Full Paper

Spontaneous superlattice formation and electrical properties of Sr-excess SrTiO₃ thin film deposited on SrTiO₃(101) by dynamic aurora pulsed laser deposition

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Epitaxial Sr-excess SrTiO₃ (ST) thin film (Sr/Ti = 1.41) was grown on ST(001) and ST(101) single-crystal substrates using dynamic aurora pulsed laser deposition (PLD) under a 200 mT magnetic field. The films spontaneously formed a superlattice structure comprising two layers having different concentrations of Ruddlesden–Popper (RP) planar faults. The superlattice periods of Sr-excess ST thin films deposited on ST(001) and ST(101) substrate were, respectively, 35 and 23 nm. For thin film deposited on ST(001), the in-plane lattice parameter coincided with the substrate, showing coherent growth. For thin film deposited on ST(101), coherent growth occurred along a direction ±45° declined against the substrate. The spontaneously formed superlattice was brought about by “up-hill diffusion” of spinodal decomposition. The direction of propagation of the composition wave of spinodal decomposition was regarded as perpendicular to the substrate and ±45° declined against the substrate for thin films deposited respectively on ST(001) and ST(101). The superlattice period of the thin film deposited on ST(101) (23 nm) is smaller by a factor of 1/√2 than that deposited on ST(001). This relation is explainable by the difference of the propagation direction of the composition wave. The thin film deposited on ST(001) is distorted tetragonally, whereas that on ST(101) is cubic. The Sr-excess ST thin film was also deposited on La-doped ST(101) (La-ST(101)) and La-ST(101) substrates to measure electrical properties. No change was found in the crystal structure and microstructure, irrespective of La-doping. The thin film deposited on La-ST(001) showed ferroelectricity. However, the film deposited on La-ST(101) shows no ferroelectricity. The difference of electrical properties is brought about by differences of crystal symmetry. The difference is also explainable from the perspective of thermodynamic phenomenology.

Key-words : Dynamic aurora PLD, Epitaxial, Ferroelectricity, Spontaneous superlattice formation, SrTiO₃(101) substrate, Superlattice period

1. Introduction

Ruddlesden–Popper (RP) homologous compounds with the general formula Srₙ₊₁TiₙO₃+n (n = 1, 2, 3, …, ∞) are known to exist in Sr–Ti–O systems. These RP compounds consist of an additional SrO layer inserted into the SrTiO₃ (ST) lattice, thereby forming a SrO bilayer.1 Stoichiometric ST can be regarded as n = ∞. Among the RP compounds, earlier reports show that only n = 1–3 members can be synthesized using a conventional solid state reaction;2,3 trials to synthesize 3 < n < ∞ members were unsuccessful.3 Haeni et al. prepared epitaxial RP thin films on ST(001) substrates with n = 1–5 using molecular beam epitaxy with both Sr and Ti sources.4 Suzuki et al. prepared epitaxial Sr-excess ST thin film (Sr/Ti = 1.5) on ST(001) substrates using pulsed laser deposition (PLD). They reported that excess SrO is accommodated as RP planar faults showing a peculiar three-dimensional mosaic structure without forming secondary phases or dislocations.5 Tokuda et al. also prepared epitaxial Sr-excess ST thin film (Sr/Ti = 1.06–1.25) on ST(001) substrates using PLD. They found that the growth direction of the RP planar faults change from normal to normal and parallel to the substrate surface with an increase in excess Sr.6 Morito et al. prepared Sr-excess ST thin films (Sr/Ti = 1.1–1.4)
on Pt/Ta/SiO₂/Si substrates using radiofrequency sputtering. They found that excess Sr was accommodated as a RP planar fault. Additionally, they found that the Sr-excess ST thin films exhibit a superior insulating property to those of stoichiometric ST thin films. This high insulating property, which serves as an effective barrier for electric conduction was inferred as deriving from the RP planar fault. Oh et al. reported recently that bulk crystals of Ca₃Ti₂O₇ and Sr-doped Ca₃Ti₂O₇ show hybrid improper ferroelectricity. However, no ferroelectricity has been reported to date for Sr₂₊₁⁺ₓTi₇₋ₓO₃₋₄₊ₓ RP homologous compounds.

We have found that epitaxial Sr-excess ST thin films (Sr/Ti = 1.20–1.46) on ST(001) substrates using dynamic aurora PLD show a spontaneously formed superlattice structure. The dynamic aurora PLD is a specially designed PLD in which an electromagnet is installed in the vacuum chamber to apply a magnetic field parallel to the direction from the target to the substrate.10,11) Spontaneous formation of a superlattice was observed only when a magnetic field of more than 100 mT was applied during deposition. Spinodal decomposition has been considered as a possible reason for the spontaneously formed superlattice structure.12–15) The spinodal decomposition is brought about by “up-hill diffusion” along a propagating composition wave.16–19) Daruka and Tersoff examined the dynamics of alloy growth by vapor deposition and bulk diffusion (up-hill diffusion) theoretically. From that examination, they found that diffusion during thin film deposition engenders spontaneous formation of a superlattice when the direction on the propagating composition wave is perpendicular to the substrate.20) Based on these reports and results of cross-sectional scanning transmission electron microscopy (STEM) analysis, we have inferred that the spontaneously formed superlattice structure comprises two alternately stacked layers with high and low concentrations of RP planar faults.9)

We have also found that the spontaneously formed superlattice of Sr-excess ST thin films (Sr/Ti = 1.20–1.46) on ST(001) substrates shows ferroelectricity,9) although bulk ST is quantum paraelectric.21) The origin of ferroelectricity was regarded as strain.22) The ferroelectricity was explained based on extension of work reported by Haeni et al.23)

To date, the spontaneous superlattice formation has been found for thin films on ST(001) substrates only. Effects of substrate orientation have not been clarified yet. The purpose of this work is to clarify whether spontaneous superlattice formation via spinodal decomposition is observed, or not, for a Sr-excess ST thin film deposited on a ST single-crystal substrate having other orientation. This work examined effects of using ST(101) substrates on crystal structure and electrical property of Sr-excess ST thin films.

### 2. Experimental

We deposited ST thin films having Sr-excess composition using PLD with a Nd:YAG laser (λ = 266 nm) at 700 °C in oxygen at a pressure of 1.33 × 10⁻² Pa. The target was synthesized using a conventional solid state reaction. Reagent grade SrCO₃ (3N) and TiO₂ (2N) powders were mixed, calcined at 1200 °C for 6 h, ground into powders, pressed into pellets, and sintered at 1350 °C for 8 h. During deposition, a 200 mT of magnetic field parallel to the direction from the target to the substrate was applied to the plume. After deposition, aging at 700 °C for 20 min in the PLD chamber was conducted without application of a magnetic field. Detailed deposition conditions are presented in Table 1. For crystal structure measurements, a pair of thin films was deposited sequentially on ST(001) and (101) single-crystals and Si substrates using identical deposition conditions. For electrical property measurements, a pair of thin films was deposited sequentially on La-doped ST (La-ST)(001) and (101) single-crystals and Si substrates using identical deposition conditions. In-plane and out-of-plane lattice parameters of thin films deposited on ST(001) and (101) were measured using reciprocal space mapping taken using high-resolution X-ray diffractometry (ATX-G; Rigaku Corp.). Cross-sectional STEM analysis was also conducted for a STEM system with accelerating voltage of 200 kV (JEM-2100F; JEOL Ltd.) equipped with an EDS detector. The sample used for STEM observations was prepared using an ion milling system (EM-09100IS; JEOL Ltd.). For the film deposited on the Si substrate, the composition and thickness were ascertained using an X-ray fluorescence spectrometer (Minipal; PANalytical B.V.) equipped with the FP Multi software module.

Electrical property measurements were conducted for thin films deposited on La-ST(001) and (101) substrates. The substrates were used as a bottom electrode. Also, Pt top electrodes (100 μm) were fabricated through the metal mask using dc magnetron sputtering. The P–E curves were measured using a ferroelectric tester (FCE-1; Toyo Corp.) operating at 1 kHz.

### 3. Results and discussion

The thickness and composition of thin films analyzed using the X-ray fluorescence spectrometer were, respectively, 400 nm and Sr/Ti = 1.41. Figures 1(a) and 1(b) respectively portrays XRD patterns of Sr-excess ST thin films deposited on ST(001) and (101) substrates. In neither

| Table 1. Deposition conditions of Sr-excess SrTiO₃ thin films |
|-------------------------|-------------------------|
| Laser | Nd:YAG laser (λ = 266 nm) |
| Repetition rate/Hz | 10 |
| Target | Sr-excess SrTiO₃ |
| Film composition | Sr/Ti = 1.41 |
| Substrate for crystal structure measurements | SrTiO₃(001), (101) and Si |
| Substrate for electrical property measurements | La-SrTiO₃(001), (101) and Si |
| Fluence/J/cm² | 2.0 |
| Magnetic field/mT | 200 |
| Substrate temperature/°C | 700 |
| Oxygen pressure during deposition/Pa | 1.33 × 10⁻² |
| Deposition time/min | 15 |
| Aging time/min | 20 |
thin film was a secondary phase detected. In both thin films, a main peak [Sr-excess ST(002) on ST(001) substrate and Sr-excess ST(101) on ST(101) substrate] and clearly defined satellite peaks labeled by open circles were observed. Because the satellite peaks are evidence of spontaneous superlattice formation, results showed that the spontaneous superlattice formation of the thin film deposited on ST(101) substrate is confirmed in addition to that on ST(001) substrate. The superlattice period \( A \) is calculable based on the following formula.

\[
\sin \theta_m = \sin \theta_B \pm m \lambda / 2A \quad (1)
\]

Therein, \( \theta_B \) represents the Bragg angle for the average film composition, \( m \) denotes an integer (the order of reflection), and \( \lambda \) stands for the X-ray wavelength (0.15406 nm). Consequently, the superlattice periods \( A \) of thin film deposited on ST(001) and (101) are, respectively, 35 and 23 nm.

**Figure 2(a)** portrays a reciprocal space map measured around ST(103) for Sr-excess ST thin film deposited on ST(001). In this figure, \( Q_x \) and \( Q_z \) respectively denote reciprocal space coordinates along [100] and [001]. Also, \( Q_x \) and \( Q_z \) are defined respectively as \( 1/d_{100} \) and \( 3/d_{001} \). The figure shows that the thin film is grown epitaxially. The \( Q_x \) value of the thin film coincides with that of the substrate. This finding agrees well with our earlier report that spontaneous superlattice formation is observed when coherent growth is realized.\(^9\),\(^10\) The white line shown in this figure is an auxiliary line along [001] to facilitate understanding of coherent growth. **Figure 2(b)** depicts a reciprocal space map measured around ST(004) for Sr-excess ST thin film deposited on ST(101). In this figure, \( Q_x \) and \( Q_z \) are defined respectively as \( 1/d_{101} \) and \( 1/d_{100} \). This figure also shows that the thin film is grown epitaxially. From these results, we infer that coherent growth is not realized because the \( Q_x \) value of the thin film differs from that of the substrate. However, drawing an auxiliary line along the [001] direction reveals that both the reciprocal points of thin film and substrate are clearly on the same line. Therefore, coherent growth is realized not along the [101] but along the [001] direction. Based on reciprocal space maps presented in Figs. 2(a) and 2(b), the out-of-plane and in-plane lattice parameters of Sr-excess ST thin films were calculated as shown in **Table 2**. Before calculation, the \( Q_x \) and \( Q_z \) values of thin film were calibrated using those of ST single crystals. For this work,
the axis ratio was defined as $a_{\perp}/a_{\parallel}$; therein, $a_{\perp}$ and $a_{\parallel}$ respectively represent out-of-plane and in-plane lattice parameters. The axis ratios for the Sr-excess ST thin film deposited on ST(001) and (101) were, respectively, 1.036 and 0.995. Therefore, the film deposited on ST(001) has tetragonal distortion, whereas that deposited on ST(101) is almost cubic.

Figure 3 presents cross-sectional STEM images of (a) HAADF and (b) EDS images of Sr-excess ST thin film deposited on ST(101). The HAADF and EDS images confirm spontaneous superlattice formation. The superlattice period observed from STEM images was 23 nm, which value agrees well with the superlattice period obtained from satellite peaks presented in Fig. 1(b) (23 nm). The EDS images also show periodical change of the element concentration having same period, especially for Ti, and slightly for O and Sr. Figure 4 shows an HRTEM image of the film. In this figure, four white lines (1), (2), (3), and (4) are drawn as auxiliary lines along [001]. On lines (1) and (2), the atoms are aligned regularly. However, on lines (3) and (4), insertion of planar faults can be observed clearly, indicating that planar faults exist along [001]. Because of the symmetry of ST(101) substrate, the planar fault is also expected to exist along [100]. Therefore, it is considered that the film deposited on ST(101) includes planar faults of two kinds along both [001] and [100]. These planar faults correspond to RP planar faults composed of SrO bilayer.5,7 As described in an earlier report, for the Sr-excess ST thin film deposited on ST(001), the spontaneously formed superlattice consists of high concentration RP planar faults layer and low concentration RP planar faults layers as presented schematically in Fig. 5(a).5,9 For the Sr-excess ST thin film deposited on ST(101), we consider that the spontaneously formed superlattice consists of the same fashion. However, for the thin film on ST(101), the RP planar faults are inserted $\pm 45^\circ$ declined to the substrate, as presented in Fig. 5(b). As described in the Introduction, spinodal decomposition is brought about by propagation of the composition wave. As depicted in Fig. 6(a), in the case of Sr-excess ST thin film deposited on ST(001), the direction of propagation of the composition wave is perpendicular to the substrate, i.e., along the [001] direction.9,10 Therefore, for the film on ST(001), the superlattice period coincides with the wavelength of the composition wave. By contrast, as depicted in Fig. 6(b), for the Sr-excess ST thin film deposited on ST(101), it is expected that the direction of propagation of the composition wave is along the [001] and [100] direction. However, because the [001] and [100] directions are $\pm 45^\circ$ declined to the substrate, the net superlattice period along the [101] direction should be $1/\sqrt{2}$ of the composition wave wavelength. Actually, as presented in Figs. 1(a) and 1(b), the superlattice periods of thin films on ST(001) and (101) are, respectively, 35 and 23 nm. When the superlattice period of thin film on ST(001) (35 nm) is divided by $1/\sqrt{2}$, we obtain 25 nm. This value is extremely close to the superlattice period of thin film on ST(101) (23 nm). Therefore, the short

| Table 2. Out-of-plane and in-plane lattice parameters and axis ratio of Sr-excess SrTiO$_3$ thin films deposited on ST(001) and (101) single-crystal substrates calculated from the reciprocal space map |
|----------------------------------------|-----------------|-----------------|
|                                       | On ST(001)      | On ST(101)      |
| Out-of-plane lattice parameter ($a_{\perp}$)/nm | 0.406           | 0.398           |
| In-plane lattice parameter ($a_{\parallel}$)/nm | 0.392           | 0.400           |
| Axis ratio, $a_{\perp}/a_{\parallel}$     | 1.036           | 0.995           |
superlattice period of the Sr-excess ST thin film deposited on ST(101) is explainable.

As Table 2 shows, for the thin film deposited on ST(001), the out-of-plane and in-plane lattice parameter are, respectively, 0.406 and 0.392 nm. The in-plane lattice parameter is almost identical to the lattice parameter of ST single-crystal (0.3905 nm). Therefore, for the thin film on ST(001), lattice parameter expansion occurs only along the out-of-plane direction to bring about tetragonal distortion. This finding agrees well with the consideration that the composition wave of spinodal decomposition propagates only along the out-of-plane direction. However, for the thin film deposited on ST(101), the lattice parameter expansion occurs along both out-of-plane and in-plane directions to bring out relaxation to become cubic. This finding agrees well with the consideration that the composition wave of spinodal decomposition propagates along both the [100] and [001] directions.

In this work, Sr-excess ST thin films were deposited on La-ST(001) and La-ST(101) in addition to ST(001) and ST(101) to measure electrical properties. No difference was found in the crystal structure or morphology for thin films deposited on ST or La-ST. Figure 7 shows $P-E$ curves of Sr-excess ST thin film having spontaneous superlattice deposited on (a) La-ST(001) and (b) La-ST(101). This figure shows that the film deposited on La-ST(001) exhibits slight ferroelectricity, as reported earlier. By contrast, the film deposited on La-ST(101) shows no ferroelectricity. This result is explainable from the point of axis ratio. As presented in Table 2, the thin film deposited on ST(001) substrates has tetragonal distortion. Therefore, strain-induced ferroelectricity is observed. However, the thin film deposited on ST(101) substrates is almost cubic. Therefore, no strain-induced ferroelectricity is observed. The results portrayed in Fig. 7 can also be explainable based on thermodynamic phenomenology. As described above, Haeni et al. reported room-temperature ferroelectricity for strained ST and predicted...
the change of transition temperature with in-plane strain. We have extended this concept using out-of-plane strain.\(^9\)

In this work, the out-of-plane strain \(\varepsilon_s\) was calculated as the following.

\[
\varepsilon_s = a_\perp \text{ (ST thin film)} - a \text{ (ST substrate)}
\]

The value of \(a_\perp\) was referred from Table 2. Figure 8 presents extension of the expected shift in transition temperature with out-of-plane strain. In this figure, red closed circles labeled (a) and (b) respectively correspond to the positions of Sr-excess ST thin film having spontaneous superlattice deposited on La-ST(001) and La-ST(101). The position of the thin film deposited on La-ST(001) is in the “range of ferroelectric transition.” That on La-ST(101) is in the “paraelectric” range. This finding agrees well with results portrayed in Fig. 7.

4. Conclusions

In Sr-excess ST thin films, excess SrO is reportedly incorporated in the ST lattice of the perovskite structure as a SrO bilayer: so-called RP planar faults. For this work, epitaxial Sr-excess ST thin film (Sr/Ti = 1.41) was grown on ST(001) and ST(101) single-crystal substrates using dynamic aurora PLD (PLD in the magnetic field) under a magnetic field of 200 mT. The films have a spontaneously formed superlattice structure. The spontaneously formed superlattice comprises two layers having different concentrations of RP planar faults. The superlattice periods of Sr-excess ST thin films deposited on ST(001) and ST(101) substrate were, respectively, 35 and 23 nm. For the thin film deposited on ST(001), the in-plane lattice parameter coincided with substrate, exhibiting coherent growth. For the thin film deposited on ST(101), coherent growth occurred along the [100] and [001] directions. These directions are declined \(\pm 45^\circ\) against the substrate. The spontaneously formed superlattice was brought about by up-hill diffusion of spinodal decomposition. The direction of propagation of composition wave of spinodal decomposition was regarded as perpendicular to the substrate and \(\pm 45^\circ\) declined against the substrate for thin films deposited respectively on ST(001) and ST(101). The superlattice period of the thin films deposited on ST(101) (23 nm) is smaller by a factor of \(1/\sqrt{2}\) than that deposited on ST(001). This relation is explainable based on the difference of propagation direction of the composition wave. The thin film deposited on ST(001) is distorted tetragonally, whereas that on ST(101) is cubic. The Sr-excess ST thin film was also deposited on La-doped ST(101) [La-ST(101)] and La-ST(101) substrates to measure electrical properties. No change was found in the crystal structure or microstructure irrespective of La-doping. The thin film deposited on La-ST(001) showed ferroelectricity. However, the film deposited on La-ST(101) shows no ferroelectricity. The difference of electric properties is brought about by a difference of crystal symmetry. The difference was also explainable from the perspective of thermodynamic phenomenology.

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