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Large tensile-strained BaTiO₃ films grown on a lattice-mismatched La-doped BaSnO₃ bottom electrode†

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Perovskite BaTiO₃ has been widely studied and utilized in various applications owing to its high permittivity, ferroelectricity, and stability. However, its low ferroelectric-paraelectric phase transition temperature (T_C , 120 °C) limits its application. The T_C can be increased by applying an epitaxial strain provided by a lattice-mismatched substrate. However, applying large tensile strain on BaTiO₃ is difficult, especially when a bottom electrode is present. In this study, we successfully fabricated large tensile-strained BaTiO₃ films using La-doped BaSnO₃ bottom electrodes. A tensile strain of 2% was achieved, which is three times larger than that previously reported for BaTiO₃ films grown on bottom electrodes. By adjusting the thickness of the BaTiO₃ layer between 20 and 300 nm, tensile strain can be varied within the range of 0.6–2%. Remarkably, the T_C of the obtained films exceeds 400 °C. In addition, although it was considered that tensile-strained BaTiO₃ films have ferroelectric polarization in the in-plane direction, the 0.6% tensile-strained film showed ferroelectric polarization in the out-of-plane direction. This finding reveals that the ferroelectric polarization direction was slightly tilted away from the predominant in-plane direction of the film.

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1. Introduction

Perovskite BaTiO₃ is one of the most promising ferroelectric materials owing to its desirable properties such as high permittivity (ϵ_r), tunability of ϵ_r , piezoelectricity, and stability.^{1,2} It is widely used in electronic components such as multilayer ceramic capacitors and microwave devices.^{3–7} The properties of BaTiO₃ can be controlled by varying the strain from the substrate. For instance, in epitaxial BaTiO₃ film grown coherently on the DyScO₃ substrate, the remnant polarization value of the ferroelectric phase is significantly higher (70 $\mu\text{C cm}^{-2}$) compared to that of the bulk (24 $\mu\text{C cm}^{-2}$).⁸ Furthermore, BaTiO₃ films demonstrate a 500 °C increase in ferroelectric transition temperature (T_C) compared with the bulk (120 °C).⁸ In addition, a flexoelectric effect occurs, causing the alignment of the polarization direction in

the out-of-plane direction without the application of an electric field.^{8–10}

The magnitude of substrate-induced strain can be controlled by selecting the substrates, bottom electrodes, and film thickness. For instance, when BaTiO₃ films were coherently grown on SrTiO₃ ($a = 3.905 \text{ \AA}$) or GdScO₃ ($a = 3.965 \text{ \AA}$) substrates, compressive strains of 2 and 0.7% were induced in the films, respectively,^{8,11} whereas bulk BaTiO₃ exhibited a tetragonal perovskite structure with $a = 3.992$ and $c = 4.036 \text{ \AA}$. Such application of compressive strain increases in remnant polarization (P_r), which is associated with an increase in the c/a ratio.^{8–12} Conversely, the application of tensile strain on BaTiO₃ films has also been investigated using substrates with large lattice constants such as MgO ($a = 4.213 \text{ \AA}$) and MgAl₂O₄ ($a/2 = 4.042 \text{ \AA}$).^{13–18} The films showed an enhancement in T_C (200–220 °C) and ferroelectricity along the in-plane direction.^{17,18} However, these substrates are insulators, and it is difficult to prepare bottom electrodes while maintaining a high tensile strain on the BaTiO₃ layer. In fact, in previously prepared BaTiO₃ films with bottom electrodes, tensile strain was limited to 0.57%.^{19,20} To achieve a large tensile strain in the BaTiO₃ film, we investigated La-doped BaSnO₃ (LBSO, hereafter) epitaxial films as electrodes because they have a cubic perovskite structure with $a = 4.116 \text{ \AA}$, which is 3% longer compared to BaTiO₃ and exhibits rather high electrical conductivity over 10^3 S cm^{-1} at room

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temperature.^{21–27} In this study, we investigated the crystal structures and ferroelectric properties of tensile-strained BaTiO₃ films grown on 50 nm-thick LBSO bottom electrodes prepared on SrTiO₃ (001) (STO) substrates. By adjusting the film thickness, the tensile strain values can be varied between 0.6 and 2%. The T_C of the 0.6 and 1.3%-tensile-strained films were ~ 400 and ~ 500 °C, respectively, which is significantly higher than that of the bulk BaTiO₃ (120 °C). In case of the polarization *versus* electric field (P - E) curves, ferroelectric behavior did not appear along the out-of-plane direction for the 1.4–2%-tensile strained films probably because the ferroelectric polarization appears in the in-plane direction. On the contrary, the 0.6%-tensile-strained film also exhibited ferroelectric polarization along the out-of-plane direction, suggesting that the ferroelectric polarization direction was slightly tilted away from the in-plane direction.

2. Experimental

Epitaxial films of BaTiO₃ were fabricated on LBSO (2% La-doped, La_{0.02}Ba_{0.98}SnO₃)-buffered SrTiO₃ (001) substrates using a pulsed laser deposition (PLD) technique.²⁴ During the deposition, the substrate temperature, laser energy, and oxygen partial pressure were maintained at 850 °C, 0.5 J cm⁻² pulse⁻¹, and 0.5 Pa for the BaTiO₃ layer and 750 °C, 2 J cm⁻² pulse⁻¹, and 20 Pa for the LBSO layer, respectively. The typical thickness of the LBSO layer is 50 nm.

The crystal structures of the obtained films were evaluated using high-resolution X-ray diffraction (XRD, ATX-G, Rigaku Co.) with Cu K α_1 radiation and variable-temperature XRD (D8 Discover, Bruker AXS GmbH) with Cu K α_1 and K α_2 radiation. The film thicknesses were determined by analyzing the Pendellösung fringes around the Bragg diffraction peaks and X-ray reflectivity. For the calculation of strain, we employed the formula: strain = $a_{\text{film}}/a_{\text{bulk}} - 1$, which is commonly used in previous literature. The surface morphology was observed by atomic force microscopy (AFM, Nanoscope, Hitachi High-tech). The ferroelectric properties of the films were measured using a ferroelectric tester (Multiferroic II, Radiant Inc.). In the measurement, an 80 nm-thick Pt electrode with a diameter of 100 μm was used as the top electrode, whereas the LBSO layer was used as the bottom electrode.

3. Results and discussion

Fig. 1 shows the out-of-plane XRD patterns of the BaTiO₃ films as functions of the BaTiO₃ thickness (t_{BTO}). The films were grown on the LBSO bottom electrodes prepared on STO substrates. The range of t_{BTO} is set to 20–300 nm. The (002) diffraction peaks of LBSO and BaTiO₃ appear at $q_z/2\pi = 4.85$ and 5.00 – 5.02 nm⁻¹, respectively. In addition, clear Pendellösung fringes were observed around the (002) diffraction peaks of LBSO, indicating the highly (001) orientation of the LBSO bottom electrode layer. On the contrary, the (002) diffraction peaks of BaTiO₃ shift toward a

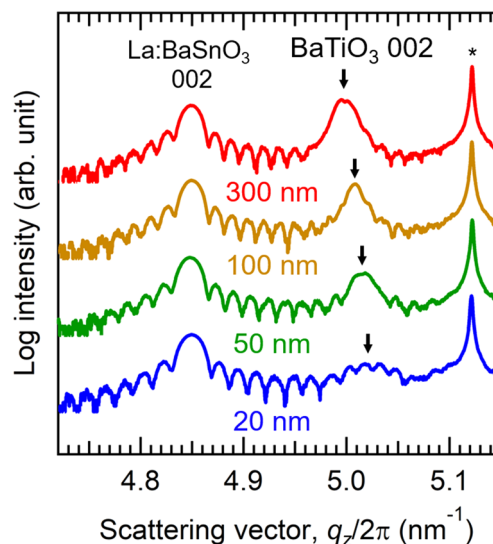


Fig. 1 Out-of-plane XRD patterns of the BaTiO₃ films with varied thickness grown on LBSO/STO substrates. The asterisk indicates the (002) STO substrate peak.

lower $q_z/2\pi$ side with increasing t_{BTO} . As the t_{BTO} increases from 20 to 300 nm, the c -axis length of the BaTiO₃ layer increases from 3.979 to 4.006 Å. The c -axis lengths were shorter than those of bulk BaTiO₃ ($c = 4.036$ Å), indicating the presence of tensile strain within the films. Fig. S1† shows the film surface morphologies. The root mean square roughness values are smaller than 0.3 nm, confirming the atomically flat surface of the films.

Fig. 2 shows the reciprocal space mappings (RSMs) around the (103) diffraction spot for the BaTiO₃ film with varied thicknesses. In case of the LBSO layer, the in-plane a -axis length (4.08 Å) is shorter than the out-of-plane c -axis length (4.125 Å) owing to the compressive strain from the STO

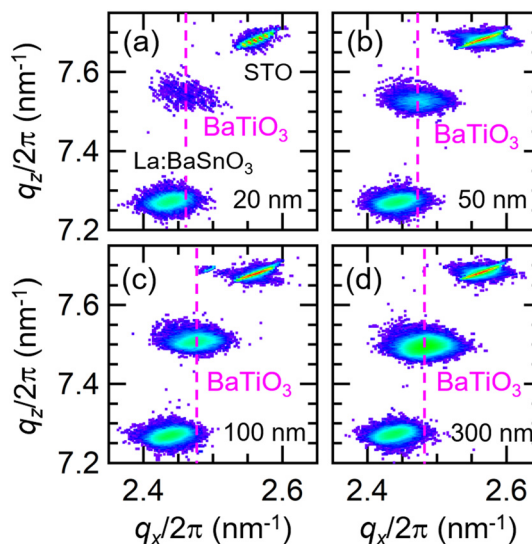


Fig. 2 Reciprocal space mappings for the BaTiO₃ film around the (103) diffraction spots. t_{BTO} = (a) 20, (b) 50, (c) 100, and (d) 300 nm.



substrate. The (103) diffraction spot of BaTiO₃ was observed as a single spot without splitting, indicating that the BaTiO₃ layer had a tetragonal structure. With increasing t_{BTO} , the diffraction spot of BaTiO₃ shifts toward the higher $q_z/2\pi$ side. The a -axis lengths of the BaTiO₃ films are in the range of 4.01–4.07 Å, which is shorter than that of the LBSO layer, whereas it is longer than that of bulk BaTiO₃. These results confirmed the presence of tensile strain in the BaTiO₃ films.

Fig. 3(a) shows the lattice constants of the BaTiO₃ films as a function of t_{BTO} . Remarkably, the c -axis was shorter than the a -axis length, in contrast to the behavior observed for bulk BaTiO₃. With increasing t_{BTO} , the a (c) values of the films monotonically increased (decreased) and approached those of the bulk single crystal. Fig. 3(b) shows the tensile strain values of the BaTiO₃ films. At $t_{\text{BTO}} = 20$ nm, the tensile strain value is as high as 2.0%, which is much higher than the previous report on epitaxially grown BaTiO₃ films on MgO substrate with the bottom electrode layer (<0.57%).^{19,20} The tensile strain value decreases with increasing t_{BTO} and reaches 0.6% at $t_{\text{BTO}} = 300$ nm. The decrease in the tensile strain with increasing t_{BTO} was attributed to the relaxation of the in-plane lattice with increasing distance from the substrate because of the generation of dislocations in the film.^{28,29}

The BaTiO₃ films were deposited using PLD at a substrate temperature (T_s) of 850 °C and an oxygen partial pressure (P_{O_2}) of 0.5 Pa, with a laser energy of 0.5 J cm⁻² pulse⁻¹. Notably, PLD conditions are known to influence the lattice strain and properties of BaTiO₃ films. For instance, the c/a values decrease with increasing T_s for BaTiO₃ films grown on multilayer-buffered Si substrates.³⁰ Additionally, it has been reported that oxygen vacancies are introduced at low P_{O_2} ,

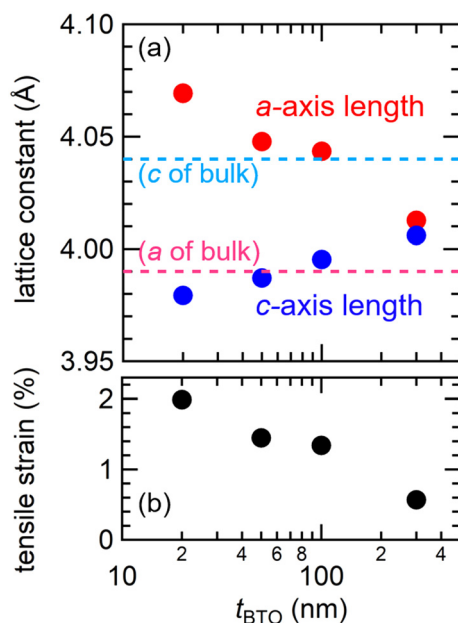


Fig. 3 (a) Lattice constants and (b) tensile strain values for the BaTiO₃ films as a function of t_{BTO} . Figure (a) also includes the a - and c -axis lengths of bulk BaTiO₃.⁸

while high P_{O_2} results in locally incoherent grain boundaries in BaTiO₃ films.³¹ Moreover, high laser energy has been shown to increase the growth-induced defect structures and create defect dipoles in BaTiO₃ films.⁹ Hence, in this study, the influence of lattice strain due to defects induced by PLD conditions may affect the properties alongside the effects of strain provided by the substrate.

Fig. 4(a) illustrates the temperature (T) dependence of the out-of-plane XRD patterns of the BaTiO₃ film with t_{BTO} of 300 nm. To facilitate an understanding of the temperature-dependent changes in the BaTiO₃ peak position, the horizontal axis is normalized by the SrTiO₃ peak position, where $2\theta_{\text{STO}}$ and $2\theta_{\text{BTO}}$ represent the 2θ values of the SrTiO₃ (002) and BaTiO₃ (002) diffraction peaks, respectively. The XRD equipment used for temperature dependence differs from that used at room temperature (refer to Fig. 1–3, see experimental section). For $t_{\text{BTO}} = 100$ and 300 nm, the curves of $2\theta_{\text{BTO}} - 2\theta_{\text{STO}}$ versus T exhibit kinks at ~ 500 and ~ 400 °C, respectively (Fig. 4(b)). Since bulk SrTiO₃ is known not to undergo phase transitions in its crystal structure, the observed kinks are attributed to changes in the lattice constants of the BaTiO₃ films. Such a change in lattice

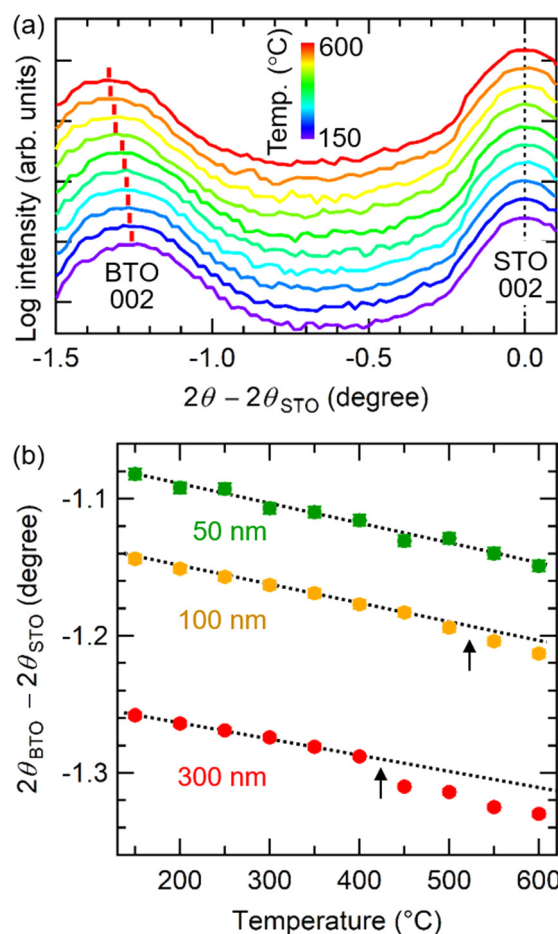


Fig. 4 (a) Temperature dependence of the out-of-plane XRD patterns for the BaTiO₃ film with $t_{\text{BTO}} = 300$ nm. (b) The $2\theta_{\text{BTO}} - 2\theta_{\text{STO}}$ values as a function of T for the BaTiO₃ films with varied thickness.

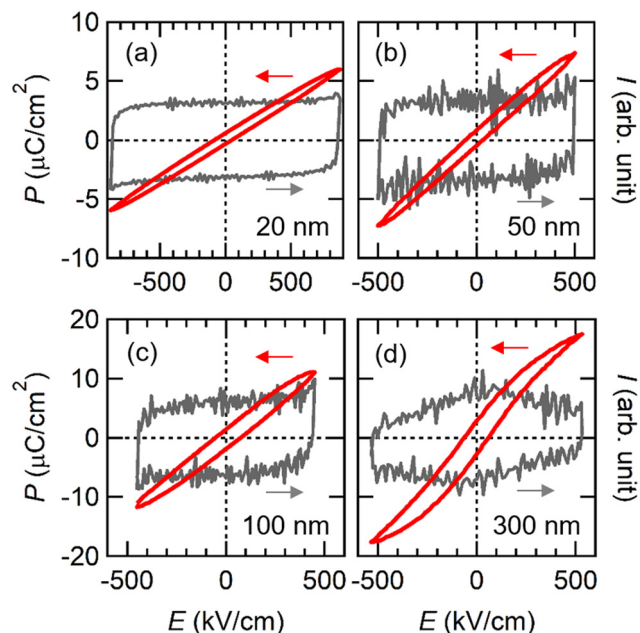


Fig. 5 P - E and I - E curves of the BaTiO₃ films with thickness of (a) 20, (b) 50, (c) 100, and (d) 300 nm.

constants has also been observed in bulk and film BaTiO₃ owing to a transition from the ferroelectric tetragonal phase ($P4mm$) to the paraelectric cubic phase ($Pm3m$).⁸ Thus, the observed kinks in the films with $t_{\text{BTO}} = 100$ and 300 nm were derived from ferroelectric-to-paraelectric phase transitions. Choi *et al.* predicted the T_{C} values of BaTiO₃ film under biaxial in-plane strain based on thermodynamic analysis;⁸ the predicted T_{C} was in the ranges of 300–500 °C and 400–800 °C when 0.6 and 1.3%-tensile strains were applied to the BaTiO₃ film, respectively. These predicted T_{C} values are consistent with our results: T_{C} for the $t_{\text{BTO}} = 100$ and 300 nm films with a tensile strain of 0.6 and 1.3% were ~ 400 and ~ 500 °C, respectively. On the other hand, no obvious kinks were observed in the $2\theta_{\text{BTO}} - 2\theta_{\text{STO}}$ values *versus* T curves for the BaTiO₃ films with $t_{\text{BTO}} = 20$ and 50 nm below 600 °C.

Fig. 5 shows the polarization *versus* electric field (P - E) curve for BaTiO₃ films with $t_{\text{BTO}} = 20$, 50, 100, and 300 nm. The measurements were conducted at 25 °C and a frequency of 10 kHz. At $t_{\text{BTO}} = 20$ nm and 50 nm, no ferroelectric hysteresis loops were observed in the out-of-plane direction. This is probably because the ferroelectric polarization was completely along the in-plane direction, as observed in a previously reported BaTiO₃ film under tensile strain.^{12,17} It is noted that bulk BaTiO₃ with a perovskite structure exhibits tetragonal, orthorhombic, and rhombohedral symmetries below the ferroelectric transition temperature. While the polarization of the tetragonal phase aligns along the c -axis, that of the orthorhombic and rhombohedral phases align along the $[110]$ and $[111]$ directions, respectively.³² The direction of polarization is primarily determined by the availability of spatial regions where Ti ions can undergo displacement. For instance, in tetragonal BaTiO₃ with $c > a$,

there is spatial freedom for Ti ions along the c -axis direction, leading to spontaneous polarization along the c -axis. In our case, the BaTiO₃ film exhibits a tetragonal structure ($a = b \neq c$) with the a -axis length longer than the c -axis length. Consequently, the location of the spatial region available for Ti ion displacement differs from that of the bulk material, resulting in a change in the polarization direction.

In contrast, at $t_{\text{BTO}} = 300$ nm, a ferroelectric hysteresis loop was observed, accompanied by polarization-switching current peaks. The P_{r} value in the out-of-plane direction was $3 \mu\text{C cm}^{-2}$. This suggests that the ferroelectric polarization direction was slightly tilted away from the in-plane direction at $t_{\text{BTO}} = 300$ nm because of the weaker tensile strain (0.6%) compared to other films (1.3–2%).

4. Conclusions

To achieve high tensile strain on the BaTiO₃ film with the bottom electrode, we fabricated BaTiO₃ films on a LBSO bottom electrode. The tensile strain values increase from 0.6 to 2% with decreasing thickness from 300 to 20 nm. The T_{C} values of the 0.6 and 1.3%-tensile strained films are ~ 400 and ~ 500 °C, respectively, which are much higher than those of the bulk (120 °C) and previously reported tensile-strained films (220–220 °C). For the 1.4–2% tensile-strained sheet, the ferroelectric hysteresis loops were not observed in the out-of-plane direction, probably because the ferroelectric polarization aligns in the in-plane direction owing to the tensile strain. On the contrary, the 0.6%-tensile strained film displayed ferroelectric behavior along the out-of-plane direction, suggesting that the ferroelectric polarization direction was slightly tilted away from the in-plane direction.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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