# *In situ* observation of crystal structure dynamics in ferroelectric films under application of an electric field

Ferroelectric materials have a switchable spontaneous polarization and also have pyroelectric and piezoelectric properties. Using such properties, they have been widely applied to many electronic devices, including sensors and actuators. Recently, they have also been applied to energy harvesting devices using mechanical vibration from an environmental source. Therefore, they have become one of the key materials for sensor network systems to a sustain an aging society, for example, by monitoring the movements of elderly people living alone.

Thin films of $Pb(Zr_{1-x}Ti_x)O_3$ combined with a microelectromechanical system (MEMS) have been extensively studied for such applications because of a superior piezoelectric and ferroelectric properties. It has been pointed out that the electromechanical response of $Pb(Zr_{1-x}Ti_x)O_3$ under the application of an electric field is not only simple lattice elongation (the so-called intrinsic contribution of the piezoresponse) (see Fig. 1(a)) but also includes extrinsic contributions, which include the reorientation of the film as shown in Fig. 1(b). For example, (100)-oriented regions (*a*-domains) switch to (001)-oriented regions (*c*-domains) in tetragonal $Pb(Zr_{1-x}Ti_x)O_3$ films consisting of a mixture of the (100) and (001) orientations. This extrinsic contribution is responsible for more than 50% of the total piezoelectric response and is required for the design of high-performance piezoelectric devices for MEMS applications.

The dynamics of the crystal structure in $Pb(Zr_{1-x}Ti_x)O_3$ films while applying an electric field have been measured by *in situ* X-ray diffraction (XRD) measurement. However, it has not yet been clarified how fast the reorientation proceeds. In particular, the relationship between the lattice elongation and geometrical domain structure deformation in tetragonal $Pb(Zr_{1-x}Ti_x)O_3$ thin films has not been determined from the viewpoint of the response speed. In our study, we investigated the change in the crystal structure under the application of an electric field in 600-nm-thick (100)/(001)-oriented epitaxial tetragonal $Pb(Zr_{0.4}Ti_{0.6})O_3$ films [1].

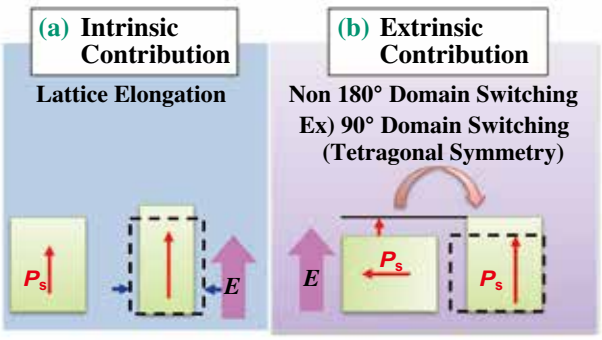


Fig. 1. Schematic drawing of two contributions to piezoelectric response in piezoelectric materials.

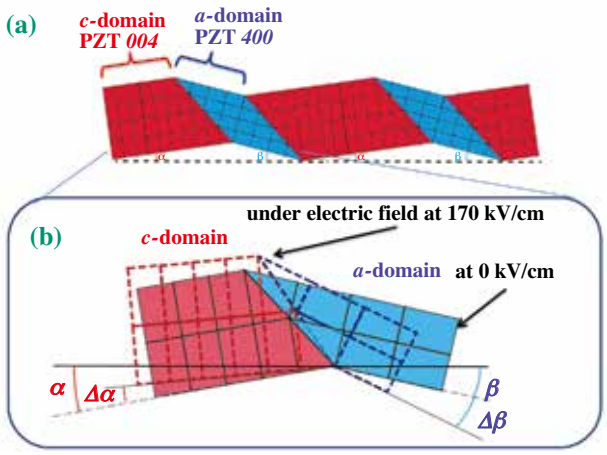


Fig. 2. Schematic drawing of crystal structures domain structures of (100)/(001)-oriented epitaxial tetragonal $Pb(Zr_{0.4}Ti_{0.6})O_3$ films.

The investigated film samples consisted of a combination of (100)-oriented domains (*a*-domains) and (001)-oriented domains (*c*-domains), as shown in Fig. 2(a), where the polar axis was perpendicular and parallel to the substrate surface for the (001)- and (100)-oriented domains, respectively. The average lattice parameters and the domain structure of the films under an electric field were measured using a time-resolved *in situ* synchrotron XRD system at SPring-8 **BL13XU** in conjunction with a high-speed pulse generator.

Figure 3 shows the XRD patterns before and under the application of an electric field. The *004* peak position of the (004) orientation shifts to a lower $2\theta$ angle under the application of an electric field, as shown in Fig. 3(a), which demonstrates the elongation of the *c*-axis lattice parameter of the (100)-oriented region. This corresponds to the intrinsic response shown in Fig. 1(a). In contrast, the *400* peak shifts in the opposite direction (to a higher angle) as shown in Fig. 3(b), thus indicating a decrease in the *a*-axis lattice parameter of the (100)-oriented region. In addition to this change in the lattice parameters, the amount of reorientation of the crystal structure from

(100) to (001) was evaluated from the changes in the *400* and *004* diffraction peak intensities resulting from the application of an electric field (see Fig. 3). These changes also accompanied a tilt in the angles of the (100)- and (001)-oriented regions from the substrate surface normal direction as schematically illustrated by the dashed line in Fig. 2(b).

Figure 4 shows the electric charge (Fig. 4(a)) and the lattice strains (Fig. 4(b)), the tilting angles (Fig. 4(c)), and the peak intensity of each domain (Fig. 4(d)) as a function of time. Figures 4(b), 4(c), and 4(d) suggest that the elastic deformation, tilting motion, and ferroelastic domain switching were completed within 40 ns. When the electric field was removed, the tilt angles and intensities also returned to their original values at zero field in less than 40 ns. These data were acquired during the repeated application of electric pulses of 800 ns duration, which confirm that a ferroelastic reorientation is perfectly repeatable. More importantly, all these changes (charging, lattice strain, domain switching, and the change in the tilting angle) occurred simultaneously without delay when the electric field across the PZT film was changed. This means that the 90° domain switching from the (100) to (001) orientation can be exploited to enhance the piezoresponse response time, even to within 10 ns order. It should be noted that the response time in this study is less than that previously reported [2,3] for a sintered body, which is on the order of 100 ns. Moreover, the reorientation of thin films does not suffer from frequency dispersion, as seen in bulk ceramics, where it becomes inactive within a short pulse time of ns order. This observation proved that the (001) orientation switches to the (100) orientation within 40 ns under a high-speed pulsed electric field. Our direct observation of such high-speed switching paves the way for the design of piezo-MEMS devices for high-frequency operation.

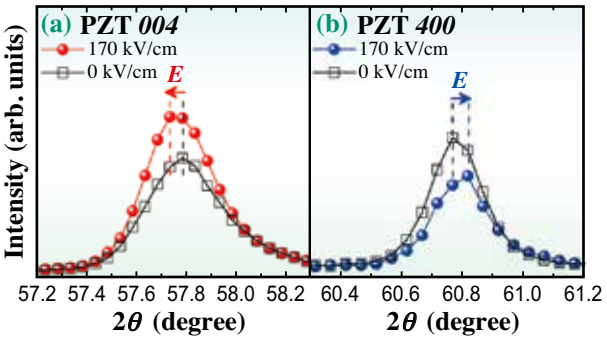


Fig. 3. HRXRD 2$\theta$ scans of (**a**) PZT *004* and (**b**) PZT *400* measured under a 200 ns pulsed electric field with amplitudes of 0 kV/cm (open squares) and 170 kV/cm (filled circles) for the $Pb(Zr_{0.4}Ti_{0.6})O_3$ films.

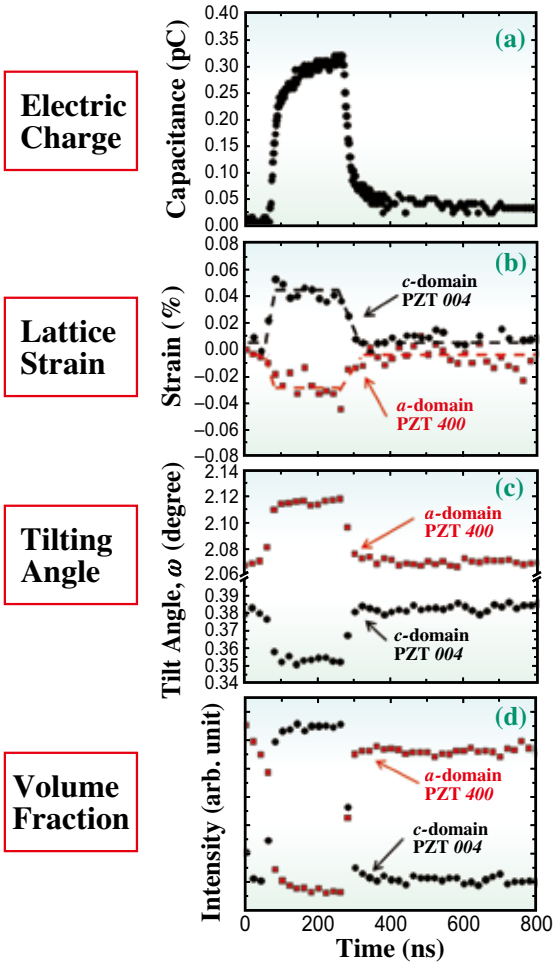


Fig. 4. (**a**) Electric charge, (**b**) lattice strains, (**c**) tilting angles, and (**d**) peak intensities of PZT *004* and PZT *400* as a function of time during the application of a 200 ns pulsed electric field with a magnitude of 170 kV/cm.

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**References**

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