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Ferroelectric materials with excellent performance without containing lead has been desired for saving human body from a harmful element, lead. The authors have reported BaTiO<sub>3</sub> (BTO) thin films with enhanced ferroelectricity by stress engineering by thermal stress assisted by LaNiO<sub>3</sub> (LNO) bottom electrodes. In the present study, we investigate the local stress state of the BTO and LNO films using TEM techniques. TEM observation reveals that the LNO film is porous structure whereas the BTO film is dense. Electron diffraction and dark field images of the films also reveal that the BTO and LNO films oriented along [001] and [100] directions perpendicular to the film plane, respectively. Another effect on the stressed BTO films, increased Curie temperature owing to the stabilized tetragonal phase, is also reported.

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Key-words : BaTiO<sub>3</sub>, LaNiO<sub>3</sub>, Stress engineering, TEM, Thin film

### 1. Introduction

Lead containing ferroelectric oxides with a perovskite structure, Pb(Zr,Ti)O3 (PZT) and PZT based materials, has been widely used as FeRAMs, actuators, and various sensing devises owing to its high ferroelectric and piezoelectric performances.<sup>1)-4)</sup> Although the excellent qualities of the PZT based materials, recently a new ferroelectric and/or piezoelectric materials which can substitute PZT are strongly desired due to a toxicity of the lead against humans. From such demands, ferroelectric materials without containing lead have been studied by many research groups.<sup>5)-8)</sup> One of a promising candidate for the non-lead ferroelectrics is a barium titanate, BaTiO<sub>3</sub> (BTO), which belongs to the pervskite structure. Even though the ferroelectric and piezoelectric properties of BTO are generally inferior to that of lead containing ferroelectrics and the transition temperature of BTO is near room temperature, which sometimes becomes problems for using as devices,<sup>9)</sup> many attempts have been made by many research groups for enhancing the properties of BTO. Besides chemical approaches,<sup>6)-8)</sup> i.e. cation doping into Aand/or B- site elements, recently a physical approach known as a 'stress engineering' attracts attention: simply applying a stress field along in plane of the film which leads lattice strain along the polarization axis, which results in an enhanced ferroelectricity.<sup>10)–13)</sup> Choi et al. reported the strained BTO film prepared on a perovskite single crystal substrate showed more than three times high ferroelectricity than that of the single crystal BTO.<sup>13)</sup> The strained BTO film also showed higher Curie temperature, i.e. the transition temperature between tetragonal and cubic, than the bulk BTO, which resulted from stabilization of the tetragonal phase owing to the strain. In the case of the report by Choi et al.,

[Received August 22, 2012; Accepted January 24, 2013]

the compressive stress applied on the single crystals was mainly caused by an epitaxial stress due to a lattice mismatching between the film and the substrate. With taking into account an industrial usefulness, however, it is ideal that the stress (or strain) which enhances the ferroelectric properties is applied on a conventional Si substrate rather than the specialized and expensive oxide single crystals, DyScO<sub>3</sub> or GdScO<sub>3</sub> etc. We have been trying another way for applying the compressive stress to the ferroelectric thin films that is applicable to various substrates including Si by using a thermal stress applied from bottom electrode, namely LaNiO<sub>3</sub> (LNO).<sup>14)-17)</sup> LNO is known as an oxide electrode with the perovskite structure (a = 0.3861 nm), which is a good lattice matching with the perovskite type ferroelectric, BTO (a = 0.3994 nm, c = 0.4038 nm).<sup>17)</sup> Also the LNO has a high thermal expansion coefficient  $(12.5 \times 10^{-6}/\text{K})$  than the ferroelectric,<sup>15)</sup> therefore the compressive is expected to be applied to the ferroelectric films from the LNO bottom electrode during cooling after an annealing process.

In our previous works, PZT films prepared on the LNO bottom electrodes obviously showed excellent ferroelectricity and piezoelectricity owing to high compressive stress applied in plane of the ferroelectric films which resulted from the high thermal expansion coefficient of the LNO bottom electrode.14)-18) We have also reported the sputtered BTO film on the LNO bottom electrode showed increasing ferroelectric properties with increasing the thickness of the LNO electrode.<sup>17)</sup> The sputtered BTO film was also applied to the increasing compressive stress in plane with increasing the thickness of the LNO bottom electrode. From the result, we considered that the high ferroelectric properties resulted from the compressive stress applied in plane by the LNO bottom electrode. It is significant to understand more precisely the stress state of the BTO film and LNO electrodes using TEM since the properties of the ferroelectric thin films are generally affected by many nano-scale factors such as micro-

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Table 1. Sputtering conditions for the BaTiO<sub>3</sub> films

Target	BaTiO <sub>3</sub>
Substrate temperature (°C)	500
Atmosphere [Ar:O <sub>2</sub> ]	8:2
Pressure (Pa)	2
RF power (W)	150
Deposition time (min)	120

structure,<sup>19)</sup> orientation,<sup>20)</sup> particle size,<sup>21)</sup> effect of electrode,<sup>22)</sup> remnant stress<sup>17)</sup> etc. In the present study, the BTO film was precisely investigated by cross sectional TEM observation and the stress distribution in the BTO and LNO films was estimated from lattice parameters at each area of the films. In order to show the high tetragonal phase stability, Curie temperature shift was also measured.

## 2. Experimental procedures

A precursor solution for the LNO thin films was prepared in the same manner as our previous work.<sup>17)</sup> Lanthanum nitrate La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and nickel acetate Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O were used as starting materials for the LNO precursor solution. These hydrates of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O were used after the dehydration at 150°C for 1 h and at 200°C for 2 h, respectively. They were subsequently dissolved and refluxed in the mixed solvent of 2-methoxy ethanol and 2-amino ethanol. Concentration of the LNO precursor solution was 0.3 M. The LNO precursor solution was deposited on a Si(100) substrate by spin coating at 3500 rpm for 30 s. The spin-coated precursor solution was dried at 150°C for 10 min in air, pre-annealed at 350°C for 10 min in air to remove residual organic components, and finally annealed at 700°C for 5 min by rapid thermal annealing (RTA) in O<sub>2</sub> atmosphere. The entire processes, spin coating, drying, pre-annealing, and annealing were repeated to increase the film thickness. The thickness of the LNO film was controlled by repeating the spin coating. An estimated thickness of the LNO film each cycle was approximately 50 nm. The BTO thin films were deposited by RF magnetron sputtering on the LNO/Si substrates with various LNO thicknesses deposited by the solution process described above. The sputtering target was prepared from commercialized BTO powder (BT-05, Sakai Chemical Industry Co). The film deposition was carried out at a substrate temperature of 500°C in an Ar and O2 mixed gas atmosphere (Ar: $O_2 = 8:2$ ) of 2 Pa. The deposition conditions are listed in Table 1. Au top electrodes were prepared on the BTO films by DC sputtering using a metal mask ( $300 \,\mu m \phi$ ). The crystalline phase of the obtained film was characterized by X-ray diffraction (XRD; Bruker D8 ADVANCE).

The ferroelectric and dielectric properties of the resultant BTO films were measured using TOYO FCE-1 and Hewlett-Packard HP-4194A, respectively. The microstructures of the thin films were investigated using a transmission electron microscopy (HRTEM, 200kV, JEM-2100F; JEOL). Bright field (BF) and dark field (DF) images and selected area electron diffraction (SAED) patterns were obtained for investigating microstructure and crystallographic analysis. For measurement of the electron diffraction, gold polycrystals were used as standard material.

#### 3. Results and discussion

### 3.1 Microstructure and orientation

**Figure 1** shows a Cross-Sectional TEM bright field image for BTO/LNO/Si thin film. The BTO film was composed of a dense



Fig. 1. Cross-Sectional TEM bright field image for the  $\mbox{BTO}/\mbox{LNO}/\mbox{Si}$  thin film.



Fig. 2. Diffraction pattern obtained from whole of the BTO/LNO/Si thin film shown in Fig. 1.

structure with about 700 nm thickness whereas the LNO film with about 200 nm thickness was porous composed of particles of about 50 nm in size. Figure 2 shows an selected area electron diffraction (SAED) obtained from the area including whole film structure (substrate, LNO layer, and BTO layer). The SAED pattern obviously shows that the LNO [100] and BTO [001] were oriented along the direction of the out of plane. The orientation of the LNO and BTO films mentioned above was confirmed by X-ray diffraction as shown in our previous report.<sup>17)</sup> From the SAED pattern of the LNO and BTO, it is understood that the LNO and BTO has similar tilt angle of about 7 degree from the direction perpendicular to the film plane. This indicates that the BTO films grown on the LNO bottom electrode are oriented to the direction of the LNO phase. The [100] orientation of the LNO layer prepared by the CSD method is already known to be [100] direction as reported in our previous report<sup>17</sup>) (not shown here). On the other hand, one can notice that the diffraction spots parallel to the film plane are weaker than those perpendicular to the plane, which indicates the film has less (or almost no) orientation in plane. This result indicates that the LNO orientation can be obtained regardless the orientation of the substrate, which implies the [100] oriented LNO can be prepared on any substrates regardless the substrate orientation.

**Figure 3** shows a dark-field image of the BTO/LNO/Si thin film obtained by the reflections of  $100_{LNO}$  and  $001_{BTO}$ . The darkfield image indicated that the [001] oriented BTO layer is columnar like structure grown from the [100] oriented LNO layer. This result implies the local epitaxial growth of the BTO crystals on the LNO layer owing to the similar crystal structures of them. It is also indicated that the percentage of the [100] orientation of the LNO layer increased with increasing the LNO layer thickness. One many notice that the BTO layer includes several dark areas in the dark-field image, but it does not indicate that the BTO has a misorientation different from [100] and [001], which can be also understood from the XRD patterns shown in our previous report.<sup>17)</sup> The reason for the disappear of the BTO particles seems to be the tilting of the BTO crystals, i.e. the diffraction spots with high tilting angle escaped from the aperture selecting the  $100_{\rm LNO}$  and  $001_{\rm BTO}$  spots.

## 3.2 Stress distribution in the film

**Figure 4** shows SAED patterns 1 through 7 obtained from the areas indicated by the corresponding numbers in the bright field image shown together. The SAED patterns were obtained with using an aperture of 100 nm in diameter. It should be noted that the areas selected in the Fig. 4 was a connected column from bottom of the LNO layer to the top of the BTO layer, and the direction of the electron beam is identical to the [010] of the column. **Figure 5** shows the measured lattice parameter of the LNO layer along directions of in plane (indicated as 200 for LNO and BTO) and out of plane (indicated as 002 for LNO and BTO) from the areas 1 through 3 at the LNO layer, as a function of the distance from LNO/Si interface. The stress state of the LNO at the interface between LNO/Si and BTO/LNO were



Fig. 3. Cross-Sectional dark-field TEM image taken using 001 reflection of BTO.





Fig. 5. Lattice parameters calculated from the electron diffraction patterns at each area for the LNO layer shown in the Fig. 4 areas 1 thorough 3 (from left to right). The result obviously indicates that the LNO is subjected to the tensile stress at the interfaces with BTO and Si owing to its large thermal expansion coefficient. The dashed line and the triangles indicate the lattice parameters in plane, and the solid line and the squares indicates that for out of plane. Lattice parameter of the bulk LNO is also shown together with the solid strate line.



Fig. 4. TEM bright field image of BTO/LNO/Si thin film and SAED patterns obtained from the areas 1 through 7 indicated by the circles indicated in the TEM image. The direction of the electron beam is parallel to the [010] of the BTO and LNO. Continuous variations of the lattice parameter of the LNO film and BTO film were measured from the diffraction patterns 1 thorough 7. The spots parallel to and perpendicular to the film plane were allocated to the directions of [100] and [001], respectively for the both case of LNO and BTO.



Fig. 6. Lattice parameters calculated from the electron diffraction patterns at each area for the BTO layer shown in the Fig. 4 areas 3 thorough 7 (from left to right). The long dashed line and the triangles indicate the lattice parameters in plane, and the solid line and the squares indicates that for out of plane. Lattice parameters of the bulk BTO were indicated by the short dashed line and the dotted line for for (100) and (001) planes, respectively. The solid line indicates the lattice parameter of the BTO (001) plane of the BTO/LNOSi film measured by XRD. The result obviously indicates that the BTO is subjected to the compressive stress at the interfaces with LNO owing to the large thermal expansion coefficient of LNO.

(therefore tensile strain appeared for the out of plane) again owing to the large thermal expansion of the LNO. The stress applied to the BTO gradually decreased with increasing the BTO layer thickness. One may notice that the lattice parameters of the BTO film does not reach that of the bulk especially for the out of plane even at the long distance away from the interface. The reason for the lattice modification of the BTO film might be high energy of the sputtering; sputtered ions have highly and may readily generate lattice defects in the films which results in the volume expansion of the lattice. It is worth noting that the lattice parameter measured by the electron diffraction is identical to that measured by XRD, which validates the lattice parameter shown here is reliable within the accuracy.

This result obviously indicate that the LNO caused the in plane compressive stress to the BTO and the stress is relaxed with increasing the BTO film thickness. From these results regarding the lattice parameter changing of the LNO and BTO, it was validated that the large thermal expansion coefficient of the LNO resulted in the compressive stress to the BTO layer. It is worth noting that the BTO film showed a good P-E hysteresis loop as reported in our previous study,<sup>17)</sup> namely the BTO film showed 2  $P_r$  of about 14.9 ( $\mu$ C/cm<sup>2</sup>) and 2  $P_s$  of about 30.2 ( $\mu$ C/cm<sup>2</sup>). As mentioned above, the LNO electrode can possess the [100] orientation regardless the substrate orientation, therefore the result also indicates that the stress engineering was demonstrated on the conventional substrates like Si.

# 3.3 Temperature dependence of dielectric behavior

**Figure 7** shows a temperature dependence of the dielectric constant measured from room temperature to 400°C for the BTO film on the LNO bottom electrode with 200 nm thickness. The data for the BTO film on the 100 nm thick LNO electrode was also indicated in the same diagram for comparison, where the compressive stress applied to the BTO film is less than that on the 200 nm LNO electrode as shown in our previous report.<sup>17)</sup> From the figure, one can notice that the Curie temperature of the BTO on the 200 nm and 100 nm thick LNO electrodes were about 310°C and 160°C, respectively. Since the original Curie temperature of the BTO is about 120°C, both of the BTO films showed



Fig. 7. Temperature dependence of the dielectric constant of the BTO thin film on the LNO electrode with different thickness, 100 nm (dotted line) and 200 nm (solid line). The Curie temperature of the bulk BTO at 120°C is indicated by the dashed line, which is exceeded by that of the stressed BTO films.

increased Curie temperatures. The reason for the temperature shift can be understood by considering stability of the tetragonal BTO phase as follows. The Curie temperature of the BTO at about 120°C indicates the transition temperature between tetragonal and cubic BTO phases. Owing to the compressive stress applied in plane to the [001] oriented BTO film, the tetragonal phase becomes more stable since the tetragonal *a*-axis length is shorter than the *c*-axis length. The Curie temperature shift to the higher temperature is not only interesting in scientific meanings but also important in an industrial usage because the dielectric and ferroelectric properties can keep stable values even if it gets heated during working as a device.

#### 4. Conclusion

In this study, the BTO thin films were deposited by sputtering on the LNO bottom electrodes prepared by the chemical solution deposition method on the Si substrate. TEM observation revealed that the LNO and BTO films had [100] and [001] orientation perpendicular to the film plane, respectively. TEM dark field image indicated that the BTO film was composed of columnar structure crystals which is grown on the [100] oriented LNO, which indicated the BTO film locally epitaxially grown on the LNO bottom electrode. Electron diffraction at each area of the BTO/LNO/Si films indicated that the tensile stresses in plane were applied to the LNO from the BTO film and the Si substrate, whereas the compressive stresses in plane were applied to the BTO film from the LNO film. These stresses were high at the interfaces and were relaxed with increasing the distance from the interfaces therefore we concluded that the stresses applied to the films were mainly caused by the thermal expansion coefficient between LNO and BTO. Owing to the compressive stress applied to the BTO film, the tetragonal phase became stable and it resulted in the increment of the Curie temperature up to 310°C from that of the bulk, 120°C. The BTO film on the LNO electrode showed a good ferroelectric properties as well owing to the applied compressive stresses. We concluded that the stress engineering for the BTO film was successfully demonstrated using the thermal stress from the LNO electrode on the conventional Si substrate.

Acknowledgments This work was partly supported by the Inter-University Cooperative Research Program of the Institute for Materials Research, Tohoku University (Proposal No. 12K0081).

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