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Single-domain treatment of potassium niobate single crystal and their piezoelectric properties

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To measure accurate piezoelectric properties of $KNbO_3$ single crystal, the method to make single-domain state and the measurement system were established. $KNbO_3$ single crystal was cut and polished. And to remove the stressed surface layers, single crystal was chemically etched. After this treatment, $KNbO_3$ crystal was poled by the 2-step poling method. As a result, the domain state was almost single-domain state. Measurement method was five-terminal method. Measurement equipment was completely shielded using by grounded metal-box. By using this equipment, the measurement system with small stray capacitance below 1 fF and low noise signal was achieved. As a result, all accurate piezoelectric constants were determined. And $KNbO_3$ single crystal was discovered to have both high electromechanical coupling coefficients and high mechanical quality factor.

Key words: potassium niobate single crystal, single-domain, piezoelectric property, stray capacitance, electromechanical coupling coefficient, mechanical quality factor

1 INTRODUCTION

Ferroelectricity of $KNbO_3$ was first founded by Mathias[1)], and up to date, a lot of studies on $KNbO_3$ have been reported[2)-6)]. However, there have been just a few reports on the piezoelectricity of $KNbO_3$ crystal [7)-9)]. There are two reasons why the reports on the piezoelectricity of $KNbO_3$ crystal were so limited. One is the difficulty in the crystal growth of $KNbO_3$ single crystal with enough electrical resistance to measure piezoelectric property due to high volatility of potassium during the growth process. The other is the difficulty in the poling treatment because of having twelve domain states and four kind of domain structures, *i.e.*, (1) 180° domain structure with W_∞ walls, (2) 90° domain structure with W_f walls of $\{100\}_c$, (3)120° domain structure with W_f walls of $\{112\}_c$, (4) 60° domain structure with W_f walls of $\{110\}_c$ (Fig. 1). Subscript c means cubic notation system.

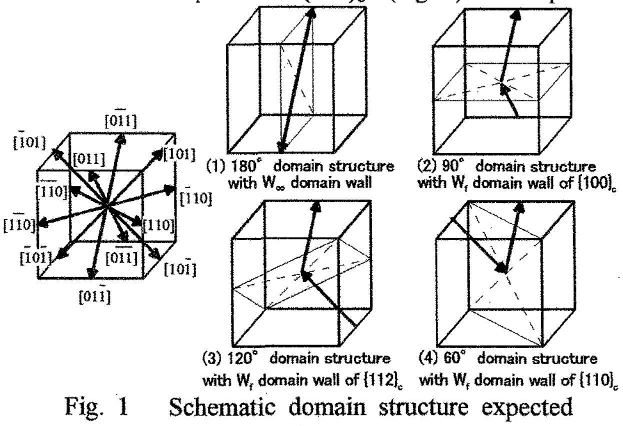

Fig. 1 Schematic domain structure expected for $KNbO_3$ single crystal.

Recently $KNbO_3$ is expected as high performance piezoelectric devices. Some of the piezoelectric properties of $KNbO_3$ single crystal were reported by Wiesendanger[7)], and all of them were reported by Zgonik[9)]. But because of those two difficulties that growing high quality single crystal and poling treatment for making single domain, accurate piezoelectric constants of $KNbO_3$ single crystal have not been reported yet.

The objective of this study is to determine accurate piezoelectric constants of $KNbO_3$ single crystal. And for this objective, to establish how to make single domain state and to establish how to measure accurate piezoelectric constants are necessary. High quality single crystal grown at Asahi Techno Glass was used.

2 EXPERIMENT

2.1 Sample preparation

The crystal system of $KNbO_3$ single crystal at room temperature is orthorhombic one. In this study,

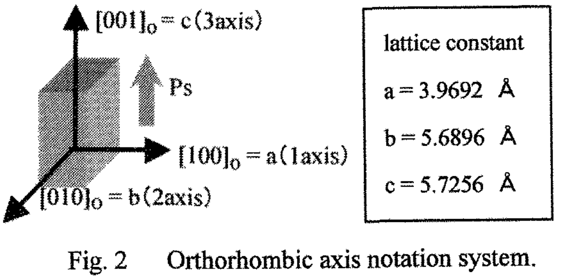

Fig. 2 Orthorhombic axis notation system.

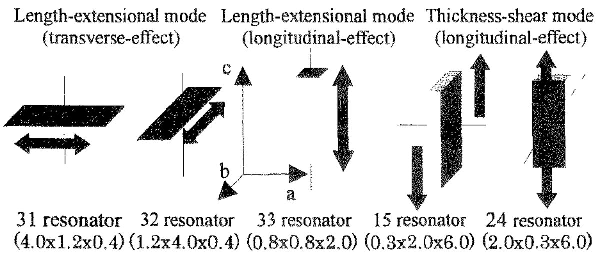

Fig. 3 Shape and size (mm) of each samples.

orthorhombic axis notation system (Fig. 2) is used. Point group is mm2, so this single crystal has five independence tensor entries. Therefore five kinds of samples (Fig. 3) were prepared. First, we established how to make single domain state using 32 resonator.

Single crystal was cut, and 6 planes were polished into a size of 4.0 x 1.2 x 0.4 mm^3, and chemically etched. Chemical etching was soaking sample for 4 hours in the etching solution. Etching solution was produced by hydrofluoric acid and nitric acid 2 to 1. Gold electrodes were sputtered on the surfaces with a size 4.0 x 1.2 mm^2. Next, sample was poled by 2-step poling method[10] (Fig. 4). After each process, domain states were observed under crossed nicols with a polarizing microscope.

2.2 MEASUREMENT SYSTEM

Piezoelectric properties were determined by resonance-antiresonance method using by impedance analyzer (Agilent 4294A).

Previous measurement system could not support sample softly and sample's vibration was prevented, so both electromechanical coupling coefficient and mechanical quality factor were measured as smaller values. The sample supported by silver wire could not be measured with reproduction because the quantity of adhesive affects the vibration of sample. In the new measurement system, sample could be supported in minimum stress by using the probe controlled by micrometer. As the result both electromechanical coupling coefficient and mechanical quality factor increased.

Sample size and the length of between proves were very short, so measurement values were not stable because of the effect of stray capacity. To remove this effect, new system's measurement method was improved by using five-terminal method. And measurement equipment was completely shielded using by grounded metal-box. By

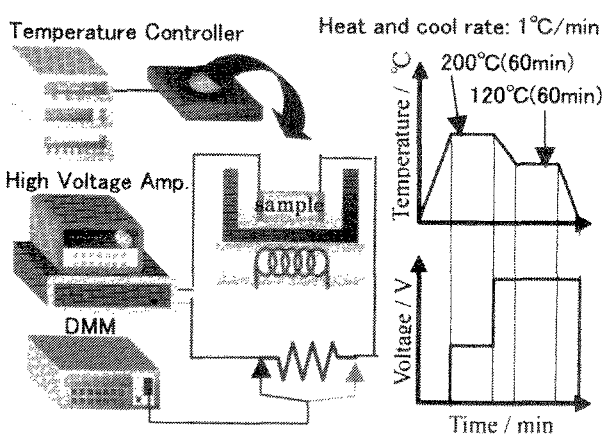

Fig. 4 2-step poling system and profile.

using this equipment, the stray capacity was decreased below 1 fF and low noise, accurate, reproductive measurement was achieved.

3 RESULT & DISCUSSION

3.1 Establishment how to make single domain state

Fig. 5 shows the domain states under crossed nicols of

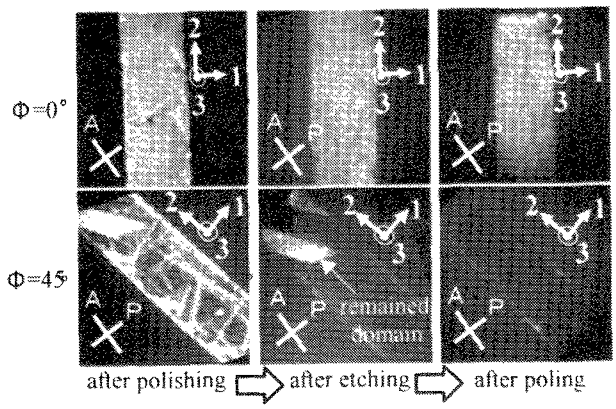

Fig. 5 The effect of each process recognized by observation under crossed nicols.

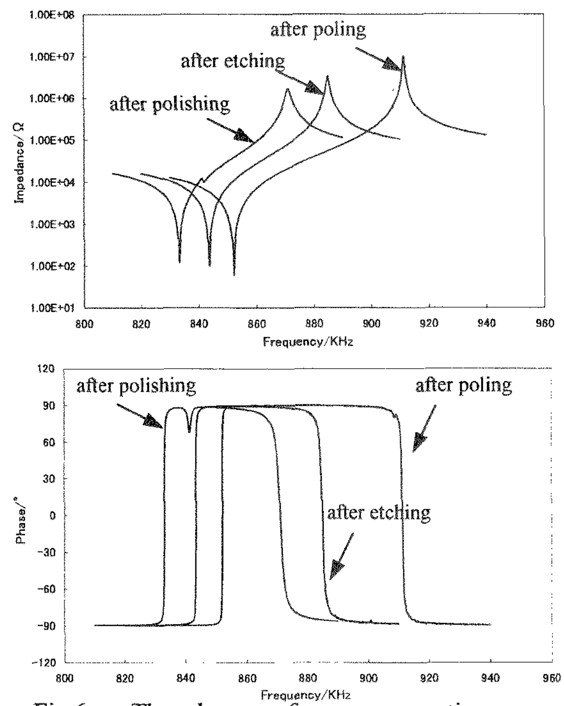

Fig.6 The change of resonance-antiresonance curve after each process

Table 1 The effect of each process recognized by measurement.

Performance	polishing	~ etching	~ poling
$\varepsilon_{33}^T/\varepsilon_0$	55.6	51.7	48.4
s_{22}^E [pm^2/N]	5.38	5.23	5.12
d_{32}[pc/N]	16.7	16.4	18.5
k_{32}	0.324	0.336	0.395
Qm	4002	4925	7613

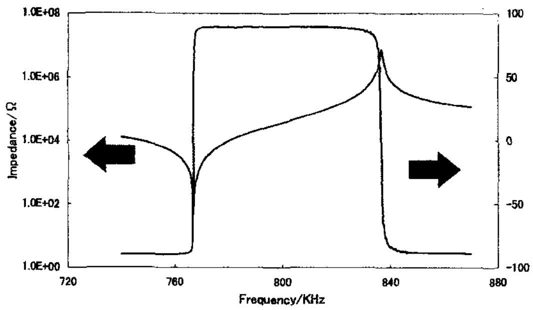

Fig. 7 Resonance-antiresonance curve of 31 resonator.

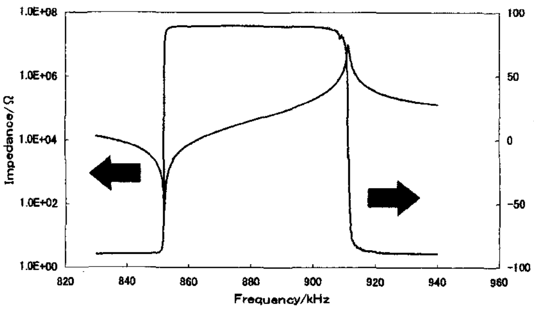

Fig. 8 Resonance-antiresonance curve of 32 resonator.

32 resonator after each process. The sample performed only polishing had many remained domain. The sample performed polishing and chemical etching had no strain layer. The strain layer was removed, but inner remained domain was not removed. The sample performed polishing, chemical etching and 2-step poling method had no remained domain. Therefore each process is necessary to make single domain state.

Next, the sample after each process was measured. The result is as Table 1 and Fig. 6. Performing each process, both electromechanical coupling coefficient and mechanical quality factor increased. Specially, mechanical quality factor increased vastly. Thus remained domain prevented sample's vibration, and making single domain state was necessary to measure accurate piezoelectric constants.

As the results, how to make single domain state was established. And to determine accurate piezoelectric constants became possible, so next each resonator was measured.

3.2 Piezoelectric properties of the length-extensional mode under transverse-effect

Table 3, Fig.s 7 and 8 show the measurement result of the 31 and 32 resonators. The resonance-antiresonance curves show no sprious peak. Each property was determined by immittance-fitting method[11]. The measurement of the sample with very high mechanical quality factor was extremely difficult using by general method[12]. But by using immittance-fitting method, the mechanical quality factor was determined exactly because the elastic compliance was represented as complex value. As shown Table 3, the piezoelectric constant in this work was larger than that measured by Zgonik et al. Especially d_{32} was twice larger than Zgonik's one. The remarkable results were that these samples had very high electromechanical coupling coefficients and mechanical quality factors compared with the PZT's ones (Table 2). Generally, the sample with high electromechanical coupling coefficient has low mechanical quality factor. And the sample with high mechanical quality factor has low electromechanical coupling coefficient. But, $KNbO_3$ single crystal had both high electromechanical coupling coefficient and high mechanical quality factor.

Table 2 Piezoelectric properties of hard and soft PZT.

	Soft-PZT[11]	Hard-PZT[11]
$\varepsilon_{33}^T/\varepsilon_0$	1340	815
s_{11}^E [pm²/N]	13.5	9.72
d_{31}[pc/N]	135	65.2
k_{31}	0.337	0.246
Qm	90	883

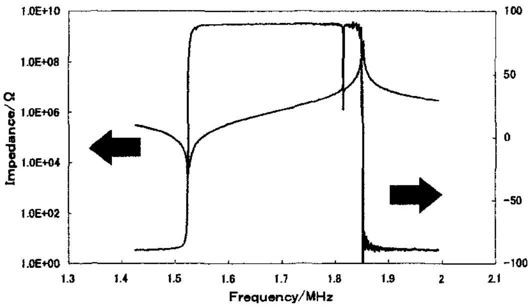

Fig. 9 Resonance-antiresonance curve of 33 resonator.

3.3 Piezoelectric properties of the length-extensional mode under longitudinal-effect

Table 3 and Fig. 9 show the measurement result of 33 resonator. The resonance-antiresonance curve was very

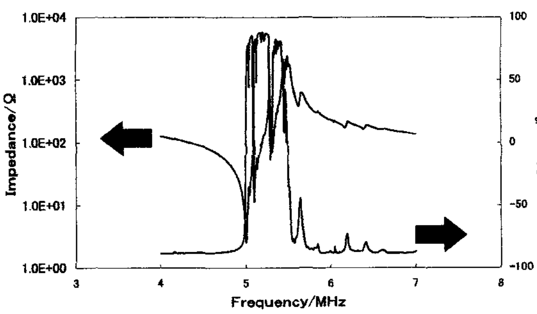

Fig. 10 Resonance-antiresonance curve of 15 resonator.

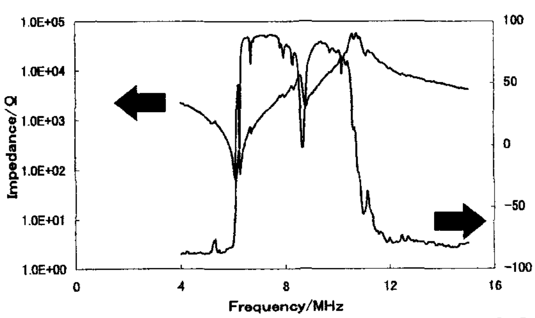

Fig. 11 Resonance-antiresonance curve of 24 resonator.

Table 3 Piezoelectric properties of $KNbO_3$ single crystal.

sample	Dielectric constant			Elastic constant			Piezoelectric constant			Electromechanical coupling coefficient			Mechanical quality factor		
		Ref.a)	This work	[pm²/N]	Ref.a)	This work	[pC/N]	Ref.a)	This work		Ref.b)	This work		Ref.	This work
31			47.5c)	S_{11}^{E}	3.70 ±0.03	5.41c)	d_{31}	19.5 ±2	22.3c)	k_{31}	0.514	0.468c)	Q_m (31)	---	7750e)
32	ε_{33}^{T}	44 ±2	48.4c)	S_{221}^{E}	4.43 ±0.04	5.12c)	d_{32}	9.8 ±0.7	18.5c)	k_{32}	0.236	0.395c)	Q_m (32)	---	7613e)
33			41.7c)	S_{33}^{D}	3.57 ±0.05	4.06c)	d_{33}	29.3 ±1.5	29.6c)	k_{33}	0.778	0.608c)	Q_m (33)	---	6773e)
15	ε_{11}^{T}	985 ±20	1103.7d)	C_{55}^{D}	1.135 ±0.01	1.16d)	d_{15}	78 ±2	140.7d)	k_{15}	0.665	0.452d)	Q_m (15)	---	460e)
24	ε_{22}^{T}	150 ±5	176.3d)	C_{44}^{D}	0.940 ±0.005	0.970d)	d_{24}	103 ±4	206.7d)	k_{24}	0.939	0.852d)	Q_m (24)	---	1906e)

a) measured by Zgonik et al.
b) calculated on basis of Zgonik's values
c) determined by immittance-fitting Method
d) determined by resonance-antiresonance method
e) determined using LCR equivalent circuit

noiseless. Each property was determined by immittance-fitting method. Electromechanical coupling coefficient was 77.8% and mechanical quality factor was 6773. These values were very high.

3.4 Piezoelectric properties of the thickness-shear mode

Table 3, Fig.s 10 and 11 show the measurement result of the 15 and 24 resonators. To make samples for this mode was very difficult because the condition of sample's surface affects the sample's vibration vastly. So, the resonance-antiresonance curves had many spurious peaks. Therefore more examination is needed. This data had many spurious and immittance-fitting method could not be used to determine the piezoelectric properties. So, the piezoelectric properties were determined by conventional resonance-antiresonance method. The mechanical quality factor was determined using LCR equivalent circuit. LCR equivalent circuit is as follows:

$$Q_m = \frac{1}{2\pi \cdot f_s \cdot C_1 \cdot R_1}, \tag{1}$$

where

$$R_1 = \frac{1}{G_{max}}, \tag{2}$$

$$C_1 = \frac{f_p^2 - f_s^2}{f_p^2} \cdot C_f. \tag{3}$$

In these equations, f_s means resonance frequency, f_p means antiresonance frequency, G_{max} means maximum value of conductance, C_f means free capacitance (the capacitance between electrodes at very lower frequency than resonance one). With these equations, mechanical quality factor could be determined as shown in Table 3.

4 CONCLUSION

To measure accurate piezoelectric properties stable, the measurement system was improved mainly in two points. One was the improvement of probes to support sample. By using the probes controlled by micrometer, the sample could be supported in minimum stress and, as the result, both electromechanical coupling coefficient and mechanical quality factor increased. The other was the improvement of stability. To remove the effect of stray capacity, the new measurement method was improved by using five-terminal method. And measurement equipment was completely shielded using by grounded metal-box. By using this equipment, the measurement system with small stray capacity below 1 fF and low noise signal was achieved. To prepare $KNbO_3$ single crystal with single domain state, the sample had to be performed three processes. First was polishing. Polishing was effective to inhibit leakage electric current in poling and spurious in measurement. Second was chemical etching. Chemical etching was effective to move domain wall smoothly in the 2-step poling method. Last process was 2-step poling method. The piezoelectric properties of $KNbO_3$ single crystal with single domain state were determined as Table 2. Generally, the sample with high electromechanical coupling coefficient has low mechanical quality factor. And the sample with high mechanical quality factor has low electromechanical coupling coefficient. But, $KNbO_3$ single crystal had both high electromechanical coupling coefficient and high mechanical quality factor. Moreover, $KNbO_3$ single crystal had lower dielectric properties than other materials with high electromechanical coupling coefficient. Therefore, $KNbO_3$ single crystal is expected as the high performance sensor or filter.

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