PULSE POLING WITHIN 1 SECOND ENHANCE THE PIEZOELECTRIC PROPERTY OF PZT THIN FILMS

T. Kobayashi[1], Y. Suzuki[1,2], N. Makimoto[1], H. Funakubo[3], and R. Maeda[1]
[1]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan,
[2]Ibaraki University, Hitachi, Japan, [3]Tokyo Institute of Technology, Yokohama, Japan

ABSTRACT

We have succeeded in enhancing the piezoelectric property of lead zirconate titanate (PZT) thin films by employing "pulse poling" technique. We have fabricated MEMS-based microcantilevers using $Pb(Zr_{0.52},Ti_{0.48})O_3$ (MPB-PZT) thin films. By applying 1 kHz and 100 V of unipolar triangle pulse voltage, the transverse piezoelectric constant $-d_{31}$ of the PZT thin film has been enhanced as high as 105 pm/V, which is larger than the dc-poled PZT thin films (78 pm/V). The $-d_{31}$ of pulse-poled the PZT thin films measured under the unipolar actuation at 0-12 V reaches 158 pm/V. The results indicate that only 1 second of pulse poling gives better piezoelectric property of the PZT thin films compared to several minutes of dc poling.

INTRODUCTION

Morphotropic phase boundary composition lead zirconate titanate ($Pb(Zr_{0.52},Ti_{0.48})O_3$, MPB-PZT) thin films are used as actuators for inkjet heads [1], optical microscanners [2], RF-switches [3], electric field sensors [4] and so on. PZT thin films usually need several minutes of dc voltage (10-20 V/µm) application for activation, which can be called as dc poling. However, such a several minutes of dc poling reduce the throughput of device fabrication. One of the promising solution for reducing the poling time is "pulse poling", where pulse voltage with higher electric field than dc voltage is applied. Recently, we have demonstrate that the pulse poling enhance the piezoelectric property of tetragonal composition $Pb(Zr_{0.3},Ti_{0.7})O_3$ thin films [5,6]. Then, in the present study, we have employed the pulse poling to MPB-PZT thin films.

MICROCANTILEVER FABRICATION

We have prepared 1.9-µm-thick MPB-PZT thin films with (001)/(100) orientation by sol-gel deposition [7]. Commercially available PZT solution (PZT-20,Kojundo Chemical Co., Saitama, Japan) with a Pb/Ti/Zr molar ratio of 120/52/48 was deposited by spin coating. Then, the as-deposited films were heated at 250°C for 5 min. on a hot plate and crystallized by rapid thermal annealing (RTA) at 650°C for 2min. The ramping rate for RTA is 100°C /sec.

We have fabricated piezoelectric microcantilevers using MPB-PZT thin films through MEMS microfabrication process, which is just the same as that reported in our previous study [5]. Figure 1 shows the MEMS microfabrication process. The process began from $Pt/Ti/PZT/Pt/Ti/SiO_2$ multilayer deposition on silicon-on-insulator (SOI) wafers with a 10-µm-thick structural Si layer. The SOI wafers, at first, were oxidized at 1100°C. After the oxidation, Pt (0.1 µm)/Ti (0.05 µm) thin films as a bottom electrode were deposited by DC magnetron sputtering. Then, 1.9-µm-thick MPB-PZT thin films were formed by sol-gel deposition as described above. Finally, Pt (0.15 µm)/Ti (0.05 µm) thin films were deposited by DC magnetron sputtering.

The obtained multilayers were etched by dry and wet etching to form microcantilevers. Through mask 1, Pt/Ti thin films as a top electrode were etched using Ar ions to determine the top electrodes. Through mask 2, PZT thin films were wet-etched using a mixture of HF, HNO_3 and HCl. Through mask 3, Pt/Ti thin films as a bottom electrode were etched using Ar ions and thermal SiO_2 thin films were etched by reactive ion etching (RIE) with CHF_3 gas to pattern bottom electrodes. Through mask 4, structural Si and buried oxide (BOX) layers were etched by RIE with SF_6 (for Si) and CHF_3 (for BOX) gases. Finally, Si substrates and BOX were etched from their back surface to form the piezoelectric microcantilevers. The fabricated microcantilevers are 1.1 mm long, 300 µm wide and 10 µm thick, respectively. Figure 2 shows the 4 inch wafer after whole microfabrication process.

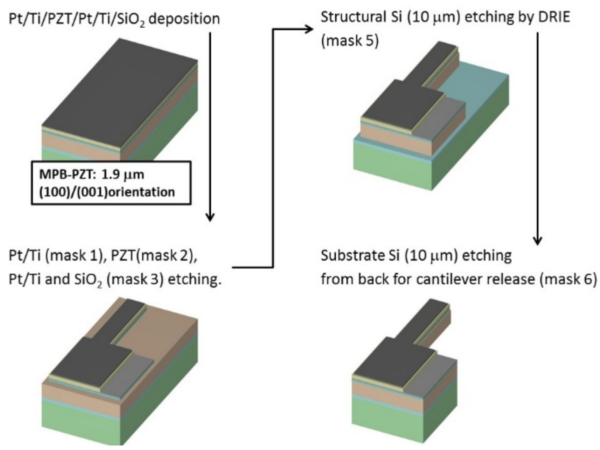

Figure 1: MEMS microfabrication process for piezoelectric microcantilevers.

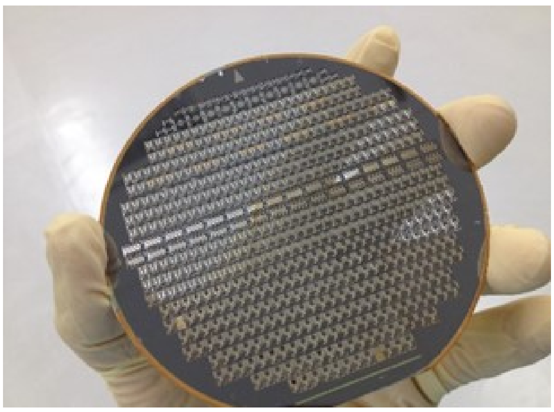

Figure 2: Photograph of 4 inch wafer after whole MEMS microfabrication process.

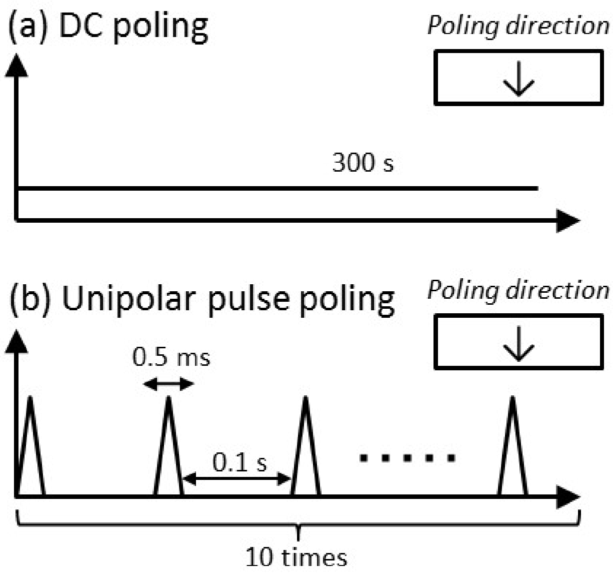

Figure 3: Waveforms of voltage for (a) dc poling and (b) unipolar pulse poling. The poling direction was downward for both cases.

The MPB-PZT thin films on the fabricated microcantilevers were poled by applying dc and unipolar triangle pulse voltage as shown in figures 3(a,b). The top and bottom electrodes were connected to signal and ground lines, respectively. The dc voltage was 20 V, which means that the poling direction is downward. For pulse poling, positive intermittent triangle waves of 40-100 V and 1 kHz were applied 10 times. The poling direction is also downward.

RESULTS

The MPB-PZT thin films on the fabricated microcantilevers were poled by applying dc and unipolar triangle pulse voltage as shown in figures 2(a,b). The top and bottom electrodes were connected to signal and ground lines, respectively. The dc voltage was 20 V, which means that the poling direction is downward. For pulse poling, positive intermittent triangle waves of 40-100 V and 1 kHz were applied 10 times. The poling direction is also downward. In order to estimate the transverse piezoelectric constant d_{31}, the tip displacement of the microcantilevers was measured. We have estimated the piezoelectric constant d_{31} using the following equations [8],

$$\delta = \frac{3AB}{K} d_{31} L^2 V \quad (1),$$

$$A = s_{11}^{\mathrm{Si}} s_{11}^{\mathrm{PZT}} \left(s_{11}^{\mathrm{Si}} t_{\mathrm{PZT}} + s_{11}^{\mathrm{PZT}} t_{\mathrm{Si}} \right) \quad (2),$$

$$B = t_{\mathrm{Si}} (t_{\mathrm{Si}} + t_{\mathrm{PZT}}) / \left(s_{11}^{\mathrm{Si}} t_{\mathrm{PZT}} + s_{11}^{\mathrm{PZT}} t_{\mathrm{Si}} \right) \quad (3),$$

$$K = \left(s_{11}^{\mathrm{Si}} \right)^2 t_{\mathrm{PZT}}{}^4 + 4 s_{11}^{\mathrm{Si}} s_{11}^{\mathrm{PZT}} t_{\mathrm{Si}} t_{\mathrm{PZT}}{}^3 + 6 s_{11}^{\mathrm{Si}} s_{11}^{\mathrm{PZT}} t_{\mathrm{Si}}{}^2 t_{\mathrm{PZT}}{}^2 + 4 s_{11}^{\mathrm{Si}} s_{11}^{\mathrm{PZT}} t_{\mathrm{Si}}{}^3 t_{\mathrm{PZT}} + \left(s_{11}^{\mathrm{PZT}} \right)^2 t_{\mathrm{Si}}{}^4 \quad (4),$$

where s_{11}, t, and L are compliance of Si (5.9 x 10^{-12} GPa^{-1}) and PZT (1.4 x 10^{-11} GPa^{-1}), thickness of Si (10 µm) and PZT (1.9 µm), length of the microcantilevers (1.1 mm), respectively. V is applied voltage to actuate the microcantilevers. In the present study, V was 1-3 V_{pp} for small displacement measurement under bipolar actuation and 0 to 2-12 V for large displacement one under unipolar actuation, where frequency was 800 Hz. The tip displacement was measured by laser displacement meter。 We have estimated the d_{31} of PZT thin films dc and pulse-poled at 20 V and 40-100 V.

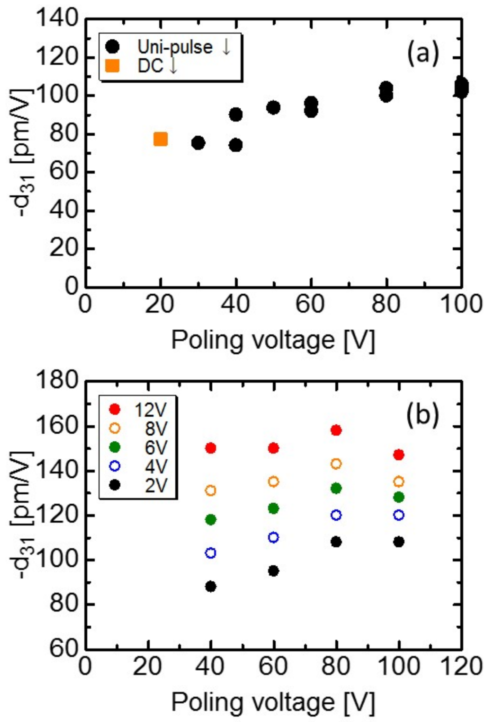

Figure 4: Piezoelectric constant -d_{31} as a function of poling voltage measured under (a) bipolar actuation at 1-3 V_{pp} and (b) unipolar actuation at 2-12 V.

Figure 4(a) shows the estimated -d_{31} values as a function of dc and pulse poling voltage measured under bipolar actuation at 1-3 V_{pp}. The -d_{31} of dc-poled PZT thin films is 78 pm/V, while that of pulse-poled PZT thin films exceeds 100 pm/V. The results indicate that only 1 second of pulse poling gives larger piezoelectric constant than several minutes of dc poling. Figure 4(b) shows -d_{31} values as a function of pulse poling voltage measured under unipolar actuation at 2-12 V. The larger actuation voltage resulted in the larger piezoelectric constant -d_{31}. The highest -d_{31} is as high as 158 pm/V. Note that the dependence on pulse poling voltage is different for actuation voltage: the -d_{31} reaches its maximum at the pulse poling voltage of 100 V for 2 and 4 V actuation, while at the pulse poling voltage of 80 V for 6, 8 and 12 V actuation.

DISCUSSION

In the following, we discuss the difference in the dependence on pulse poling voltage. It is well known that the piezoelectric response of PZT thin films is a summation of intrinsic and extrinsic contribution. The former originate from the piezoelectric response of single domains, and the latter from the domain wall motion. Since the coercive voltage of the present PZT thin films is 7 V, the d_{31} measured at 2 V originate from intrinsic contribution, while that measured at 12 V from both intrinsic and extrinsic contributions. Therefore, we assume that the piezoelectric constant measured at 12 V $d_{31,12V}$ is expressed as follows,

$$d_{31,12V} = d_{31,2V} + (d_{31,12V} - d_{31,2V}) \quad (5),$$

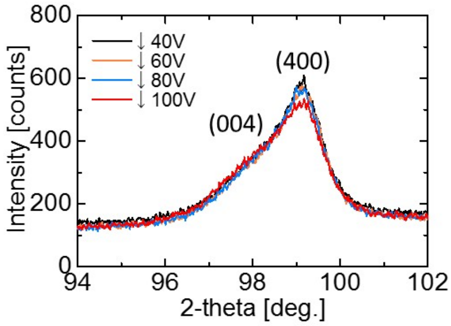

Figure 5: XRD patterns of the PZT thin films pulse-poled at 40-100 V around PZT(004)/(400) peak.

Table 1: $d_{31,12V}$, $d_{31,2V}$, $d_{31,12V}$-$d_{31,2V}$, $V_{(001)}$ and $V_{(100)}$ of PZT thin films pulse-poled at 40-100 V

Poling [V]	$d_{31,12V}$ [pm/V]	$d_{31,2V}$ Intrinsic piezo.	$d_{31,12V}$-$d_{31,2V}$ Extrinsic piezo.	$V_{(001)}$ [%]	$V_{(100)}$ [%]
40	150	58.7	41.3	37.4	62.6
60	150	63.3	36.7	38.8	61.2
80	158	68.5	31.5	39.0	61.0
100	147	73.5	26.5	41.6	58.4

where $d_{31,2V}$ is that measured at 2 V. In equation (5), the first term corresponds to the intrinsic piezoelectric effect, and the second term to the extrinsic piezoelectric effect.

As described above, the present PZT thin films consist of (001) and (100) oriented domain. The intrinsic piezoelectric effect is related to lattice distortion of (001) domain, while the extrinsic one to switching of (100) domain to (001) domain. Thus, we have investigated the degree of (001) and (100) orientation of the PZT thin films by using X-ray diffractometry (XRD). Figure 5 shows XRD patterns of PZT thin films around PZT(004)/(400) peak. From the XRD pattern, we have estimated the degree of (001) and (100) orientation $V_{(001)}$ and $V_{(100)}$ by the pseudo-Voigt function fitting.

Table 1 summarize $d_{31,12V}$, $d_{31,2V}$, $d_{31,12V}$-$d_{31,2V}$, $V_{(001)}$ and $V_{(100)}$ of PZT thin films pulse-poled at 40-100 V. The degree of (001) orientation $V_{(001)}$ increased with pulse poling voltage, which leads to the increase in the intrinsic contribution to piezoelectric constant $d_{31,2V}$. On the other hand, the extrinsic contribution to piezoelectric constant $d_{31,12V}$-$d_{31,2V}$ decrease with increasing pulse poling voltage. With increase in unipolar actuation voltage, the extrinsic contribution to the total piezoelectric constant becomes more dominant. Thus, the large decrease in $V_{(100)}$ occurred by 100 V of pulse poling have resulted in the lower $d_{31,12V}$ than that of the PZT thin films pulse-poled at 40-80 V.

The other possibility of the lower $d_{31,12V}$ of the PZT thin films pulse-poled at 100 V is crack formation observed in the case of tetragonal composition PZT thin films [5,6]. Figures 6(a-d) show cross-sectional SEM images of the PZT thin films pulse-poled at 40-100 V. Only the PZT thin films pulse-poled at 100 V have crack which go along the thickness direction (shown by white arrow in the picture). In the present case, 14 similar cracks were observed in 300 μm. The cracks may also lower the $d_{31,12V}$ of the PZT thin films pulse-poled at 100 V. As shown in the SEM images, the cracks go through along the small pores generated during PZT deposition. If the deposition conditions are

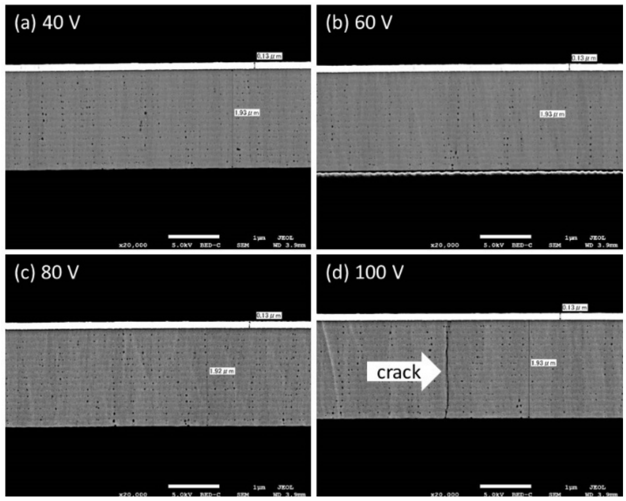

Figure 6: Cross-sectional SEM images of the PZT thin films pulse-poled at 40-100 V.

improved to reduce the generation of pores, the crack formation can be avoided. The improvement of the deposition condition is now underway.

CONCLUSION

In the present study, we have employed pulse poling to activate the MPB-PZT thin films on the MEMS-based microcantilevers. The transverse piezoelectric constant -d_{31} of the PZT thin film, measured under the actuation condition of 1-3V_{pp}, has increased with pulse poling voltage and reached 105 pm/V at the pulse poling voltage of 100 V. While the -d_{31} measured under the unipolar actuation at 12V has reached its maximum (158 pm/V) at the pulse poling voltage of 80 V. Through XRD analysis, it has been turned out the that large decrease in $V_{(100)}$ occurred by 100 V of pulse poling has led to lower $d_{31,12V}$ than that of the PZT thin films pulse-poled at 40-80 V. Although the mechanism of the difference in the dependence on pulse poling voltage is not fully understood, the results indicate that only 1 second of pulse poling gives better piezoelectric property of the PZT thin films compared to several minutes of dc poling.

ACKNOWLDGEMENTS

This research is granted by the Japan Society for the Promotion of Science (JSPS) through the "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)," initiated by the Council for Science and Technology Policy (CSTP).

CONTACT

takeshi Kobayashi: takeshi-kobayashi@aist.go.jp

REFERENCES

[1] M. Murata, T. Kondoh, T. Yagi, N. Funatsu, K. Tanaka, H. Tsukuni, K. Ohno, H. Usami, R. Nayve, N. Inoue, S. Seto, and N. Morita, "High-resolution piezo inkjet printhead fabricated by three dimensional electrical connection method using through glass via", *Proc. MEMS 2009,* pp. 507-510.

[2] M. Tani, M. Akamatsu, Y. Yasuda, and H. Toshiyoshi, "A two-axis piezoelectric tilting micromirror with a

newly developed PZT-meandering actuator", *Proc. MEMS 2007,* pp. 699-702.

[3] K. Matsuo, M. Moriyama, M. Esashi, and S. Tanaka, "Low-voltage PZT-actuated MEMS switch monolithically integrated with CMOS circuit", *Proc. MEMS 2012,* pp. 1153-1156.

[4] T. Kobayashi, S. Oyama, H. Okada, N. Makimoto, K. Tanaka, T. Itoh, and R. Maeda, "An electrostatic field sensor driven by self-excited vibration", *Proc. MEMS 2012,* pp. 527-530.

[5] T. Kobayashi, N. Makimoto, T. Oikawa, A. Wada, H. Funakubo, and R. Maeda, "Linear actuation piezoelectric microcantilever using tetragonal composition PZT thin films", *Proc. MEMS 2013,* pp. 413-416.

[6] T. Kobayashi, N. Makimoto, H. Funakubo, T. Oikawa, A. Wada, T. Itoh, and R. Maeda, "Enhanced performance of sensor/actuator integrated piezoelectric microcantilever by using tetragonal composition PZT thin films", *Proc. Transducers 2013,* pp. 1879-1812.

[7] T. Kobayashi, M. Ichiki, J. Tsaur, and R. Maeda, "Effect of multi-coating process on the orientation and microstructure of lead zirconate titanate (PZT) thin films derived by chemical solution deposition", *Thin Solid Films*, vol. 489, pp. 74-78, 2005

[8] J. G. Smits and W. S. Choi, "The constituent equations of piezoelectric heterogeneous bimorphs", IEEE Trans. Ultrason. Ferroelectr. Freq. Control, vol. 38, pp. 256-270, 1991