

Enhanced Piezoelectric Property of Barium Titanate Single Crystals by Domain Wall Engineering using Patterning Electrodes

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For the [111] oriented barium titanate (BaTiO_3) single crystals, the patterning electrode was used to induce the finer engineered domain configurations with domain size below $5 \mu\text{m}$. The poling treatment was performed at 134.0°C under electric fields below 6 kV/cm to inhibit the burning of the patterning electrode with photoresist. As the results, the gradient domain sizes from $3 \mu\text{m}$ (high voltage side) to $8\text{-}9 \mu\text{m}$ (ground side) were induced into the 31 resonator along thickness direction. For this resonator, the d_{31} was measured at -243.2 pC/N using a resonance-antiresonance method. Thus, this study was revealed that the patterning electrode was very powerful tool to induce much finer domain sizes below $5 \mu\text{m}$. However, this value of -243.2 pC/N was almost 70 % of the expected d_{31} of -337.7 pC/N for the resonator with domain size of $3 \mu\text{m}$. It was considered that this difference was originated from lower applied electric field below 6 kV/cm in this study than that over 10 kV/cm for the study using the whole plane electrode.

Key words: barium titanate, engineered domain configuration, domain engineering, piezoelectric property

1. INTRODUCTION

From the viewpoint of environmental problem, environmental friendly materials are currently required. However, practical piezoelectric materials such as PZT ceramics with high piezoelectric properties¹⁾ are always including lead. Therefore, lead-free piezoelectric materials with higher piezoelectric properties than PZT ceramics must be required.²⁻⁴⁾ BaTiO_3 is one of the typical lead-free piezoelectric materials, but its piezoelectric properties were much lower than those of PZT ceramics. Thus, if the piezoelectric properties of BaTiO_3 are drastically improved, BaTiO_3 becomes to one of the promising lead-free piezoelectric materials which can partially replace PZT ceramics. To achieve much higher piezoelectric constants, it is known that the introduction of the engineered domain configuration into ferroelectric single crystals is very useful.⁵⁻⁷⁾

The engineered domain configuration is one of the domain engineering technique using the crystallographic anisotropy and can be induced by electric field applied along crystallographically special directions different from the polar direction. The direction of electric field which introduces the engineered domain configuration is dependent on the crystal structure. BaTiO_3 is tetragonal structure at room temperature and has 6 equivalent spontaneous polar directions along $\langle 100 \rangle$ directions. The engineered domain configuration of BaTiO_3 crystals consisted of three kinds of polarizations and are obtained by electric field applied along [111] direction as shown in Fig. 1.⁸⁾ Recently, in BaTiO_3 single crystals with engineered domain configuration, it was reported that the piezoelectric constants significantly increased with increasing domain wall densities, i.e., decreasing domain sizes.⁹⁻¹⁰⁾ However, in this poling treatment, the whole plane electrode was used, and the minimum domain size

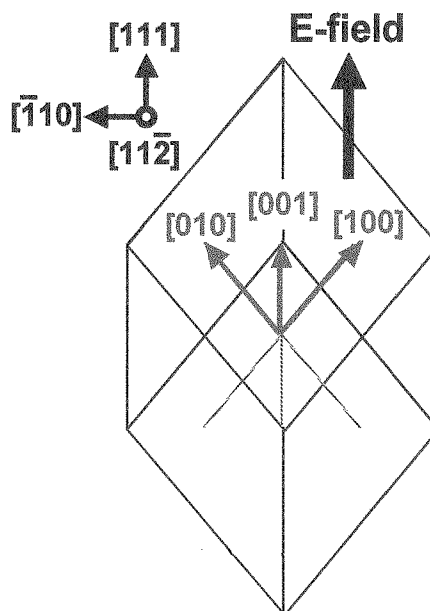


Fig. 1 Schematic engineered domain configuration of tetragonal BaTiO_3 crystal.

was limited to greater than $5 \mu\text{m}$. Therefore, it is important to establish a new poling method to induce much smaller domain sizes below $5 \mu\text{m}$ into the BaTiO_3 single crystals. Urenski *et al.* reported that for the KTiOPO_4 single crystals, the periodic domain structure was successfully induced using the patterning electrodes.¹¹⁾ Thus, using the patterning electrode, it can be possible to induce much smaller domain sizes below $5 \mu\text{m}$ into the BaTiO_3 single crystals.

The objective in this study is to prepare the 31 resonators of BaTiO₃ crystals with a high piezoelectric constant (d_{31}) by introducing finer engineered domain configurations. For this purpose, a new poling method using a patterning electrode was established to induce the engineered domain configuration with smaller domain sizes below 5 μm , and piezoelectric properties were also investigate as a function of domain size.

2. EXPERIMENTAL

BaTiO₃ single crystals were grown by a top seeded solution growth (TSSG) method at Fujikura, Ltd.¹²⁾ These crystals were oriented along [111] direction using a back-reflection Laue method. For the piezoelectric measurement using the 31 resonators, BaTiO₃ single crystals were sized into 4.0x1.2x0.4 mm³ (4.0mm // [1-10], 1.2mm // [11-2], 0.4mm // [111]) by cutting and polishing using fine Al₂O₃ powders. The patterning electrode with gold strip line of 3 μm width per 6 μm spacing parallel to [1-10] direction was prepared on the top surface using a photolithography technique while the whole electrode was prepared on the bottom surface. First, on the top surface of the resonator, the photoresist (Kayaku Microchem, SU-8 3000) layer with 2 μm in thickness was coated. Then, mask alignment, UV radiation and development were performed. After this process, gold electrode was sputtered on both surfaces with 1.2x4.0 mm². The fine engineered domain configuration was induced by using the patterning electrode at various electric fields (0-10 kV/cm) and temperatures (20-140 °C). In this process, the domain structure was observed under crossed-nicols using a polarizing microscope (Nikon, LAB-OPHOTO2-POL). After poling, piezoelectric properties were measured by a resonance-antiresonance method¹³⁾ using impedance analyzer (Agilent, 4294A).

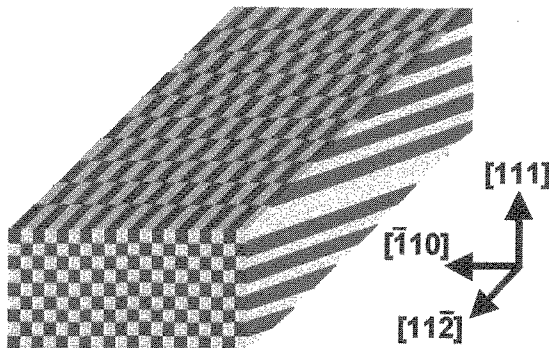


Fig. 2 Schematic desirable finer engineered domain configuration.

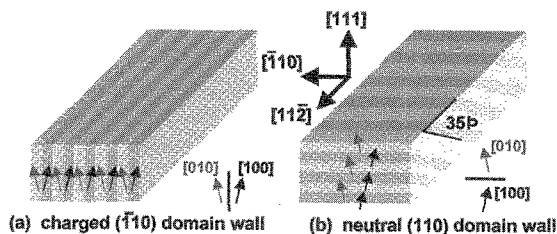


Fig. 3 Domain configurations with (a) 90° charged and (b) 90° neutral domain walls composed of two kinds of polar vectors along [010] and [001] directions.

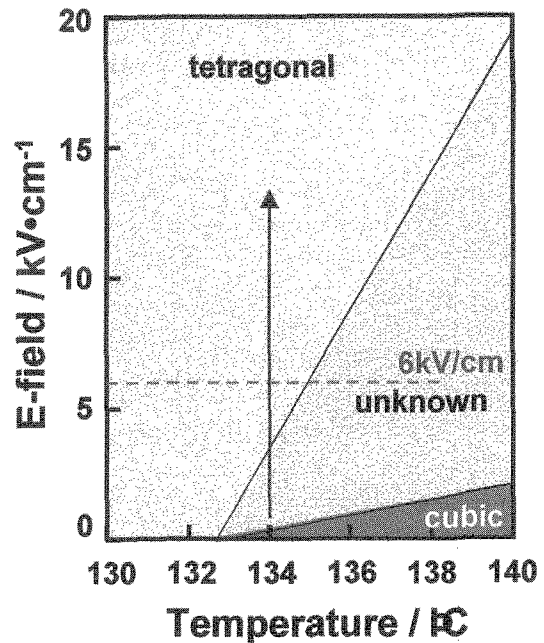


Fig. 4 Phase transition diagram as functions of temperature and electric field for [111] oriented BaTiO₃ single crystals.

3. RESULT AND DISCUSSION

Figure 2 shows the desirable engineered domain configuration for tetragonal BaTiO₃ single crystals in this study. This domain configuration is composed of just two kinds of polarizations along [010] and [100] directions as shown in Fig. 3. The d_{31} of each domain region with polar direction of [010] and [100] directions was estimated at -62 pC/N, respectively, by transformation of axis using single domain data reported by Zgonik *et al.*¹⁴⁾ Thus, if there is no piezoelectric contribution from domain wall region, it is expected that the d_{31} of the 31 resonator with the engineered domain configuration as shown in Fig. 2 can be just -62 pC/N. Moreover, the previous study revealed that in the engineered domain configuration, the d_{31} from domain wall region with a thickness of around 10 nm was estimated at a ultrahigh d_{31} value of -82,700 pC/N.¹⁵⁾ This suggested that if the engineered domain configuration with average domain size of 3 μm is induced into BaTiO₃ single crystals, it is expected that the d_{31} can become to -337.7 pC/N. In general, it is known that d_{33} value can be expressed as $[2*d_{31}]$. Thus, when the d_{31} becomes to -337.7 pC/N, it is expected that the d_{33} also can become to 675.4 pC/N. Thus, a poling treatment was performed to induce the engineered domain configuration with domain size of 3 μm .

Fig. 4 shows the temperature-electric field program used for a new poling method using patterning electrode. The phase transition temperature from tetragonal to cubic was 132.2 °C for BaTiO₃ crystals. Thus, first, temperature increased up to 140.0 °C without electric field, and the appearance of the optical isotropic state was confirmed. Then, temperature decreased slowly down to 134.0 °C, and electric field was applied along [111] direction at 134.0 °C. The patterning electrode prepared in this study was composed of (1) photoresist strip line of 3 μm width per 6 μm spacing and (2) gold electrode deposited on both the patterned photoresist and the crystal surface. Thus, it should be noted that in the patterning electrode, photoresist



Fig. 5 Photograph of burned patterning electrode during poling treatment at 134.0 °C and 6.1 kV/cm.

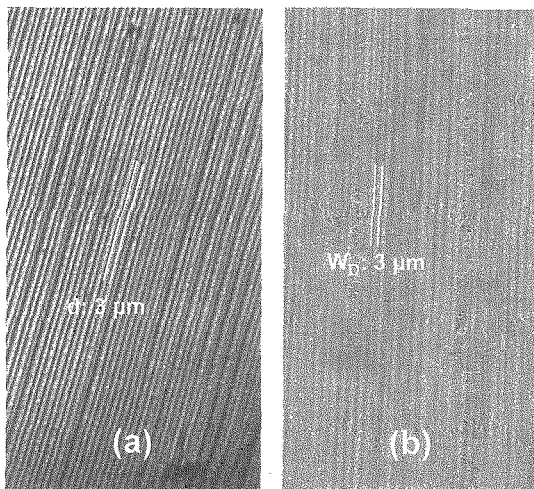


Fig. 6 Photograph of (a) the patterning electrode with gold electrode width of 3 μm and (b) the poled domain structure with average domain size of 3 μm.

was still remained between crystal surface and gold electrode. This is because this photoresist is stable up to 250 °C. However, when electric field over 6 kV/cm was applied at 134.0 °C, photoresist was burned with a large leakage current over 300 μA as shown in Fig. 5. Thus, in this study, the electric field applied at 134.0 °C was limited below 6 kV/cm.

To induce the engineered domain configuration into BaTiO₃ crystals, electric field-induced phase transition from cubic to tetragonal phases above the Curie temperature of 132.2 °C must be required. Thus, the following poling method was applied in this study. At 134.0 °C, electric field was slowly applied up to 2 kV/cm, and then rapidly increased up to 5.6 kV/cm. Without soaking at 5.6 kV/cm, temperature decreased down to 50 °C at a cooling rate of -10 °C/min under electric field of 5.6 kV/cm. Fig. 6 shows optical microscope photographs of patterning electrode itself with a pattern width of 3 μm and the induced engineered domain configuration. In Fig. 6-b, average domain size was estimated at around 3 μm. When the whole plane electrode was used to induce the finer engineered domain configuration, minimum domain size was always limited above 5 μm. However, in this

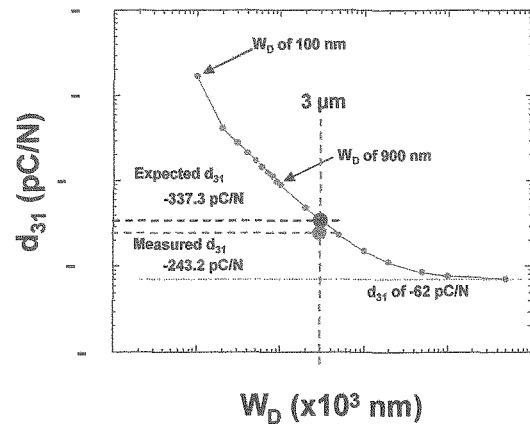


Fig. 7 Domain size dependence of the d_{31} for the [111] poled BaTiO₃ single crystals.

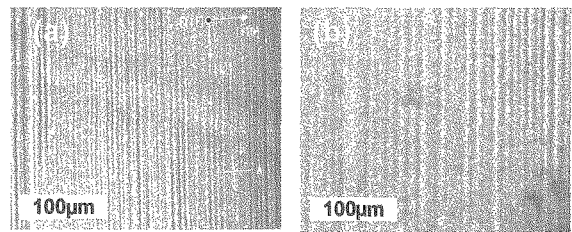


Fig. 8 Domain structures of the 31 resonator near (a) the top surface (high voltage side) and (b) the bottom surface (ground side).

study, using the patterning electrode with gold strip width of 3 μm, the engineered domain configuration with domain size of 3 μm was successfully induced into BaTiO₃ crystals. This revealed that for the poling treatment of BaTiO₃ crystals, the patterning electrode is very powerful technique.

Finally, for this 31 resonator with 3 μm domain width, the piezoelectric properties were measured using resonance-antiresonance technique. As mentioned before, it is expected that the d_{31} of -337.7 pC/N can be measured for the 31 resonator of the engineered domain configuration with domain width of 3 μm.¹⁵⁾ The measured d_{31} was -243.2 pC/N as shown in Fig. 7, and if regarded d_{33} as $[2 \cdot d_{31}]$, the d_{33} can be estimated at 486.4 pC/N. However, this measured value was just 70 % of the expected value of -337.7 pC/N. Thus, the origin of this lower d_{31} than the expected d_{31} was investigated. Fig. 8 shows domain structures near top and bottom electrodes of the 31 resonator. The domain size near the top patterning electrode (high voltage side) was estimated at 3 μm while that near the bottom electrode (ground side) was estimated at 8-9 μm. The gradient domain sizes from 3 to 8-9 μm along thickness direction ([111] direction) were first observed. As mentioned previously, when the whole plane electrode was used for the poling treatment, the minimum domain size was limited to 5 μm, but there was no gradient domain size.^{9-10,15)} This difference might be originated from different electric fields. When the homogeneous domain size of 5.5 μm using the whole plane electrode, the applied electric field was 10.1 kV/cm. This electric field was almost twice larger value than that of 5.6 kV/cm used in this study. Urenski *et al.* reported that for the introduction of the expected periodic domain structure

similar to the patterning electrode, the much higher electric field than the coercive electric field (E_c) was required.¹¹⁾ Therefore, if the high electric field over 10.1 kV/cm is applied to the 31 resonator using the patterning electrode with 3 μm width, it is considered that the homogeneous domain size of 3 μm can be induced into the resonator. At present, the patterning electrode without photoresist is designed for this purpose, and near future, we will challenge to induce much finer homogeneous domain sizes into the resonator to prepare a lead-free piezoelectrics with higher d_{31} over -500 pC/N.

4. CONCLUSIONS

In this study, the patterning electrode was used to induce the finer engineered domain configurations with domain size of 3 μm . The poling treatment was performed at 134.0 °C under electric fields below 6 kV/cm to inhibit the burning of the patterning electrode with photoresist. As the results, the gradient domain sizes from 3 to 8-9 μm were induced into the 31 resonator. Up to date, when the whole plane electrode was used, the minimum domain size was limited to 5 μm . However, using patterning electrode, the smaller domain size than 5 μm was successfully induced into the resonator. The d_{31} was measured at -243.2 pC/N, and this value was almost 70 % of the expected d_{31} of -337.7 pC/N for the resonator with domain size of 3 μm . This difference was originated from lower applied electric field below 6 kV/cm. This problem can be solved by development of the patterning electrode without photoresist. In the future, the developed patterning electrode with much finer pattern than 3 μm will be prepared, and much higher d_{31} will be challenged.

5. ACKNOWLEDGMENT

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