The $a$ $\langle 100 \rangle$ misfit dislocations are likely to be formed at the edges of the growing islands to release misfit strain. The $a/2$ $\langle 101 \rangle$ partial misfit dislocations were observed to be formed by the dissociation of $a$ $\langle 100 \rangle$ misfit dislocations, in agreement with the observation of Suzuki et al. [30] in BaTiO$_3$ films.
Vectors \( a/2 \{ 1 1 0 \}, a/2 \{ 1 0 1 \}, a/2 \{ 0 0 1 \} \) and \( a/2 \{ 1 \bar{1} 1 \} \) were identified as the possible displacement vectors of the abundant \( \pi \) stacking faults. Among these, the in-plane displacement vectors of the type \( a/2 \{ 1 1 0 \} \) were most frequently observed using diffraction contrast imaging. It is highly likely that the origin for the formation of the high density of planar defects is the coalescence of islands during 3-D island growth. They might also arise from the lattice collapse by a shear vector \( a/2 \{ 1 1 0 \} \) through \( \{ 1 0 0 \} \) and \( \{ 1 1 0 \} \) planar arrays of Pb and O vacancies [38].

Cation ordering domains are observed in a disordered matrix, indicating that the cation ordering occurred by a nucleation and growth mechanism [44]. The size of the cation ordering domains is smaller in comparison to that of bulk PST, which may be attributed to a lead-deficient stoichiometry in PST thin films [16].

The state of the structural disorder in PST relaxor thin films is characterized by a high density of \( \pi \) stacking faults and a rather small size (<10 nm) of the cation ordering domains, and is therefore markedly distinct from the state of disorder in bulk relaxor-type PST. We postulate that this leads to an extremely small size and high fluctuation frequency of the polar nanoregions. Polar nanoregions, supposed to be essential to explain the relaxor properties, could not be detected here using TEM, possibly due to the high fluctuation frequency of the polar nanoregions. The dielectric constant of the relaxor PST thin films is about an order of magnitude smaller than that of bulk PST, which is attributed to the large density of \( \pi \) stacking faults in the PST thin films.

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