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Surface characteristics of tetragonal PZT ceramics

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Ferroelectric domain structures of tetragonal PZT ceramic surface were evaluated by the poling field dependence of relative XRD intensity of (002) peak and planar coupling factor. From our domain configuration model, it was confirmed that there are two peaks of 90° domain rotation and one peak of 180° domain rotation. On the ceramic surface the 90° domain switching was easy to occur in comparison with the bulk, the amount of which was larger than the one of the bulk. Furthermore, while the 90° domain changed into the 180° domain, the 90° domain switching decreased and 180° domain switching increased with alternating the poling field.

1. INTRODUCTION

Since PZT ceramics are ferroelastic and ferroelectric materials, the domain switching can be caused by mechanical stress and electric field. In tetragonal phase there are 90° and 180° domains, among which the ferroelastic domain switching is occurred only by the 90° rotation. This ferroelastic domain switching can be detected by the change in X-ray diffraction(XRD) peak intensities of (002) and (200)[1-3]. In PZT ceramics the surface alignment by poling also occurs. The surface layer is not constrained like bulk, thus the texture change during poling or under the stress may be easier than the bulk[4-5]. Recently as a FRAM memory device great attention was paid in PZT thin films, however, for the applications the degradation of the films must be improved. Study on this surface layer characteristics may be useful for understanding the degradation characteristics of thin films. From this study we found the existence of surface layer showing different behavior from bulk in poling.

2. EXPERIMENTAL PROCEDURE

The ceramic composition used for this study was $0.05Pb(Sn_{1/2}Sb_{1/2})O_3 - 0.62PbTiO_3 - 0.33PbZrO_3$ with 0.4 wt% MnO_2. The powder was uniaxially pressed at 150 MPa, and fired at 1240 ℃ for 2 hours. The fired sample disks were 14 mm in diameter and 1 mm thick. Poling was conducted at 80℃ for 30 minutes. Polishing was done with SiO_2 polishing slurry (Glanzox 3700, Fujimi Co., Japan). Samples in several conditions of surface treatments and poling were examined using XRD. The XRD intensity is expressed as the relative ratio of I_{002} (=I(002)/{I(002)+I(200)}). Further, the poling field dependence of planar coupling factor(kp) was measured by a impedance/gain-phase analyzer(HP4194A).

3. RESULTS AND DISCUSSION

3.1. Effect of poling field on kp and I002.

Figure 1 shows the poling field(E) dependence of kp[6] and I002, when the E varied from 1.0→4.5→-1.0→-4.5→1.0 to 3.0kV/mm. The samples consist of PZT ceramic disks with as-fired surface(① in Fig.1) and with polished surface(② in Fig.1). The disk of ② was polished every poling treatment, because of the elimination of a surface layer. Therefore, the sample of ② is said to possess a bulk property of PZT ceramics. Since the relations between kp and E had the same tendency independent of the surface condition, the E dependence of kp was due to the bulk property. The I002, however, depended on the surface condition. As the variation in I002 of ① was larger than the one of ②, the ceramic surface caused the increase in I002 of ① in comparison with I002 of ②. We believe the surface was easy to orient in c-axis direction by 90° rotation because of the relaxation of induced stress by poling. Although the kp(bulk property) approached to 0% at E=±2kV/mm in Fig.1, the I002 of ② was almost constant. After the poling of the virgin ceramics, 180° rotation was dominant to affect the kp in the ceramic bulk by applying alternating poling fields.

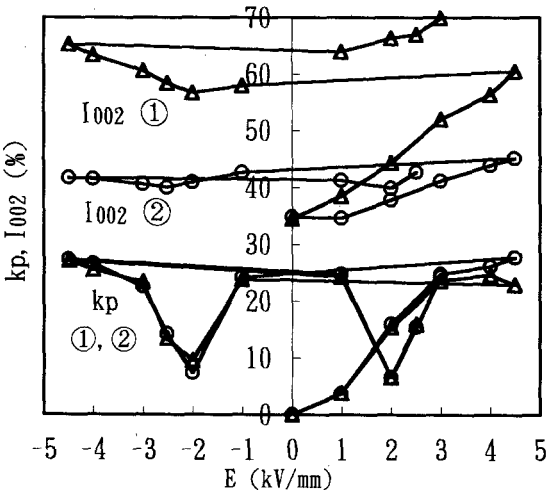

Fig. 1 The poling filed(E) dependence of planar coupling factor (kp) and relative intensity of I002; ①as-fired surface and ② bulk.

3.2. Poling field dependence of ferroelectric domain structure

Figure 2 shows a typical domain configuration model composed of c, c*, b and b* axes. Alternating poling fields were applied to c(+) and c*(-); a subscript of * shows the opposite direction of c axis. We believe the change in the domain structure by poling can be explained to evaluate the change in the area with the individual axis. The total amount of the domains oriented to c and b axes was calculated by the relations between I002, kp and E, further, a normalized polarization(P) from P-E hysteresis loop using the following equations[7].

$$I_{002} \propto (ct+c^*t) \quad (1)$$

$$I_{200} \propto (bt+b^*t) \quad (2)$$

$$r' = c^*/c = b/b^* = (1-P)/(1+P) \quad (3)$$

$$c = (c+c^*)/(1+r') \quad (4)$$

$$c^* = (c+c^*)/(1+1/r') \quad (5)$$

$$b = (b+b^*)/(1+r') \quad (6)$$

$$b^* = (b+b^*)/(1+1/r') \quad (7)$$

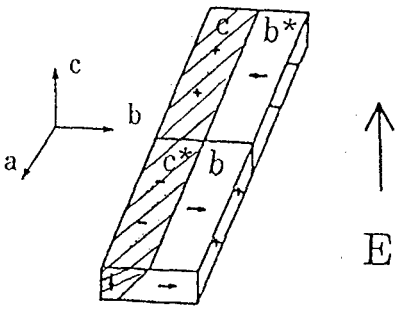

Fig.2 Domain configuration model of tetragonal PZT ceramics .

where I_{002} and I_{200} are the relative intensities of XRD on (002) and (200) lines; P is the polarization normalized(Pmax.=1); c, c*, b and b* are the amount(area) of the domains oriented to c, c*, b and b* axes; ct, c*t, bt and b*t are the total amount of the domains.

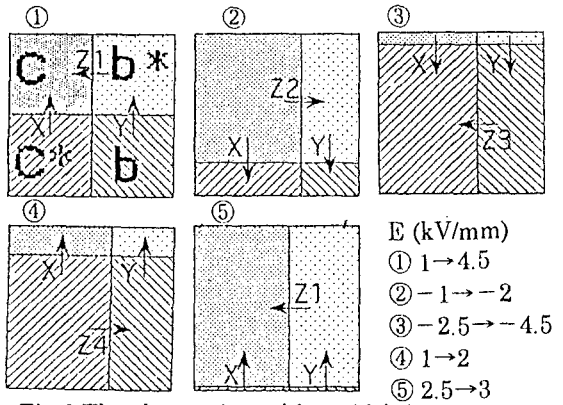

Fig.3 The change in c,c*,b and b* domains at various poling fields(①→⑤).

Figure 3 shows the E dependence of c, c*, b and b*. ①; when the E was applied in c axis direction from 1.0 to 4.5kV/mm, c* and b change into c and b* by 180° rotation (X and Y), and b* changes into c by 90° rotation(Z1) at the initial stage of poling. The c in the same direction of the E, however, still exists. ②; while the E was applied to the highly oriented c axis domain in the opposite direction(c* axis) of the initial poling field from -1.0 to -2.0kV/mm, c changes into b* by 90° rotation(Z2). Simultaneously, c and b* change into c* and b by 180° rotation (X and Y). Furthermore, ③; increasing E from -2.5 to -4.5kV/mm, it was mainly occurred b changed into c* axis by 90° rotation(Z3). ④; when the E was applied to the highly oriented c* axis domain in the same direction(c axis) of the initial poling field from 1.0 to 2.0kV/mm, c* changes into b by 90° rotation (Z4) and c* and b change into c and b* by 180° rotation (X and Y). Finally, ⑤; with the increase of the E over 2.5kV/mm, b* was mainly oriented in c axis direction by 90° rotation(Z1).

3.3. Domain rotations of ceramic surface

From our domain configuration model, we evaluated the E dependence of the amount of 90° and 180° rotations on the surface(as-fired surface) and bulk(polished surface) as shown in Fig.4 and 5, respectively. It was thought that there were two peaks of 90° rotation at E=±2kV/mm and ±3kV/mm.

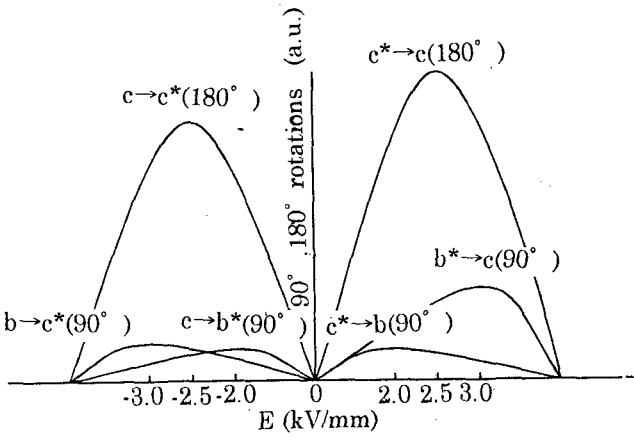

Fig.4 Schematic chart for 90° and 180° rotations on ceramic surface at various poling field(E).

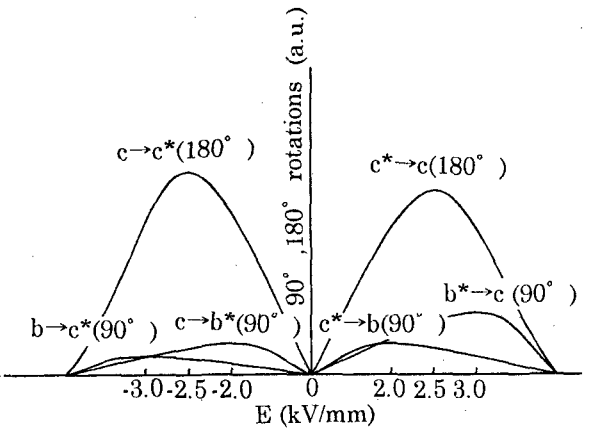

Fig.5 Schematic chart for 90° and 180° rotations on ceramic bulk at various poling field(E).

While the peaks at E= ± 3kV/mm corresponded to b*→c and b→c* orientations, the peaks of the surface were larger than the peaks of the bulk. In contrast, the peaks at E= ±2kV/mm corresponded to c*→b and c→b* orientations, there was no difference between the peaks of the surface and bulk. From our result, the 90° domain switching of b*→c and b→c* on the ceramic surface occurred easily to orient in c and c* directions, which is perpendicular to the surface, in compassion with the bulk. After the 90° domain switching on the surface, the domains in c and c* directions were changed only by 180° domain switching with further applying the electric field. Since the 90° domain changes into the 180° domain, the 90° domain switching decreased and the 180° domain switching increased with alternating the field, especially on the surface. The evaluation of the domain switchings as mentioned here corresponded with the results of the E dependence of kp and I_{002}.

4. SUMMARY

The ferroelectric domains in tetragonal PZT ceramics were investigated by the poling field dependence of crystal orientations in the ceramics. The crystal orientations regarding the ceramic surface and bulk were evaluated by the (002) and (200) peak intensities of XRD. The relative intensity I_{002} was about 34-35% in respect to as-fired samples just after firing. The I_{002} increased with increasing the poling field(E) because of c-axis orientation by 90° domain rotation. The I_{002}'s of the ceramic surface and bulk were 45 and 60% at E=4.5kV/mm, respectively. Since the kp was almost same(27%) independent of the surface conditions, the difference in the I_{002} was due to the surfaces. From our domain configuration model and the E dependence of kp and I_{002}, the amount of 90° domain rotation was affected by the surface conditions. We believe the evaluation of ceramic surface was an effective tool for analyzing the domain structures of PZT thin films.

ACKNOWLEDGEMENT

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