Transactions of the Materials Research Society of Japan 33[4] 1243-1245 (2008)

Direct domain writing in CSD-derived PZT thin films by AFM

H. Suzuki, N. Wakiya, N. Sakamoto, Y. Hoshi, and J. Akedo*
Graduate School of Materials Science and Technology, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu 432-8561, Japan, Fax: 81-53-478-1157, e-mail: tchsuzu@ipc.shizuoka.ac.jp
* AIST,1-2-1 Namiki, Tsukuba, Ibaraki 305-8564, Japan
Fax: +81-29-861-7091, e-mail: akedo-j@aist.go.jp

In this study, PZT thin films with different compositions were deposited by a chemical solution deposition on Si wafer with or without Electric-Field-Assisted Annealing (EFA-A) for the easy control of domain switching by Atomic Force Microscope (AFM) to develop the advanced memory. As a result, it was demonstrated that the EFA-A was very effective to enhance the electrical properties of the PZT thin films and the coercive field of the resulting PZT thin films increased with increasing amount of Ti concentration. Therefore, we tried to switch the domain structure of the PZT thin films with a Zr/Ti ratio of 30/70 annealed with EFA-A by AFM to exhibit the possibility of the direct domain writing in the CSD-derived PZT thin film for the advanced AFM memory.
Key words: PZT tin film, Direct domain writing, AFM, memory, CSD

1. INTRODUCTION

Lead zirconate titanate (PZT) ferroelectric thin films have attracted great attention in recent years as promising materials for use in nonvolatile memories and in microelectromechanical systems (MEMS).[1-3] Their dielectric and ferroelectric properties have been intensively investigated. However, the piezoelectric properties of PZT films are lack of understanding. This is mainly due to the following two factors. One is that the thick-film deposition technique has not been established. For the actuator application, over several μm thick film is necessary. This thickness extends well beyond the upper limit of current thin film fabrication methods such as chemical solution deposition (CSD), pulse laser deposition and well below the lower limit of conventional tape-casting and screen printing thick film techniques.[4] Another problem is the measurement technique. The standard resonance method cannot be used directly for the thin film measurements, since the film is constrained on the substrate. In addition, when film thickness is less than 1 μm, the resonant frequency will be too high to be measured. Recently, quasi-static methods, such as continuous charge integration and double beam interferometer, have been proposed to solve this problem.[5,6]

For PZT thin films, in addition to the compositional factor, the orientation also controls the film properties. In our previous studies, excellent piezoelectric behaviors have been observed in the oriented PZT films.[7,8] In this study, we report structural effects of the CSD-derived PZT thin films on the ferroelectric and domain switching behavior, mainly in the region of the tetragonal symmetry and investigate the influences of the composition and the film orientations on their domain switching responses. We observed the response charges of the poled films induced by electric field applied by a atomic force microscope (AFM), and estimated the contribution of the composition and the film orientation on the total response in the ferroic domain.

2. EXPERIMENTAL PROCEDURE

Lead acetate trihydrate, titanium iso-propoxide and zirconium n-propoxide were used as starting materials, and absolute ethanol was used as a solvent to prepare the precursor solution for CSD. The Zr/Ti ratio was changed from 30/70 to 53/47, and excess Pb (20 mol%) was added to the precursor solution to compensate lead depletion during processing by the evaporation and diffusion into the platinum electrode. Therefore, the nominal composition of the precursor solution was equivalent to that of $Pb_{1.2}(Zr_xTi_y)O_3$. Details of the precursor solution preparation are described elsewhere [9]. The concentration of the PZT precursor solution was controlled at 0.6 M.

Orientation control of the PZT films were carried out by using in-situ seeding layers of (001)-oriented PbO, which could be deposited during pre-annealing at 420 °C. We also used EFA-A to increase the (001)-oriented grains in the films [10]. Final annealing was performed at 650 °C for 5 min. in air by the rapid thermal annealing (RAT). Figure 1 shows the schematic illustration for the thin film deposition using in-situ seeding layers.

Crystalline phases in the resultant PZT thin films were identified by X-ray diffraction (XRD). For electrical measurement, Au top electrode was sputtered through the metal mask with 200 or 50 μ m circular holes. To control the residual stress in the films, we used the back-etching technique to prepare the diaphragm structure with different residual Si substrate thickness [11].

Dielectric behavior of the PZT thin films was measured by LCR meter (HP-4284A). P-E hysteresis loops and the piezoelectric property for the resultant thin film were measured by the ferroelectric thin film test system combined with scanning probe microscope (Toyo corporation, FCE-PZ and SII Nanotechnology Inc., SPI3800N).

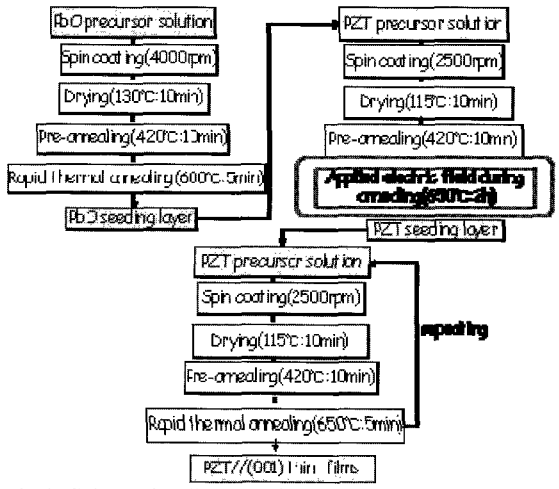

Fig.1 Schematic diagram for deposition of PZT thin films by EFA-A.

3. RESULTS AND DISCUSSION

3.1 Electrical properties of CSD-derived PZT thin films

Figure 2 shows the change in the remanent polarization of the resulting PZT thin films with different orientation or degree of the (001)-orientation, caused by the different annealing processes. As a result, EFA-A resulted in the higher (001)-orientation of the resulting PZT films and, therefore, leading to the higher remanent polarization independent of the composition in the tetragonal region. In addition, PZT(30/70) film deposited by the EFA-A exhibited almost the same remanent polarization as those of the PZT films with ZrO_2 rich compositions. This shows that the PZT(30/70) by EFA-A is suitable for the domain switching by the AFM. Furthermore, the coercive field of the resulting PZT thin films increased by the EFA-A as shown in Fig. 3, suggesting that the PZT(30/70) thin film deposited by EFA-A is easy to maintain the switched domain for a long time. All these results indicates that PZT(30/70) thin film by a EFA-A is good for the film that can be used for the direct domain writing by AFM.

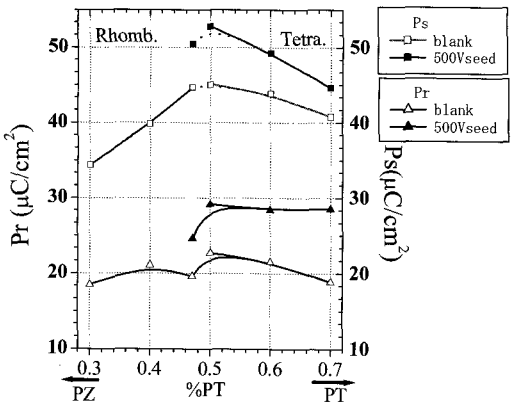

Fig. 2 Relation between remanent polarization and the film orientation of the resultant PZT films with different compositions.

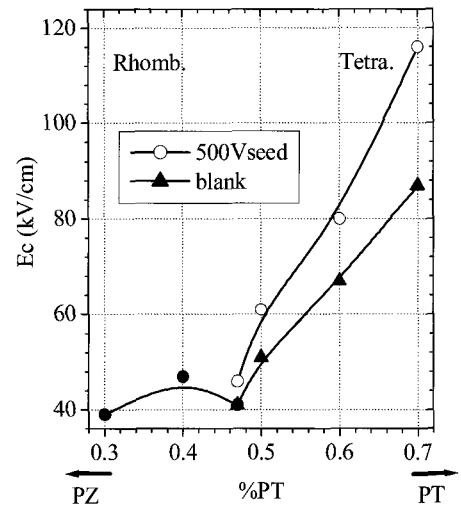

Fig. 3 Relation between coercive field and the film orientation or applied electric field during annealing of the resultant PZT films with different compositions.

3.2 Direct domain writing by AFM

From the above results, we elucidate the domain switching behavior of the PZT(30/70) thin film by a EFA-A. Figure 4 exhibited the domain switching behavior of the PZT(30/70) film by applying the electric field with AFM. As shown in figure 4, PZT(30/70) film by a EFA-A shows very good direct domain writing property, showing the possibility for the AFM memory. Further investigation is essential to confirm the possibility for the AFM memory using highly (001)-oriented PZT(30/70) film by a EFA-A.

4. CONCLUSIONS

In this paper, ferroelectric and domain switching behavior of the highly (001)- & (100)-oriented PZT films deposited with and without EFA-A. EFA-A increased the remanent polarization of the resultant PZT thin films independent of the composition in the tetragonal region as well as the coercive field. These results indicated that PZT(30/70) thin film by a EFA-A was suitable for the direct domain writing film for a AFM memory. In fact, piezo-images for the resultant PZT(30/70) thin film by a EFA-A exhibited very good domain switching behavior, showing the possibility for the direct domain writing by the PZT thin films deposited by a EFA-A.

ACKNOWLEDGEMENTS

This work was supported in part by Grants-in-Aid for Scientific Research (B) (No.16360325) from Japan Society for the Promotion of Science.

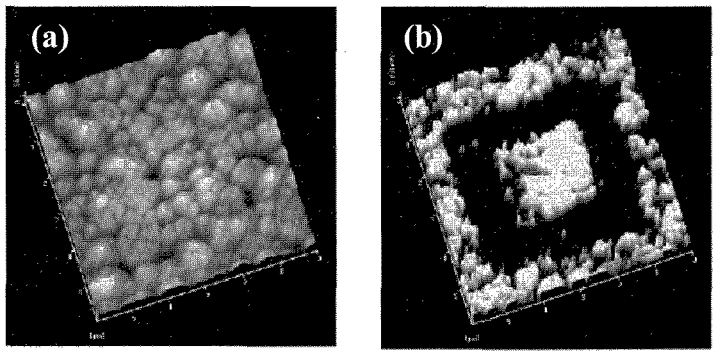

Fig. 4 Piezo-images of the PZT(30/70) thin film surface deposited by a EFA-A, before (a) and after applying the electric field

REFERENCES

[1] J. F. Scott and C. A. Paz deAraujo, Science 246, 1400(1989).
[2] P. Muralt, J. Micromech. Microeng. 10, 136(2000).
[3] D. Damjanovic, Rep. Prog. Phys. 61, 1267(1998).
[4] H. D. Chen, K. R. Udayakumar, C. J. Gaskey, L. E. Cross, J. J. Bernstein, and L. C. Niles, J. Am. Ceram. Soc. 79, 2189(1996).
[5] D. S. Fu, K. Ishikawa, M. Minakata, and H. Suzuki, Jpn. J. Appl. Phys. 40, 5683 (2001).
[6] A. L. Kholkin, Ch. Wütchrich, D. V. Taylor, and N. Setter, Rev. Sci. Instrum. 67, 1935(1996).
[7] D. S. Fu, K. Ishikawa, Y. Yoshimi, and H. Suzuki, Jpn. J. Appl. Phys. 41, L580(2002).
[8] D. S. Fu, H. Suzuki, T. Ogawa, and K. Ishikawa, Appl. Phys. Lett. 80, 3572 (2002).
[9] H. Suzuki, Y. Kondo, S. Kaneko, and T. Hayashi, Mater. Res. Soc.Sym. Proc. 596, 241 (2000).
[10] H.Nakayama, et. al., Jpn.J.Appl.Phys., 43 (2004)
[11] T. Ohno, et. al. , Jpn. J. Appl. Phys., 43, 6549-6553 (2004)

(Recieved December 7, 2007 ; Accepted November 14, 2008)