Domain Switching and Piezoresponse Properties of PZT Thin Films

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Abstract

$Pb(Zr_{0.53}Ti_{0.43})O_3$ (PZT) thin films with various preferred crystallographic orientations were deposited on various substrates using pulsed laser deposition techniques. The piezoelectric displacement that involved the bending vibration of the PZT thin film on substrate was observed in randomly oriented PZT thin film, and the piezoelectric displacement of randomly oriented PZT thin film is larger than those of (100) and (111) preferred texture films. This result was discussed by correlation with the number of effective spontaneous polarization axes in the morphotropic phase boundary of the PZT system. Moreover, polarization fatigue was found to lower the electric-field-induced displacement significantly, indicating large contribution of ferroelectric domain motion to the piezoelectric response of PZT thin films under bipolar drive.

Key words: PZT thin film, MPB, polarization fatigue, piezoelectric response, domain motion

1. INTRODUCTION

LEAD ZIRCONATE TITANATE ($Pb(Zr_{1-x}Ti_x)O_3$; PZT) thin films with large piezoelectric displacement at lower applied voltage are desirable for micro electromechanical systems (MEMS).[3-5] It has been reported that the dielectric and electromechanical response of PZT is maximum for compositions corresponding to a morphotropic phase boundary (MPB) around $x=0.47$, which separates a tetragonal titanium rich crystallographic phase from a rhombohedral zirconium rich phase.[6,7]

In this study, PZT thin films with compositions corresponding to the MPB were prepared using a pulsed laser deposition (PLD) technique onto various bottom electrode/seed layers for control of the crystal orientation of PZT. We measured the electric-field-induced displacement of the thin films using various crystal orientations in the MPB region to investigate the dependence of the film texture and domain motion on the piezoelectric properties.

2. EXPERIMENTAL

Standard ceramic processing methods were used to prepare PZT bulk targets for the PLD source, including mixing of PbO, ZrO_2, and TiO_2 fine grained reagent powders, uni-axial compaction, and sintering to near theoretical density by heating up to 1,200°C. The composition of the PZT bulk target was adjusted to have 18% excess PbO and 7% excess ZrO_2 to the MPB composition. It was an optimum target composition for preparing a PZT thin film with a composition corresponding to the MPB onto a substrate. The PZT bulk target was positioned at 46 mm away from substrate in the PLD process.[8,9] The light source of the PLD was an yttrium aluminum garnet (YAG) laser beam with a wavelength of 266 nm (the fourth harmonic generation, FHG). The fluence of the incident laser beam, repetition rate and substrate temperature were 1.5 J/cm², 10 Hz and 700°C, respectively. The PLD was conducted under an oxygen partial pressure ambient of 5 Pa. The PZT thin films were deposited on substrates with size of 10 mm × 10 mm.

The substrates used for PZT film deposition were (1) a Pt(200 nm)/Ti/SiO_2/Si substrate, (2) a Pt/Ti/SiO_2/Si substrate coated with a 200 nm thick sol-gel derived PZT seed layer using the same commercial source and procedure as reported by Maki et al.,[10] (3) a SiO_2/Si substrate coated with a 200 nm thick $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) bottom electrode layer fabricated using the PLD technique, and (4) a conducting Nb (0.05 wt%) doped $SrTiO_3$ (Nb : STO) single crystal (111) substrate. The thickness of the PZT thin films deposited on these substrates was 1 μm except for the case of substrate (2) ; i.e., an 800 nm thick PZT thin film was deposited using the PLD technique on the 200 nm thick sol-gel derived PZT seed layer. For electrical measurement, top electrodes were fabricated using multi-spot deposition of a 200 nm thick Pt, IrO_2 and $SrRuO_3$ (SRO) films (200 μm in diameter) using radio frequency (RF) magnetron sputtering for Pt and PLD for IrO_2 and SRO.

The electric field (E) was applied for the film thickness between the top and bottom electrodes. The polarization (P) versus E ($P-E$) hysteresis curves and fatigue properties were examined by a ferroelectric testing system (Radiant Technologies) using pulse wave in 8 V at 500 kHz. The electric field induced displacement at the center of the top electrode was measured using a laser Doppler displacement measuring system (Model AT7211, Graphtec Co., Japan) under unipolar and bipolar alternating current (ac) electrical fields at 1 kHz. The basic principle of this method is described elsewhere.[11,12]

3. RESULTS AND DISCUSSION

Figure 1 shows the P fatigue performance of Pt/PZT/Pt/TiO_x/SiO_2/Si, IrO_2/PZT/Pt/TiO_x/SiO_2/Si and SRO/PZT/Pt/TiO_x/SiO_2/Si thin film capacitors, at switching cycles of ±8 V (at 500 kHz).

As shown in the figure, the remnant polarization (P_r) value of the PZT thin film of Pt/PZT/Pt/TiO_x/SiO_2/Si thin film capacitor decreases to 50% of initial value at 10^8 switching cycles,
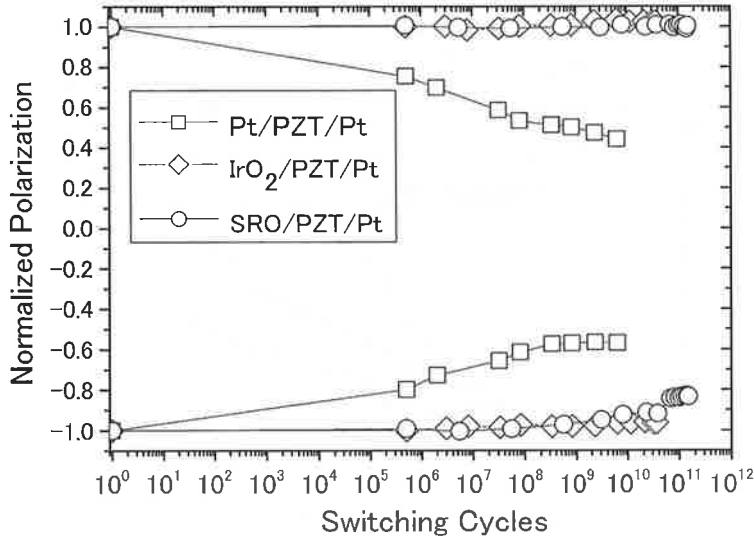
Fig. 1   The polarization fatigue performance of Pt/PZT/Pt/TiO$_x$/SiO$_2$/Si, IrO$_2$/PZT/Pt/TiO$_x$/
SiO$_2$/Si and SRO/PZT/Pt/TiO$_x$/SiO$_2$/Si thin film capacitors at the bipolar voltage switch-
ing cycles of ±8 V (at 500 kHz).

while P_r value of PZT thin films of SRO/PZT/Pt/TiO$_x$/SiO$_2$/Si and IrO$_2$/PZT/Pt/TiO$_x$/SiO$_2$/
Si thin film capacitors remained constant at more than 10^{11} switching cycles.   The Degradation
of the PZT thin film is not observed while using the SRO and IrO$_2$ thin film electrodes as buffer
layers.

The loss of switching P with repeated P reversal is due to pinning of the domain wall,
which inhibits switching of the domain affected by induced internal space charge at domain
boundaries.   However, a variety of mechanisms for domain wall pinning have been proposed,
including pinning due to electron charges trapped by oxygen vacancies.

From these results, it is confirmed that the polarization ferroelectric fatigue property of the
PZT thin film is improved by using the SRO and IrO$_2$ thin film electrodes as buffer layers.

Figure 2 shows the electric field induced displacement of the PZT thin films.

Displacement has been calculated using the top amplitude of the time dependent output
wave recorded at an elevated applied voltage under bipolar drive up to 20 V_{p-p}.   Although the
output wave under the unipolar drive is observed in a frequency that is same as that of the input
sine wave, the doubling of the frequency appears under the bipolar drive.   The output signal
is caused from the bending vibration of the PZT film on substrate, i.e., the PZT film expands
or shrinks in the horizontal direction, which leads to the deflection of the film on substrate
structure in the vertical direction.   The vibration response measured from one side of the
sample using a single beam interferometer is known to include a large contribution of the
bending motion of the substrate.[11]   Therefore, the center position on each wafer is always
utilized to compare the film displacement among various samples to eliminate the bending
effect of the substrates distributing across the entire wafer.   However, the PZT thin film
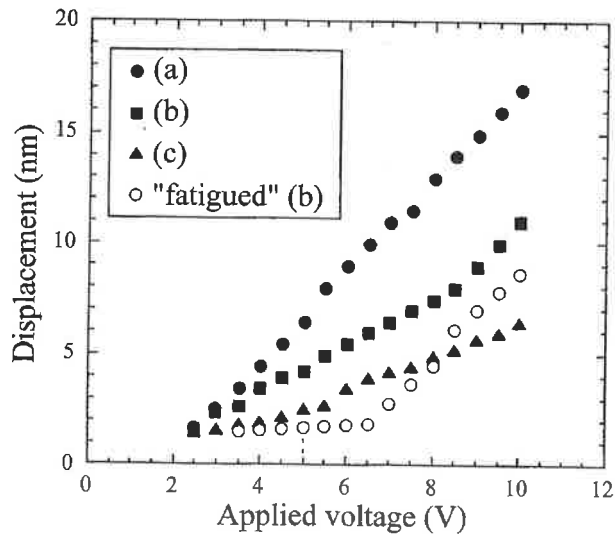
Fig. 2　Piezoelectric displacement of PZT thin films under bipolar drive up to 20 V_{p-p} (positive drive voltage of about 10 V) at 1 kHz : (a) random orientated sample, (b) (111) preferred orientated sample, and (c) (100) preferred orientated sample. Open circles are obtained from (b) (111) preferred orientated sample after polarization fatigue testing up to 10^8 periodic switching by application of the drive amplitude with ± 5 V.

deposited on the Nb : STO substrate displays a weak output signal similar to frequency noises in the entire region of the applied voltage, because the thickness of the Nb : STO serving as both bottom electrode and substrate is 500 μm, which was 2.5 times thicker than the 200 μm thickness of the other silicon-based substrates coated with the seed/bottom-electrode layers. The other samples have the same shape and dimensions in film/substrate. The bipolar drive voltage of 20 V_{p-p} ($-10/+10$ V) for 1 μm film thickness corresponds to the electric bias field of about $3E_c$. Experiments throughout this work did not use a poling procedure prior to piezoelectric measurement; therefore, the films were run through the butterfly strain curve caused by polarization reversal during the bipolar drive. Specifically, PZT thin films have critical problems, such as P "fatigue" with periodic pulses, i.e., the decrease in the P value with periodic pulses. The fatigue has been frequently reported in PZT thin films deposited on platinum electrodes. Also in piezoelectric measurement with periodic pulses, the degradation of the transverse piezoelectric coefficient of PZT thin films deposited on Pt/Ti/SiO$_2$/Si substrates has been reported, which is correlated with the magnitude of applied bipolar electric fields.[13] Although the P fatigue mechanism has not been clarified, the main source is thought to be the pinning of domain walls by the charged ionic defects accumulated at grain boundaries, domain boundaries and film/electrode interfaces. Oxygen vacancies that are mobile in PZT are considered to be the most probable charged ionic defects.[14] In this study, the PZT thin film deposited on the Pt/Ti/SiO$_2$/Si substrate lost about 25% of the initial polarization after 10^8 periodic switching by application of the bipolar drive amplitude with ± 5 V.

The electric-field-induced displacement is also compared in Fig. 2, which was measured

before and after the fatigue testing of PZT film deposited on the $Pt/Ti/SiO_2/Si$ substrate. For the fatigued sample, a plot of displacement versus applied voltage gives distinct relationships separated at about 6.5 V. This measurement clearly shows that the piezoelectric response is considerably restricted up to about 6.5 V beyond the positive amplitude with 5V in the fatigue test. Subsequently, the domain motion is "waked-up" by a sufficient applied charge that is capable of large piezoelectric response.

As shown in Fig. 2, a larger displacement is observed for the films with the various crystal orientations in the order of random > (111) > (100) preferred orientations.[2]

Taylor et al.[15] have reported that larger piezoelectric displacement is observed for Zr rich rhombohedral $Pb(Zr_{0.6}Ti_{0.4})O_3$ thin films in the order of (100) > random > (111) preferred orientations. In the present work, the (100) oriented PZT thin film deposited on the LSCO/SiO_2/Si substrate with columnar grains and a longitudinal axis orientation is perpendicular to the electric field applied between the upper and bottom electrodes. Therefore, these specific axis relationships rather than the preferred crystallographic orientation seem to have significantly affected the piezoelectric response of the PZT film deposited on the LSCO/SiO_2/Si substrate. For the film composition near the MPB, the largest piezoelectric displacement is observed in the randomly oriented film. This can be explained from the multiple polarization directions caused by the coexistence of rhombohedral and tetragonal phases. The reason for the maximum dielectric and electromechanical response at the MPB composition remains unsettled, even now,[16] but one of the possible explanations is that the rhombohedral and tetragonal crystallographic domains coexist in PZT around the MPB composition, which results in an increase of the number of the effective polarization axes compared with the case of single phase. Resonance frequency analysis and neutron diffraction studies have confirmed that the rhombohedral and tetragonal phases coexist near the MPB.[17,18] The present experimental results certainly have demonstrated that the larger piezoelectric displacement is
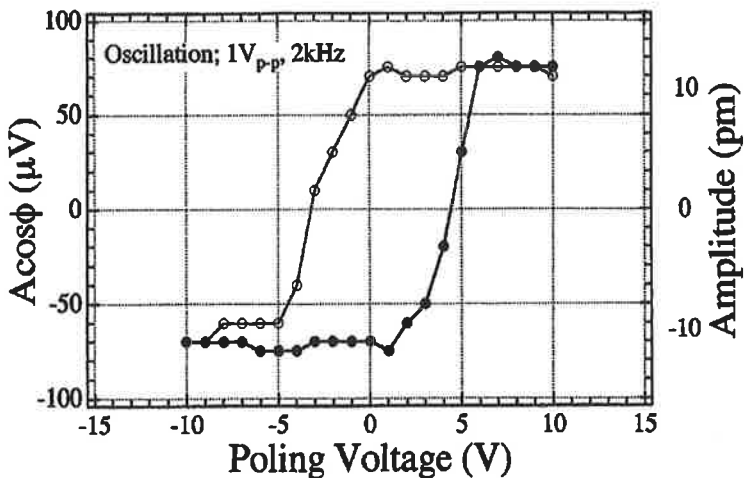

Fig. 3　Bias dependence of $A\cos\phi$ and displacement amplitude measured for the PZT flim.

observed in the randomly oriented PZT thin film than in other preferred texture films.

Figure 3 shows the poling voltage dependence of $A\cos\phi$ and electrostriction displacement measured in the PZT film.[1] The curve is similar to the shape of P-E hysteresis loop. From this measurement data, piezoelectric modulus (M_{31}) is estimated to be about $3.1 \times 10^{-21} \mathrm{m^2/V^2}$. This value is of the same order as that of PZT ceramics.

4. CONCLUSION

The preferred crystallographic orientation of pulsed laser deposition deriving $Pb(Zr_{1-x}Ti_x)O_3$ thin films near the morphotropic phase boundary were found to be depended strongly on the selection of silicon-based substrates coated with seed/bottom electrode layers.

The $Pb(Zr_{1-x}Ti_x)O_3$ thin films deposited on the $Pt/Ti/SiO_2/Si$, $Pb(Zr_{1-x}Ti_x)O_3$(sol-gel)/Pt/Ti/SiO_2/Si, $LSCO/SiO_2/Si$ and Nb doped $SrTiO_3$ substrates showed (111), randomly, (100), and (111) preferred crystallographic orientations.

The largest electric-field-induced piezoelectric displacement was found in the randomly oriented thin film. This seemed to be correlated with some of the effective spontaneous polarization axes attributed to the film composition near the morphotropic phase boundary.

Acknowledgements

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