

Investigation of crystallographic deformation by converse piezoelectric effect of piezoelectric thin films

Piezoelectric materials, such as lead zirconate titanate Pb(Zr,Ti)O₃ (PZT), can convert mechanical energy to electrical energy, and vice versa, through direct and converse piezoelectric effects. For PZT, it is known that the morphotropic phase boundary (MPB) composition, which is the interface between the tetragonal (P4mm) and rhombohedral (R3m)phases, provides superior dielectric and piezoelectric properties [1]. PZT thin films have been widely developed for use in microelectromechanical systems (MEMS) such as sensors, actuators, and energy harvesters [2]. The piezoelectric properties of PZT thin films are different from those of their bulk ceramic counterparts because they are affected by many factors, including crystal quality, crystal orientation, and internal stresses from substrates [3]. Therefore, investigation of the fundamental properties of piezoelectric thin films is of great significance to improve MEMS devices.

Continuous efforts have been made to evaluate the origin of piezoelectric effects by in situ characterization methods. Recently, we have developed a simple and precise method to measure the effective piezoelectric coefficients $(e_{31,f})$ of PZT thin films using unimorph cantilevers [4]. Their piezoelectric properties are considered to arise from intrinsic and extrinsic contributions. Intrinsic contributions are associated with crystal lattice deformation (such as elongation and shrinkage), whereas extrinsic contributions originate from collective lattice distortions caused by domain rotations or phase transitions. Our previous study demonstrated that the piezoelectric properties of polycrystalline PZT thin films are better than those of epitaxial PZT thin films, probably because of the large extrinsic contributions to such films.

In this study, we investigated the crystallographic

deformation of PZT thin films by *in situ* X-ray diffraction (XRD) measurements using synchrotron radiation to clarify the crystallographic factors contributing to their piezoelectric properties. We evaluated both epitaxial and polycrystalline PZT thin films with MPB compositions. Our study demonstrated the change in the crystal structure under applied direct current (DC) voltage, which is consistent with the polarization-electric field (*P-E*) hysteresis loop [5].

We prepared epitaxial PZT thin films on (001) Pt/MgO substrates and polycrystalline PZT thin films on (111)Pt/Ti/SiO₂/Si substrates. Both films were approximately 3 µm thick and were fabricated by rf-magnetron sputtering. The Zr/Ti ratio was approximately 52/48, which is same as to the MPB composition. In situ XRD measurements were carried out using synchrotron radiation ($\lambda = 0.1$ nm) at SPring-8 BL19B2 and BL46XU. Figure 1 shows a schematic illustration of the experimental setup for in situ XRD measurements in the surface normal (outof-plane) direction and the vertical (in-plane) direction. Here, specimens were not subjected to electrical poling treatments before measurement. Figure 2(a) shows the PZT 004 peak at various DC voltages and the variation in the *c*-axis lattice parameter determined from the observed peak positions. The diffraction peaks shifted toward lower angles with increasing negative voltage and vice versa. The relative changes in the *c*-axis lattice parameter as a function of electric field represent the reversible elongation and contraction of the crystal structure along the electric field bias magnitude and direction. We also ascertained the reversible in-plane peak shifts in Fig. 2(a). The reversible contraction and elongation behavior of the *a*-axis lattice parameter was confirmed, as shown in Fig. 2(b). The electric field dependence





at various DC voltages and a-axis lattice parameters as functions of electric field.

of the in-plane lattice parameter indicates behavior opposite to that of the out-of-plane case. This result is consistent with the observation that when the outof-plane crystal lattice is stretched along the forward electric field, the in-plane crystal lattice shrinks and vice versa.

We then investigated the polycrystalline PZT thin film on a Si substrate. Figure 3(a) shows a synchrotron XRD θ -2 θ pattern around the PZT 004 peak at various applied DC voltages. The polycrystalline PZT 004 peak is much broader than the epitaxial PZT peak (Fig. 2(a)). This broad peak is successfully decomposed into a rhombohedral 004 and tetragonal 400 and 004 peaks, as shown in the right graph of Fig. 3(a), indicating a slight amount of the tetragonal phase coexists. Figure 3(a) shows a clear shift in the diffraction peak for both positive and negative biases, and the peaks are shifted toward higher angles only when a voltage of +5 V is applied. Figure 3(b) shows the field-induced

variation of the *c*-axis lattice parameter superimposed with the P-E hysteresis loop measured at 1 kHz. The *c*-axis lattice parameter exhibits a butterfly curve that arises from the inverse polarization effect. This behavior is consistent with the coercive electric field determined from the P-E hysteresis loops. Note that the coercive electric field of the polycrystalline PZT thin film is much smaller than that of the epitaxial PZT thin film. It was also confirmed that the field-induced strain of the polycrystalline PZT thin film was much larger than that of the epitaxial PZT thin film. This was probably due to the large extrinsic effects such as a crystalline phase transition and domain reorientation. These large extrinsic effects are considered to enhance the macroscopic piezoelectric properties. Our direct observation of crystallographic deformation paves the way to improving the piezoelectric properties of piezoelectric thin films for the application of novel piezoelectric MEMS devices.





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