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# Direct observation of 90° domain switching in lead zirconate titanate thick films using x-ray diffraction

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Using an x-ray diffraction with reciprocal space mapping, 90° domain switching in tetragonal lead zirconate titanate (PZT) thick films under an applied field was studied. An increase in the $c$-axis lattice constant and a decrease in the $a$-axis lattice constant due to the piezoelectric effect and switching from $a$ domain to $c$ domain (90° domain switching) were observed under an applied field. The contribution from 90° domain switching to the total strain was estimated to be 60%–100%, which is almost the same as that for bulk PZT. High value is consistent with the intrinsic nonlinearity in a tetragonal film. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2752104]

Ferroelectric films are widely studied because of their high potential applicability in piezoelectric actuators, micromirrors, optical waveguides, ferroelectric random access memories, infrared sensors, and resonators.[1] Lead zirconate titanate (PZT) is the leading ferroelectric material due to its high Curie temperature and high piezoelectric constant of $d_{33}=223$ pm/V at the morphotropic phase boundary for the bulk PZT. However, thin films with a thickness of several hundred nanometers often exhibit low $d_{33}=50$ pm/V.[2,3] Therefore, there is an increased interest in thick films of thickness in microns that have a $d_{33}$ value comparable with bulk PZT.[4] There is a high demand for thick films for applications and the study of piezoelectric properties is a requirement for thick films.

Piezoelectric properties comprise the intrinsic effect of piezoelectricity and the extrinsic effect of 90° domain switching in tetragonal films. The 90° and 180° domain switchings have been indirectly observed with the temperature dependence of the dielectric constant and $d_{33}$ values for the bulk PZT.[5] By applying a voltage, 90° domain switching and piezoelectricity can be directly observed in (002)/(200) of the x-ray diffraction (XRD) spectrum. There is no (111) domain in tetragonal films. Polycrystalline materials form a Debye-Scherrer ring. Conventional $\theta$-$2\theta$ scans measure a part of the ring. A reciprocal space mapping is required in order to estimate the volume ratio of $c$ domain. The XRD spectrum of the tetragonal bulk PZT obtained using a conventional $\theta$-$2\theta$ scan under an applied field exhibited an increase in the $c$-axis lattice constant, i.e., piezoelectric effect and the switching from $a$ domain to $c$ domain, i.e., 90° domain switching.[6–8] An XRD spectrum of tetragonal PZT epitaxial films obtained from synchrotron emissions with a reciprocal space mapping under an applied field exhibited changes in the lattice constant of $c$ axis and the $c$-domain volume ratio.[9] The XRD spectrum of PZT thin films with conventional $\theta$-$2\theta$ scan taken before and after the applied field exhibited a switching from $a$ domain to $c$ domain.[10] However, direct observations of 90° domain switching and piezoelectricity with reciprocal space mapping have not been done for PZT thick films. A normal x-ray source requires a long time to perform reciprocal space mapping, and a good thick film has not been made in order to withstand the voltage for a long time duration. Synchrotron emissions require a short time duration to perform reciprocal space mapping; however, XRD with synchrotron emissions has not been studied for thick films.

In this study, dense and crack-free 5 $\mu$m thick PZT films have been successfully prepared, and the XRD spectrum obtained from a normal x-ray source with reciprocal space mapping under the applied field was measured.

PZT thick films were deposited onto a 2 in. Pt(111)/Ti/$SiO_2$/Si substrate using a chemical solution deposition process. Lead acetate trihydrate (99.9%, Nakarai Tesque), titanium isopropoxide (97%, Kanto Chemical), zirconium $n$-propoxide (70% in propanol, Azmax), and 2-methoxyethanol (99.7%, Aldrich) were used as the starting materials. The nominal composition of the precursor solution is $Pb(Zr_{0.3}Ti_{0.7})O_3$. The details of the preparation process of PZT films have been previously described elsewhere.[11] A 9 mm square Pt top electrode was sputter deposited onto the PZT thick film through a metal mask. In order to measure the reciprocal space mapping, D8Discover Hybrid (Bruker AXS, Germany) was used. The measurement condition was set as $2\theta=34°-48°$ for (200) and (002). The full width at half maximum of $\psi$ was 12° for a defined value of $\theta$ and the measurement condition was set as $\psi=\pm 6°$ for each value of $\theta$. The time duration for each measurement was 5 min. The integrated XRD spectrum with $\psi$ was used for this experiment. The state at which the voltage has not been applied is referred to as the initial state. At first, the XRD spectrum is measured at the initial state. Next, a dc electric field of 40 kV/cm was applied for 2 min to ensure sufficient time for domain switching to occur,[12] followed by an XRD measurement under 40 kV/cm. Further, the applied voltage was decreased to 0 kV/cm, and the XRD spectrum under 0 kV/cm was measured. This sequence was repeated, wherein the applied dc field was increased in a step of 40 up to 160 kV/cm, for example, a sequence of 0, 40, 0, 80, 0, 120, 0, 160, and 0 kV/cm. In this study, the coercive field $E_c$ of the film was

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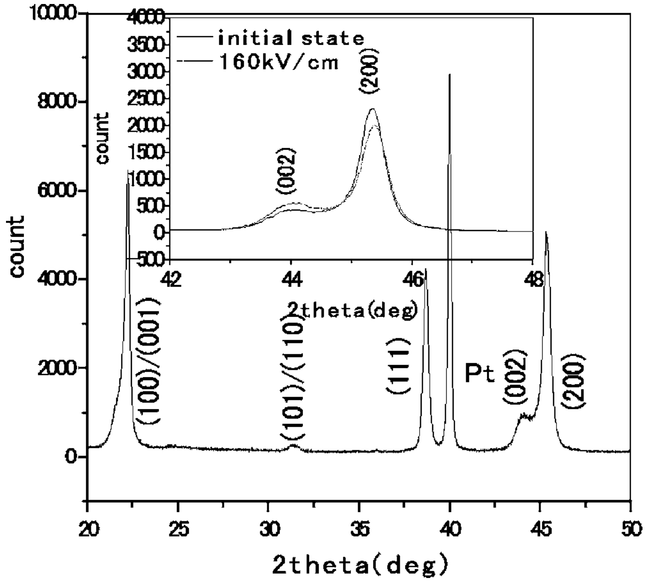


FIG. 1. XRD spectrum from 20° to 50° taken by conventional $\theta$-$2\theta$ scans (outer figure) and integrated XRD for (200) and (002) with $\psi$ taken by reciprocal space mapping (inner figure).

$67.5 \pm 1.2$ kV/cm. Errors are introduced by different electrodes of the same film.

The XRD spectrum obtained by the conventional $\theta$-$2\theta$ scans from 20° to 50° is shown in Fig. 1. The PZT thick film is entirely randomly oriented. The integrated XRD spectrum with $\psi$ obtained by reciprocal space mapping for (200) and (002) is also shown in Fig. 1. The peaks for (200) and (002) can be distinguished. A decrease in the peak intensity of (200) and an increase in the peak intensity of (002) under an applied voltage are observed in Fig. 1. This demonstrates 90° domain switching from *a* domain to *c* domain. The shift in the (200) peak to a higher diffraction angle on application of a voltage can also be observed in Fig. 1. A decrease in the lattice constant of *a* axis can be attributed to the piezoelectric effect.

Cu $K\alpha_1$ and $K\alpha_2$ were used as x-ray source in the detector. For each of the peaks of both (200) and (002), two functions were used as $K\alpha_1$ and $K\alpha_2$. These functions were connected with intensity and diffraction angle. Peaks of (200) and (002) were simultaneously fitted with four functions. When an XRD spectrum of the initial state was fitted with a Gaussian function, $X^2$/degree of freedom (DOF) was 3.61. When this spectrum was fitted with a PsdVoigt2 function, which is defined in the analysis tool origin, $X^2$/DOF was 1.27. When the spectrum was fitted with a PsdVoigt1 function, $X^2$/DOF improved as 1.15. Therefore, a PsdVoigt1 function was used.

The intensity of the peak exhibits a multiplicity of four for *a* axis and two for *c* axis. Considering this, the volumes of the *a* domain $V_a$ and *c* domain $V_c$, which removed the multiplicity were calculated. The *c*-domain volume ratio $V_c/(V_a+V_c)$ is given by $2I_c/(I_a+2I_c)$;. Here, $I_a$ and $I_c$ are the peak intensities for *a* axis and *c* axis, respectively. The *c*-domain volume ratio is shown in Fig. 2. The error is a 68% confidence level statistical error from the model fit. The *c*-domain volume ratio at the initial state was $36.3\% \pm 0.4\%$. When an electric field of 120 kV/cm was applied, the *c*-domain volume ratio increased up to $42.7\% \pm 0.4\%$ due to the switching from *a* domain to *c* domain. When the applied

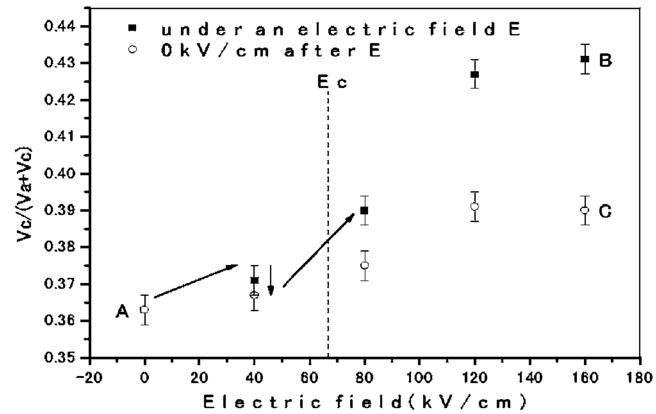


FIG. 2. *c*-domain volume ratio with the electric field *E*.

voltage was removed, the switched *c* domain did not return to the initial state and the *c*-domain volume ratio became $39.1\% \pm 0.4\%$. When the applied field was less than the coercive field, $E_c = 67.5$ kV/cm, there was no significant increase in the *c*-domain volume ratio, as shown in Fig. 2. This result is consistent with the domain switching theory. The changes in the lattice constants for *a* axis and *c* axis were calculated from the peak shifts of (200) and (002), as shown in Fig. 3. A 68% confidence level statistical error is observed in the model fit. When an electric field was applied, the lattice constant of *a* axis decreased and that of *c* axis increased.

There are two types of strains: one from 90° domain switching and the other from piezoelectricity. Here, the strain from 90° domain switching is calculated with a *c*-domain volume ratio deduced from (200)/(002). The (111) does not contribute to a strain by 90° domain switching because 90° domain wall has the same projection along the applied field.[1] The schematic view of the strain from 90° domain switching is shown in Fig. 4. The initial state, the state under an electric field, and the state in which the electric field is removed are denoted by *A*, *B*, and *C*, respectively. These symbols correspond to those shown in Fig. 2. At first, when an electric field was applied to the initial state ($A \rightarrow B$), a strain from the initial state $S(B-A)$ was calculated. Next, when the electric field was removed ($B \rightarrow C$), a strain from the initial state $S(C-A)$ was calculated. The subtraction of these two strains $S(B-A)-S(C-A)$ was obtained as the strain at which the on-off cycle of the electric field was repeated ($B \leftrightarrow C$). We have used the idea of the average length of the lattice in the

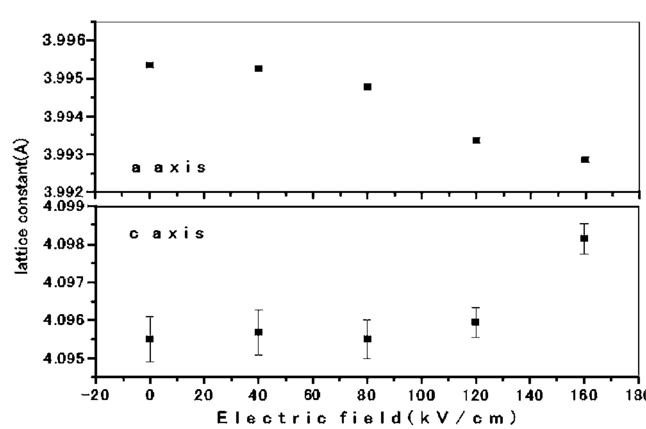


FIG. 3. Lattice constants of *a* axis and *c* axis with electric field. The lattice constant of *a* axis is 3.96 A and that of *c* axis is 4.13 A for the bulk PZT.

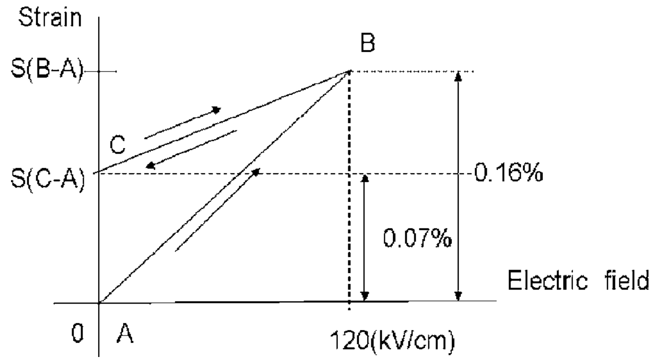


FIG. 4. Schematic view of relationship between a strain from 90° domain switching and the electric field. The initial state, the state under an electric field, and the state in which the electric field is removed are denoted by *A*, *B*, and *C*, respectively.

direction of the thickness of the film.[7] We suggest that *a* domain and *c* domain are superimposed in the direction of the thickness of the film as bulk PZT. The average length of the lattice at the initial state $L(A)$ is $(1-V(A))a(A)+V(A)c(A)$. Here, $a(A)$ and $c(A)$ are the lattice constants of *a* axis and *c* axis at the initial state, respectively, and $V(A)$ is the *c*-domain volume ratio at the initial state. When an electric field is applied, the change in the average length of lattice from the initial state is given as follows: $\Delta L(B-A)$ is $(V(B)-V(A))(c(A)-a(A))$, where $V(B)$ is the *c*-domain volume ratio under an electric field $E$. $S(B-A)=\Delta L(B-A)/L(A)$. When the electric field is removed, the change in the average lattice constant from the initial state is given as follows: $\Delta L(C-A)$ is $(V(C)-V(A))(c(A)-a(A))$, where $V(C)$ is the *c*-domain volume ratio after the removal of the electric field $E$. $S(C-A)=\Delta L(C-A)/L(A)$. The strains $S(B-A)$, $S(C-A)$, and $S(B-A)-S(C-A)$ are $0.16\% \pm 0.02\%$, $0.07\% \pm 0.02\%$, and $0.09\% \pm 0.04\%$, respectively, for a dc electric field of 120 kV/cm. The strain from the piezoelectric effect could not be calculated accurately. The lattice constants of *a* axis and *c* axis were expected to return to the initial state upon the removal of the electric field. However, it did not and this requires further study. The total strain was measured by an atomic force microscope (AFM) or laser displacement, and the total strain versus the calculated strain from 90° domain switching were compared. When a dc electric field of 120 kV/cm was applied to a 5 $\mu$m thick $Pb(Zr_{0.3}Ti_{0.7})O_3$, a strain of $0.15\% \pm 0.00\%$ was measured using laser displacement for the film with an electrode with dimensions of $9\times 9$ $mm^2$ and a strain of $0.08\% \pm 0.00\%$ was measured by the AFM for a film with an electrode of 20 $\mu$m diameter. Poling was performed for 2 min before the measurement. Errors are introduced by different electrodes of the same film. The contributions of domain switching to the total strain were estimated to be 60% and 100%. The correspondence value for $Pb(Zr_{0.52}Ti_{0.48})O_3$ bulk was 68% from an indirect observation of the 90° domain switching at room temperature.[5] The high value obtained for the thick film is almost the same as that for bulk PZT. In addition, this high value for thick film is consistent with the suppression of piezoelectricity by intrinsic nonlinearity in tetragonal films.[1]


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