Domain Size Dependence on Piezoelectric Property of BaTiO₃ Single Crystals with Engineered Domain Configuration

Satoshi Wada, Koichi Yako, Hirofumi Kakemoto and Takaaki Tsurumi
Department of Metallurgy and Ceramics Science, Graduate School of Science and Engineering,
Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, JAPAN.
Fax: +81-3-5734-2514, e-mail: swada@ceram.titech.ac.jp

For tetragonal barium titanate (BaTiO₃) single crystals, an electric field (E-field) applied along $[111]_c$ direction can induce an engineered domain configuration into the crystal. In this study, the engineered domain structure with different domain sizes was induced into BaTiO₃ single crystals, and their piezoelectric properties were investigated as a function of a domain size. Prior to this study, the dependence of domain configuration on temperature and E-field was investigated using a polarizing microscope in order to understand the optimum condition for fine domain structure and coarse domain structure. As a result, above Curie temperature of 132°C, when the E-field over 6kV/cm was applied along [111] $_c$ direction, the engineered domain configuration with fine domain structure appeared. Moreover, it was also found that this fine domain structure was still stable at room temperature without E-field. On the other hand, the coarse domain structure was obtained by poling below Curie temperature. Finally, the piezoelectric properties were measured using the 31 resonators with different kinds of domain sizes. As the result, it was found that the piezoelectric properties such as d_{31} and k_{31} increased significantly with decreasing domain sizes.
Key words: barium titanate, engineered domain configuration, domain size, piezoelectric property

1. INTRODUCTION

Domain engineering is very important technique to obtain the enhanced piezoelectric and ferroelectric related properties for ferroelectric single crystals. In $[001]_c$ oriented rhombohedral PZN-PT single crystals, ultrahigh piezoelectric activities were found by Park *et al.*[1,2] and Kuwata *et al.*[3,4] with the strain over 1.7 %, the piezoelectric constant d_{33} over 2,500 pC/N, the electromechanical coupling factor k_{33} over 93 % and the hysteresis-free strain *vs* electric-field behavior. These ultrahigh piezoelectric properties were originated from one of the domain engineering techniques, *i.e.*, "the engineered domain configuration". This engineered domain configuration technique uses the anisotropy of the ferroelectric single crystals. The crystal structures are also very important factor for the engineered domain configurations[5].

BaTiO₃ single crystals have a tetragonal *P4mm* phase at room temperature. To induce an engineered domain configuration into tetragonal crystals, E-field should be applied along $[111]_c$ direction. Thus, the piezoelectric properties were investigated using the $[111]_c$ oriented tetragonal BaTiO₃ crystals[6,7]. As the results, the d_{33} of the $[111]_c$ poled tetragonal BaTiO₃ crystal with the engineered domain configuration was almost 203 pC/N, and this value was almost twice larger than 90 pC/N of the $[001]_c$ poled BaTiO₃ single-domain crystal. On the other hand, the d_{33} of the $[001]_c$ poled rhombohedral PZN-PT crystal with the engineered domain configuration was almost 30 times larger than 83 pC/N of the $[111]_c$ poled PZN-PT single-domain crystal[2]. What is the origin of this significant difference? To explain this huge difference, we focused on a domain size in the engineered domain configuration. This is because that the domain structure of the $[001]_c$ poled PZN-PT crystal was composed of the fine fiber-like domain with a domain width of around 1 μm[8,9] while that

of the $[111]_c$ poled BaTiO₃ crystal was made of very course domain with a wide domain width of 300~400 μm[6]. Thus, when the fine domain structure induces into the $[111]_c$ poled tetragonal BaTiO₃ crystals with the engineered domain configuration, it can be possible to obtain much enhanced piezoelectric property.

In this study, the piezoelectric properties of BaTiO₃ crystals were investigated as a function of a domain size. For this objective, in the $[111]_c$ oriented tetragonal BaTiO₃ crystals with an engineered domain configuration, the domain size dependence on the E-filed and the temperature was investigated.

2. EXPERIMENTAL

BaTiO₃ single crystals were grown by a top-seeded solution growth (TSSG) method at Fujikura, Ltd. In TSSG-grown BaTiO₃ single crystals, the concentration of most impurities (Cr, Mn, Fe, Co, Ni, Cu) was below 2-3 ppm. The details of preparation of BaTiO₃ single crystals and their characterization were described elsewhere[10,11]. These crystals were oriented along $[111]_c$ direction using a back-reflection Laue method.

For in-situ domain observation at various E-fields and temperatures, the crystals were prepared by cut and polishing to an optimum size of approximately 0.2x0.5x2.0 mm³ (0.2mm // $[1\text{-}10]_c$, 0.5mm // $[111]_c$, 2mm // $[11\text{-}2]_c$). Their top and bottom surfaces (0.5x2.0 mm²) were mirror-polished, with its thickness between top and bottom approximately 200 μm along an incident direction of light. Gold electrodes were sputtered on both sides (0.2x2.0 mm²) parallel to the light. Domain configuration was always observed under crossed-nicols using a polarizing microscope (Nikon, LABOPHOTO2-POL). A unipolar E-field exposure was done along $[111]_c$ direction, being normal to incident polarized light, using a Kepco BOP-1000M high voltage DC amplifier. The crystal was placed

in a cryostat with an optical-isotropic glass window (Linkam, LK-600PM) in dry air. Temperature just below the bottom of the crystal was measured, and then changed from 0°C to 200 °C at a rate of 0.4~1 °C/min. The temperature in the cryostat was measured with an accuracy of ±0.1 °C and controlled within ±0.1 °C.

For the piezoelectric measurement using the 31 resonators, BaTiO₃ single crystals were sized into 4.0x1.2x0.4 mm³ (4.0mm // [1-10]$_c$, 1.2mm // [11-2]$_c$, 0.4mm // [111]$_c$) by cutting and polishing using fine Al₂O₃ powders. Gold electrodes were sputtered on both sides (4.0x1.2 mm²). Poling treatment for the preparation of BaTiO₃ crystals with different domain sizes was performed on the basis of the observation results of domain size dependence on the E-fields and the temperatures. After the poling treatment, their domain configuration was investigated using the polarizing microscope. Finally, their piezoelectric properties were measured using an impedance analyzer (Agilent, HP-4294A) by a conventional resonance-antiresonance method[12].

3. RESULT AND DISCUSSION

3.1 Domain size dependence on E-filed and temperature

To understand domain size dependence on E-filed and temperature for [111]$_c$ oriented BaTiO₃ crystals, the domain structures were observed at various temperatures from 0 to 200 °C and various E-fields from 0 to 20 kV/cm. Prior to all domain observation, BaTiO₃ crystals were heated up to 140 °C, and then cooled down to the observation temperatures at a cooling rate of 0.4 °C/min without E-field. At the constant temperature, E-fields were applied along [111]$_c$ direction very slowly.

Figure 1 exhibited the domain size dependence on E-filed and temperature for [111]$_c$ oriented BaTiO₃ crystals with the engineered domain configuration. Moreover, Fig. 2 showed the typical domain structures observed at the various regions in Fig. 1. In Fig. 1, the "A" and "B" regions were assigned to orthorhombic *mm2* phase. At 25 °C, E-field exposure along [111]$_c$ direction for tetragonal BaTiO₃ crystals resulted in the E-field induced phase transition from *4mm* to *mm2*, and this result was almost consisted with some reports[5-7,13]. Figures 2-(a) and (b) exhibit that these domain structures were composed of fine domains, but when E-field was removed, domain structure was easily returned to the normal tetragonal domain
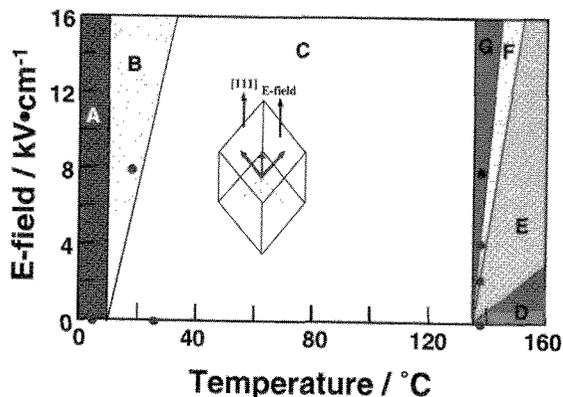
configuration as shown in Fig. 2-(c). Thus, the fine domain structure in the "A" and "B" regions cannot exist stably at room temperature without E-field. The "C" region was assigned to tetragonal *4mm* symmetry. By the poling treatment in this region, domain structure was slightly changed, but the observed all domain walls were completely assigned to 90° domain walls of {110}$_c$ planes as shown in Fig. 2-(c). The "D" region was assigned to the optical isotropic state with cubic *m3m* symmetry as shown in Fig. 2-(d). On the other hand, the "E" region was very unclear. The brightness in the "E" region suggested that this domain state was not optical isotropic, but anisotropic state. When E-field was applied along [111]$_c$ direction for cubic *m3m* symmetry, it is expected that the cubic *m3m* symmetry can be slightly distorted to rhombohedral or monoclinic symmetry. At present, the origin of this birefringence is unknown. In the "F" region,
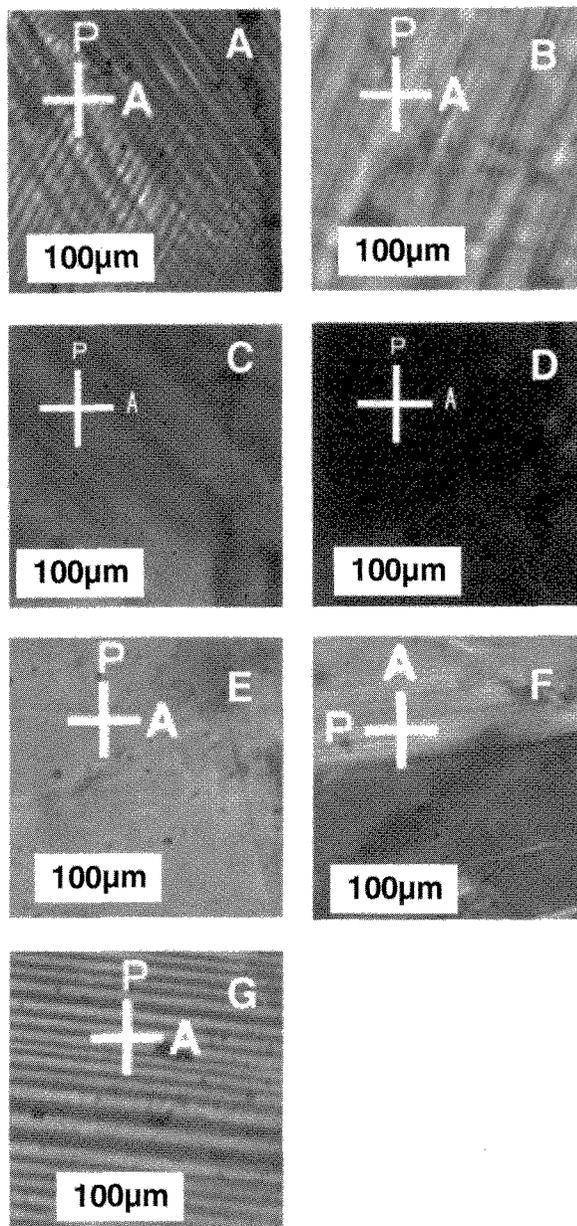

Fig. 2. Domain configurations in (a) the "A" region, (b) the "B" region, (c) the "C" region, (d) the "D" region, (e) the "E" region, (f) the "F" region and (g) the "G" region
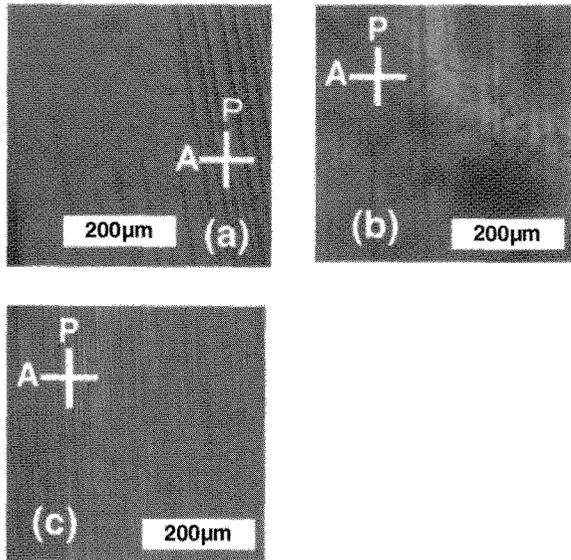

Fig. 1. Domain size dependence on the E-fields and the temperatures for [111]$_c$ oriented BaTiO₃ single crystals with the engineered domain configurations.

Fig. 3.   Domain configurations with the different domain sizes. *i.e.*, (a) greater than 40 μm, (b) 13.3 μm, and (c) 6.5 μm.
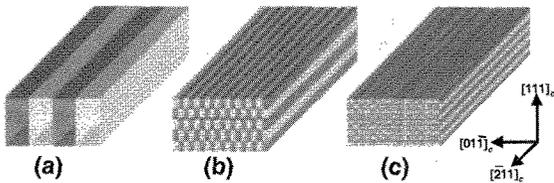

Fig. 4   Schematic engineered domain configurations induced by the poling treatment; (a) a domain size over 40 μm, (b) a domain size of 13.3 μm and (c) a domain size of 6.5 μm.

a coexistence of the bright state without domain walls and fine domain state was observed. In the "G" region, only fine domain structure was clearly observed, and these all domain walls were assigned to $\{110\}_c$ planes.

In the "A", "B", "C" and "D" regions, these symmetries were assigned on the basis of some reports[5-7,13]. However, there is no information about the "E", "F" and "G" regions. Thus, these symmetries will be measured using the in-situ measurement, which can be combined with the polarizing microscopy.

3.2 Domain size dependence of piezoelectric property using the 31 resonators

On the basis of the result of the domain size dependence on E-filed and temperature, three kinds domain sizes were induced into $BaTiO_3$ single crystals with the engineered domain configuration. The engineered domain $BaTiO_3$ crystal with the large domain size was poled at just below T_c while that with the finer domain size was poled at just above T_c. Figure 3 shows the $BaTiO_3$ single crystals with three kinds domain sizes, *i.e.*, (1) domain size of 40 μm or over 40 μm (Fig. 3-(a)), (2) that of 13.3 μm (Fig. 3-(b)) and (3) that of 6.5 μm (Fig. 3-(c)). All of domain walls observed in Fig.3 were assigned to the 90° domain walls of $(011)_c$. In Fig. 3-(a), the color of this picture under crossed nicols was monochrome, which suggested that these domain walls were continuous from top to bottom as shown in Fig. 4-(a). On the other hands, in Figs.
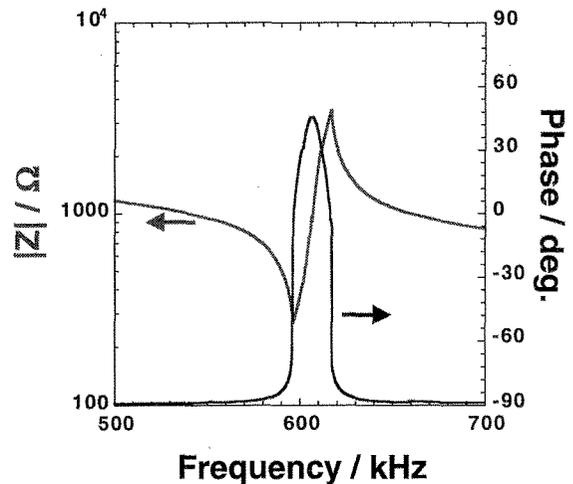

Fig. 5   The frequency dependence of the impedance and the phase for $[111]_c$ poled $BaTiO_3$ crystals with a domain size over 40 μm.
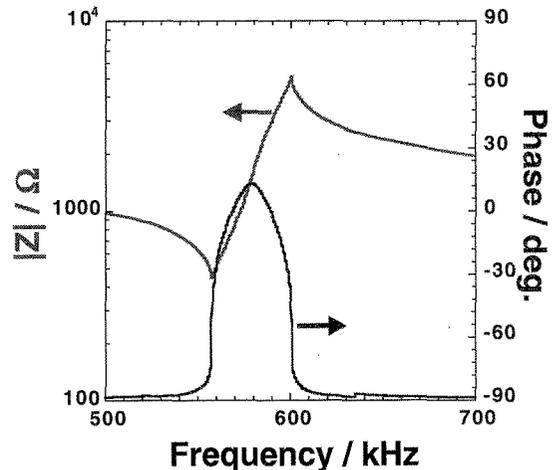

Fig. 6   The frequency dependence of the impedance and the phase for $[111]_c$ poled $BaTiO_3$ crystals with a domain size of 6.5 μm.

3-(b) and (c), the distribution of various colors, *i.e.*, birefringence, was clearly observed, which suggested that along $[111]_c$ direction, there were laminated fine domain structures as shown in Figs. 4-(b) and (c). At present, we consider that the above poling treatment induced the schematic engineered domain configurations as shown in Fig. 4 into the $[111]_c$ poled $BaTiO_3$ single crystals.

Using these three 31 resonators with the different domain sizes, piezoelectric properties were measured by a conventional resonance-antiresonance method. Figures 5 and 6 show the frequency dependence of the impedance and the phase for the 31 resonators with a domain size over 40 μm and that with a domain size of 6.5 μm, respectively. If the poling treatment is completely succeeded, the phase between resonance and antiresonance frequencies should be closed to +90°. In these figures, the maximum phase angle was almost +50° and +15°, respectively. It seems that these low phase angles suggested the insufficient poling treatment. Using the resonance and antiresonance frequencies, piezoelectric related constants were calculated and summarized in Table I. The measurement results by

Table I   Piezoelectric properties of the poled $BaTiO_3$ single crystals

BaTiO₃ single crystals	$\varepsilon_{33}{}^T$	$s_{11}{}^E$ (pm²/N)	d_{31} (pC/N)	k_{31} (%)
[001]$_c$ (single-domain)	129	7.4	-33.4	---
[111]$_c$ (single-domain)	---	---	-62.0	---
[111]$_c$ (domain size > 40 μm)	2,185	7.37	-97.8	25.9
[111]$_c$ (domain size of 13.3 μm)	2,087	7.68	-134.7	35.7
[111]$_c$ (domain size of 6.5 μm)	2,441	8.80	-180.1	41.4

Zgonik *et al.* for [001]$_c$ oriented $BaTiO_3$ single-domain crystal[14] and the d_{31} value calculated using those reported by Zgonik *et al.*[14] for [111]$_c$ oriented $BaTiO_3$ single-domain crystal were also listed in Table I. The Engineered domain $BaTiO_3$ crystal with a domain size over 40 μm possessed much higher piezoelectric properties than those of [001]$_c$ & [111]$_c$ oriented $BaTiO_3$ single-domain crystal. The most surprising thing is the fact that the piezoelectric properties significantly depend on the fineness of the domain size. The piezoelectric properties such as d_{31} and k_{31} increased significantly with decreasing domain sizes. These results revealed that 90° domain walls can contribute significantly to piezoelectric property for the engineered domain configuration. Thus, we must consider about a role of 90° domain wall on the piezoelectric property. Liu *et al.* reported a model for the role of non-180° domain walls in the engineered domain configurations[15]. Now, we consider that to explain the enhanced piezoelectric property with increasing non-180° domain wall density, this model is very useful.

4. CONCLUSION

In this study, the engineered domain configuration with different domain sizes was induced into tetragonal $BaTiO_3$ single crystals, and their piezoelectric properties were investigated as a function of a domain size. Prior to this study, the dependence of domain configuration on temperature and E-field was investigated using a polarizing microscope in order to understand the optimum condition for fine domain structure and coarse domain structure. As a result, at 133.0 °C, when the E-field over 6kV/cm was applied along [111]$_c$ direction, the engineered domain configuration with a fine domain size of 6.5 μm appeared. Moreover, it was also found that this fine domain structure was still stable at room temperature without E-field. On the other hand, the coarse domain structure was obtained by poling at 128.0 °C. Finally, the piezoelectric properties were measured using the 31 resonators with different kinds of domain sizes. As the result, $BaTiO_3$ single crystals with the engineered domain configuration exhibited much enhanced piezoelectric properties. Moreover, it was found that the piezoelectric properties such as d_{31} and k_{31}

increased significantly with decreasing domain sizes. These results revealed that non-180° domain walls can contribute significantly to piezoelectric property for the engineered domain configuration.

5. ACKOWLEDGWMENT

6. REFERENCES

1) S .-E. Park and T. R. Shrout, Mater. Res. Innovat., 1 (1997), p.20.
2) S.-E. Park and T. R. Shrout, J. Appl. Phys., 82 (1997), p.1804.
3) J. Kuwata, K. Uchino and S. Nomura, Ferroelectrics, 37 (1981), p.579.
4) J. Kuwata, K. Uchino and S. Nomura, Jpn. J. Appl. Phys., 21 (1982), p.1298.
5) S. Wada, H. Kakemoto, T. Tsurumi, S.-E. Park, L. E. Cross and T. R. Shrout, Trans. Mater. Res. Soc. Jpn., 27 (2002), p.281.
6) S. Wada, S. Suzuki, T. Noma, T. Suzuki, M. Osada, M. Kakihana, S.-E. Park, L. E. Cross and T. R. Shrout, Jpn. J. Appl. Phys., 38 (1999), p.5505.
7) S. Wada and T. Tsurumi, Trans. Mater. Res. Soc. Jpn., 26 (2001), p.11.
8) S. Wada, S.-E. Park, L. E. Cross and T. R. Shrout, J. Korean Phys. Soc., 32 (1998), p.S1290.
9) S. Wada, S.-E. Park, L. E. Cross and T. R. Shrout, Ferroelectrics, 221 (1999), p.147.
10) O. Nakao, K. Tomomatsu, S. Ajimura, A. Kurosaka and H. Tominaga, Jpn. J. Appl. Phys., 31 (1992), p.3117.
11) O. Nakao, K. Tomomatsu, S. Ajimura, A. Kurosaka and H. Tominaga, Ferroelectrics, 156 (1994), p.135.
12) EMAS-6100: Standard of Electronic Materials Manufacturers Association of Japan (1993).
13) S.-E. Park, S. Wada, L. E. Cross and T. R. Shrout, J. Appl. Phys., 86 (1999), p.2746.
14) M. Zgonik, P. Bernasconi, M. Duelli, R. Schlesser, P. Gunter, M. H. Garrett, D. Rytz, Y. Zhu and X. Wu, Phys. Rev. B, 50 (1994), p.5941.
15) S.-F. Liu, S.-E. Park, L. E. Cross and T. R. Shrout, Ferroelectrics, 221 (1999), p.169.