Liquid-Phase Epitaxial Growth of BaTiO₃ Doped (Na₀.₅Bi₀.₅)TiO₃ Single Crystals on a SrTiO₃ Single Crystal Substrate

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1. Introduction

Perovskite-type sodium bismuth titanate \( (Na_{0.5}Bi_{0.5})TiO_3 \) (NBT) is a ferroelectric material with a rhombohedral perovskite structure \( (a = 0.389 \text{ nm} \text{ and } c = 89.4^\circ) \) at room temperature. It has been reported that NBT exhibits two phase-transitions at certain temperatures.\(^2\) Because of its lead-free chemical composition, NBT is thought to be one of the possible substitutes for lead-based piezoelectric materials. However, NBT has a high coercive field \( (E_c) \) of 7.3 kV/mm and it is difficult to fully poled NBT. Takenaka and his coworkers\(^3\)-\(^5\) extensively studied binary or ternary solid-solution systems of NBT in search of solid-solution compounds that can be poled with a relatively low electric field. They also reported the chemical composition at the morphotropic phase boundary (MPB) in these compounds. For example, they found that the MPB composition for the binary system comprising NBT and BaTiO₃ (BT) is located at 6% BT. They suggested that a solid solution based on NBT has similar properties to lead-based perovskite oxides; namely, a high dielectric constant and high piezoelectric constant. Thus, NBT-based solid-solution compounds have the potential to provide good piezoelectric performance with a non-toxic composition.

In the recent years, much attention has been paid to piezoelectric-oxide single crystals.\(^6\),\(^7\) Because of the absence of grain boundaries, it is expected that such single crystals of piezoelectric materials will provide higher actuation than polycrystalline materials. Moreover, a concept for controlling the domain structure of a piezoelectric single crystal, a so-called engineered domain structure,\(^8\) has been proposed. Accordingly, the device technology for piezo-electric single crystals is currently one of the hot issues in the field of piezoelectricity. In our previous study, we grew an NBT crystal doped with BT (NBT–BT) by using a flux method with excess Na₂O and Bi₂O₃ as the flux, and we found that one of the grown crystals exhibited a piezoelectric coefficient \( (d_{33}) \) of up to 450 pC/N.\(^9\) Moreover, a co-doped system, \( (Na,Bi,Ba)(Ti,Zr)O₃ \), showed large piezoelectric displacements.\(^1₀\) The strain produced in this system was much higher than that in NBT–BT\(^9\) crystals. We therefore concluded that single crystals of NBT-based solutions are promising materials for actuator applications. The flux method is, indeed, useful for growing NBT–BT crystals. However, random nucleation is not suitable for commercial mass production. Therefore, in the current study, we tried epitaxial growth of NBT–BT on single-crystalline substrates of strontium titanate \( (SrTiO₃\text{, ST}) \) with the aim of controlling the crystal growth process. In particular, we used a liquid-phase epitaxy (LPE) technique in order to grow NBT–BT single crystals in thick films. Strontium titanate has a perovskite structure and its melting temperature, i.e., 2600°C, is much higher than that of NBT, i.e., 1260°C. Thus, ST is a possible substrate material for growing NBT–BT by the LPE method. However, it has cubic structure \( (a = 0.3998) \) at room temperature; consequently, lattice mismatch between ST and NBT–BT is expected. It is well known that the lattice mismatch as well as thermal expansion coefficient (TEC) mismatch between the substrate and the grown crystal causes internal stress. For example, a thin film of \( (Sr₀.₅Ba₀.₅)TiO₃ \) grown on a MgO substrate has a tetragonal cell at room temperature, while bulk \( (Sr₀.₅Ba₀.₅)TiO₃ \) has a cubic cell.\(^1¹\) Moreover, it has been reported that ST and NBT form solid-solution compounds in the whole compositional range.\(^1₂\) This means that...
it is necessary to control the reaction between the substrate and the grown crystal in order to obtain high-quality NBT–BT crystals on ST substrates. Thus, in this study, we paid careful attention to lattice mismatch and mutual diffusion between substrate ST and grown NBT–BT.

2. Experimental procedure

The precursor for the LPE growth was prepared by a solid-state reaction. The molar ratio of the source materials, Na$_2$CO$_3$, Bi$_2$O$_3$, BaCO$_3$, and TiO$_2$, was Na:Bi:Ba:Ti = 0.5–x+y:0.5–x+y:x:1.0. Here, x and y correspond to doping with BT and addition of Na–Bi–O flux, respectively. The value of x was set to zero or 0.06 and y was fixed at 0.10. The weighed powders were mixed by ball milling with ethanol for 20 h. The mixture was calcined at 800°C for 3 h and the resultant powder was milled again. The calcination and milling were repeated several times to ensure homogeneity of the precursor. The major phase in the obtained precursor was identified as a perovskite oxide by X-ray powder diffraction (XRD).

The single-crystal substrates of ST used in this study were 10×10×0.5 mm in size with well polished (001) or (111) faces. Three types of sample arrangements for conventional LPE growth were examined: open-cell, closed-cell, and crucible-cell. The open-cell consists of a platinum dish, 12×12×5 mm in size, without a lid. In the closed-cell, the substrate and precursor were enclosed in a platinum envelope sealed by welding. The crucible-cell comprises a standard platinum crucible with a volume of 25 cm$^3$. Schematic drawing of the three types of the cells are shown in Fig. 1. By comparing the closed-cell and the open-cell, we expected to identify the effect of evaporation of the source materials during growth. The amount of precursor was about 20 g for the crucible-cell and 3–5 g for the other two arrangements. All three kinds of sample cell were heated at 1260°C for 1–4 h and cooled to 1100–1150°C at a rate of 6–12°C/h.

The morphology of the grown crystals was observed by optical microscopy (OM) or scanning electron microscopes (SEM). The chemical composition of the grown crystals was analyzed by electron probe microanalysis (EPMA) with a wavelength-dispersion (WDX) or an energy-dispersion (EDX) X-ray detector. For EPMA–WDX analysis, standard samples were used for quantitative analysis, and line profiling was used to produce compositional fluctuation along the growth direction. The crystalline phase of the grown crystal was examined by XRD, and the orientation of the crystal lattice was examined by using a polarized-light optical microscope as well as the XRD.

Dielectric and electromechanical properties of the grown crystals were measured after removing the ST substrate by polishing. Gold electrodes were formed by sputtering. The samples with the electrodes were then annealed at 400°C for 1 h to form strong adhesion between the electrodes and the specimen. Impedance spectra as functions of both frequency and temperature were measured with an LF impedance analyzer (4192A, Hewlett Packard). The parallel circuit mode of the 4192A was selected for the evaluation of dielectric constant (ε) and dielectric loss factor (tan δ). Electrical poling was carried out by the field-cooling procedure. An electric field of 2 kV/mm was applied at 200°C, and the field was suppressed when temperature reduced to 50°C. During the poling process, leakage current was recorded in order to evaluate the dc electrical resistivity. The electromechanical coupling factor, $k_t$, was evaluated by the resonance/anti-resonance method with the HP4192A.

3. Results and discussion

3.1 Crystal growth

NBT–BT crystal was successfully grown on the ST substrates in the open-cell and closed-cell sample arrangements. In contrast, in the case of the crucible-cell, the substrate was dissolved into the melt during the soaking process and no trace of the substrate material was found after the growth process. The difference between the crucible cell and the other sample assemblies is discussed in the latter part of Section 3.2.

The grown crystals are shown in Fig. 2. They had a perovskite crystal structure and their symmetry, i.e., tetragonal or rhombohedral, depends on their barium concentration. The grown crystals were examined by XRD, and the orientation of the crystal lattice was examined by using a polarized-light optical microscope (OM) or scanning electron microscopes (SEM). The chemical composition of the grown crystals was analyzed by electron probe microanalysis (EPMA) with a wavelength-dispersion (WDX) or an energy-dispersion (EDX) X-ray detector. For EPMA–WDX analysis, standard samples were used for quantitative analysis, and line profiling was used to produce compositional fluctuation along the growth direction. The crystalline phase of the grown crystal was examined by XRD, and the orientation of the crystal lattice was examined by using a polarized-light optical microscope as well as the XRD.

Observation with a polarized optical microscope (P–OM) revealed the domain configuration in the grown crystals. Figure 3 shows cross-nicols images of a barium-doped crystal grown on a (001) substrate in the closed-cell set up. The darkest image of the grown crystal (Fig. 3(a)), corresponding to the extinction position, was produced when the polarizer of P–OM was set parallel to the growth direction, which
is parallel to the ST [001] direction, while the brightest image was shown when the polarizer and the growth direction made an angle of 45° as shown in Fig. 3(b). This means that the optical axis of the grown crystal is parallel to the growth direction. However, as shown in Fig. 4, an extinction sequence was also observed when the polarized light was directed along the growth direction. This means that one more optical axis must lie perpendicular to the growth direction. Figures 3 and 4 indicates that a NBT–BT crystal, having a tetragonal symmetry, was epitaxially grown on the ST substrate and that the grown crystal has a multi-domain structure (90° domains). On the other hand, an undoped crystal grown on the (001) substrate showed extinction when the polarizer was set parallel to either [101], [110], or [011] directions of the substrate. This means that the undoped crystal has a rhombohedral unit cell whose c-axis is also that of the ST substrate at room temperature. The domain structures of both tetragonal NBT–BT and rhombohedral NBT grown on ST are illustrated in Fig. 5. The epitaxial growth of NBT–BT on the ST (111) substrate was also confirmed. For example, the undoped NBT crystal exhibited extinction when the polarizer was set parallel to the [111] direction of the substrate (see Fig. 6), indicating the grown crystal was rhombohedral NBT, whose c-axis was shared by the ST. Therefore, it can be said that liquid phase epitaxial growth of NBT–BT-based solid solutions on an ST substrate is possible, when the Na–Bi–O self flux is applied.

### 3.2 Composition analyses

The averaged ratio between sodium and bismuth concentrations (Bi/Na) was determined to be 1.182 by EPMA–WDX analyses, and its standard deviation was 0.034. Taking the expected experimental error into account, we can safely say that the Bi/Na ratio is independent of the barium concentration and the temperature profile for the crystal growth. This means that a pair of bismuth and sodium ions was substituted by two barium ions and that the ionic charge balance was well maintained during the grown NBT–BT crystals. The results of line profiling by EPMA–WDX analysis are shown in Figs. 7 and 8. Figure 7 represents the compositional profile of the NBT–BT crystal grown in the closed-cell set up under a relatively long soaking time and high soaking temperature. In contrast, Fig. 8 represents the NBT–BT crystal grown in the open-cell set up under a relatively low soaking temperature and short soaking time. The differences between Figs. 7 and 8 are shown by the profile of the strontium and barium concentrations. In Fig. 8, the concentration of barium is significantly inhomogeneous. This is typical feature of the crystal grown...
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We presume that the evaporation of the flux components during the crystal growth is the reason for the inhomogeneity of the barium concentration. In contrast, strontium concentration at the interface region does not depend on the sample-cell configuration. Contamination by strontium in the grown crystal was evident when the soaking temperature was higher and the soaking time was longer.

Fig. 5. Domain structure of the NBT crystal grown on a ST (001) substrate.

Fig. 6. Polarized-light microscope images (cross section) of the undoped NBT crystal grown on a ST (111) substrate.

It is also notable that neither sodium nor bismuth was found in the substrate. This means ST dissolved into the Na-Bi-(Ba-)Ti-O melt was deposited again onto the substrate by forming a solid solution whose A-sites were partly occupied by strontium and that inter-diffusion between the grown crystal and the substrate hardly occurs during the crystal growth process. This behavior can be understood from the viewpoint of charge compensation. Because of the charge neutrality, sodium or bismuth has to associate with another defect, as shown in the following reactions.

\[ 2\text{Sr}^{x⁺} + \text{Na}_2\text{O} \rightarrow 2\text{NaSr} + 2\text{SrO} + V_0^* \]
\[ 2\text{Sr}^{x⁺} + \text{Bi}_2\text{O}_3 \rightarrow 2\text{BiSr} + 2\text{SrO} + O_i^* \]
\[ 4\text{Sr}^{x⁺} + \text{Na}_2\text{O} + \text{Bi}_2\text{O}_3 \rightarrow 2\text{NaSr} + 2\text{BiSr} + 4\text{SrO} \]

Fig. 7. Line profiling by EPMA-WDX for an NBT crystal doped with BT grown in the closed-cell configuration. The soaking temperature and time for LPE growth were 1260°C and 6 h.

Fig. 8. Line profiling by EPMA-WDX for an NBT crystal doped with BT grown with the open-cell configuration. The soaking temperature and time for LPE growth were set to 1240°C and 2 h.

It is thus plausible that the inter-diffusion is prevented by kinetic effects, even if the solid solution of (Na, Bi, Sr)TiO₃ is a thermodynamically stable phase, because there is no simple reaction path. From the above-described results of compositional analyses, we can conclude (a) that the closed-cell configuration is necessary to obtain a homogeneous crystal and (b) that lower soaking temperature and shorter soaking time are required to prevent the formation of a solid solution contaminated with strontium.

As described earlier, the crucible cell is not appropriate for the growth of NBT on a ST substrate. The reaction between the melt and the ST substrate was enhanced by using the crucible cell. It is speculated that the convection took place in the crucible, and the large amount of melt results in an acceleration of the reaction between the ST substrate and the melt. In other words, coexistence of the NBT melt and the ST crystal is unstable, and the thermodynamically stable state is that ST is dissolved into the melt. It is therefore important to control the reaction kinetics to ensure that the LPE method can be applied to the growth of NBT-BT on a ST substrate.

3.3 Internal stress at the interface

The chemical composition at the interface, i.e., barium and strontium concentrations, is related to the crack formation behavior at the NBT-BT/ST interface. Regarding the undoped NBT, a lot of macroscopic cracks were found on both the ST side and the NBT side (as shown in Fig. 9). This means that the stress caused by the mismatch between cubic-ST and rhombohedral-NBT was released by forma-
tion of macroscopic cracks at both sides of the interface. In contrast, such macroscopic cracks were not found at the substrate/crystal interface in the BT-doped samples.

Figure 10 shows typical polarized optical-microscope images of the interface in the NBT-BT samples. Neither microscopic nor microscopic cracks were found in the sample shown in Fig. 10(a), while a lot of microscopic cracks were found in the sample shown in Fig. 10(b). Another difference between Figs. 10(a) and 10(b) was observed in the images of the ST substrates. That is, strong contrast is seen in Fig. 10(a), but not in 10(b). Since ideal ST crystal has cubic cell at room temperature, double refraction is not expected. However, the ST substrate shown in Fig. 10(a) has a brighter section. This means that the ST substrate in Fig. 10(a) exhibits double refraction, i.e., it is not a cubic cell, as a result of internal stress. Therefore, it is plausible that the internal stress caused by lattice mismatch was released by formation of micro cracks in the sample shown in Fig. 10(b) and the internal stress caused strain in the ST substrate in the sample shown in Fig. 10(a). It is worth noting here that the samples shown in Figs. 10(a) and (b) correspond to the results in Figs. 7 and 8, respectively. Corresponding to their chemical compositions, the crystalline phase of the NBT-BT around the interface, which was determined by polarized-light observation and XRD, was tetragonal in Fig. 10(a) and rhombohedral in Fig. 10(b).

The results in Figs. 10(a) and 10(b) indicate that the appearance of the effect of internal stress depends on the composition of the NBT–BT crystal around the crystal/substrate interface. Regarding the rhombohedral phase, i.e., NBT–BT with low barium concentration, the internal stress at the substrate/crystal interface results in formation of cracks at the interface. In contrast, regarding the interface between the tetragonal phase and the ST substrate, the internal stress results in the lattice distortion of the substrate and a grown crystal as illustrated in Fig. 10(a). Further studies are necessary to understand the mechanism of this crack generation. However, it is likely that the symmetry mismatch between the structures of the grown crystal and the substrate, i.e., rhombohedral and cubic, causes the shear stress that results in the formation of cracks, since the cracks were not found in the crystal with a tetragonal symmetry at room temperature. Therefore, it can be said that the ST substrate is more appropriate for growth of the relatively heavily barium-doped crystal, which has a tetragonal form at room temperature.

3.4 Dielectric and piezoelectric properties

Figures 11 and 12 show the temperature (T) dependence of relative dielectric constants ($\varepsilon_r$) and tan $\delta$ of the NBT–BT crystals in rhombohedral form (2.5% barium) and tetragonal phase (8% barium), respectively. The properties under the low electric field seem to be similar to those of the other single crystals grown by the flux method reported in our previous study. Frequency dependence of dielectric constant, a typical feature of a relaxor material,
was observed, and the dielectric constant showed maximum values at two temperatures of around 150 and 280°C. The tetragonal crystal was poled by applying a high electric field, and the \( k_t \) value was evaluated to be 30-35%. This result means that the effect of the ST substrate was not significant.

4. Conclusions

The growth direction of a NBT-BT single crystal was successfully controlled by using liquid phase epitaxy (LPE) with a ST single-crystal substrate. By using a sealed capsule for the growth cell, a relatively homogeneous crystal could be grown. It was also found that inter-diffusion between the grown NBT-BT crystal and the ST substrate is negligible, indicating that the ST single crystal is an appropriate substrate material for LPE growth of NBT and its solid solution. The obtained crystal exhibited dielectric and electromechanical properties, which are similar to the previously reported ones of NBT crystals grown by the normal flux method. Since random nucleation was prevented and the orientation of the grown crystal was controlled by using the ST single crystal substrate, we can conclude that the LPE method using a ST substrate is appropriate for growing a highly oriented thick film of NBT and its solid solution.

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