

Preparation of Texture Controlled Lead Zirconate Titanate Thin and Thick Films Using Chemical Solution Deposition Process

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Texture control of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films, $x = 0.45, 0.53$ and 0.6 , and crack free $10\text{-}\mu\text{m}$ -thick $\text{Pb}_{1.1}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT) film were successfully fabricated using a chemical solution deposition process. 0.5 M PZT precursor solution were prepared from trihydrated lead acetate, titanium iso-propoxide, zirconium n-propoxide, and 2-methoxyethanol as the solvent. The process of spin coating and pyrolysis at $400\text{-}520^\circ\text{C}$ was repeated five times, before the precursor films were fired at $650\text{-}700^\circ\text{C}$, and the process sequence was repeated several times to prepare the films. In pyrolysis process, the precursor films heat-treated less than 450°C indicated the (100) dominant orientation, whereas the precursor films heat-treated above 450°C showed the (111) dominant orientation. Furthermore, to prepare the thick film, the process sequence was repeated 30 times. The fabricated crack-free PZT thick films showed (100) preferred orientation. A flat surface and dense microstructure was observed. The electrical properties were comparable with the bulk PZT ceramics. The dielectric constant and dissipation factor were $\epsilon_r = 1453$ and $\tan\delta = 0.039$, and the remnant polarization and coercive field were $P_r = 25\ \mu\text{C}/\text{cm}^2$ and $E_c = 30\ \text{kV}/\text{cm}$, respectively.

Key words: PZT, chemical solution deposition, thin film, texture control, ferroelectric property

1. INTRODUCTION

Lead zirconate titanate (PZT) films are in demand for applications in many fields like memories, sensors and actuators. Combining the preparation technique for ferroelectric films with Si micro machining process is an effective way to fabricate microelectromechanical systems (MEMS), such as piezoelectric micro actuator devices for applications in the electrical and medical fields [1, 2]. One of the effective techniques to increase the ferroelectric and piezoelectric properties is supposed to be arrangement of the polarization direction using a texture control process. Various possibilities of the texture control of PZT thin film were investigated for a sol-gel [3, 4], sputtering [5, 6] and MOCVD process [7, 8]. On the other hand, various processes were investigated to fabricate thick PZT films up to $100\ \mu\text{m}$ [9-14] to increase the amount of displacement and force of PZT films. Moreover, a low process temperature for the PZT thick films is required to ensure compatibility with the Si micro machining process. In the case of thick films prepared by the powder source technique, such as screen printing [1, 15], the usual firing temperature is more than 800°C , and the density of the thick films are not so high because of imperfect sintering. Compared with a screen printing process, thin film preparation process using chemical solutions, like

sol-gel, have the advantage of low firing temperature and dense microstructure in spite of low film deposition rate. Therefore, a chemical solution deposition (CSD) process is considered to be an attractive way to ensure the compatibility with the Si micro machining and to control the texture orientation of PZT films. In this study, we investigated the condition of the texture control process of PZT thin films and preparation of a $10\text{-}\mu\text{m}$ -thick PZT film using the CSD process.

2. EXPERIMENTAL PROCEDURES

Trihydrated lead acetate (99.9%, Nakarai tesque), titanium iso-propoxide (97%, Kanto chemical) and zirconium n-propoxide (70% in propanol, Azmax) were used as starting materials, and 2-methoxyethanol (99.7%, Aldrich) was used as a solvent to prepare the CSD precursor solutions. The nominal compositions of the solutions were equivalent to those of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, $x = 0.45, 0.53$ and 0.6 , and $\text{Pb}_{1.1}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$. Details of the precursor solution preparation process are described elsewhere [16]. Concentration of the Pb-Zr-Ti precursor solution was controlled at 0.5M . Figure 1 shows preparation process of the PZT films. First, the precursor solution was deposited on a Pt(111)/Ti/SiO₂/Si substrate using a spin coater operating at $3000\ \text{rpm}$ for $40\ \text{s}$. A sequence of spin coating, drying at room temperature and

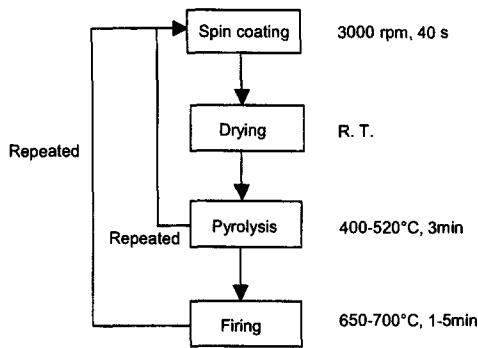


Fig. 1 Flow diagram for film fabrication process.

pyrolysis treatment at 400-520°C for 3 min was performed five times, and the samples were fired at 650-700°C for 1-5 min. This sequence was repeated to increase the film thickness from 280nm to 10 μm . In the case of the 10- μm -thick PZT film, pyrolysis treatment at 500°C and firing at 700°C were performed.

The crystal structure of the thin films was examined with an X-ray diffractometer (XRD). The microstructure of the films was observed with scanning electron microscope (SEM, S-5000, Hitachi). To evaluate the ferroelectric properties, a 0.5-mm-diameter Pt electrode was sputter-deposited onto the PZT thin films through a metal mask. *P-E* hysteresis curves were measured with RT66A (Radiant Technology). The dielectric permittivity was measured using a LCR meter (HP4284A) at 10kHz-10mV.

3. RESULTS AND DISCUSSION

3.1 Texture control of PZT thin film

Fig. 2 shows the result of XRD analysis of the PZT thin film for $x=0.45$ fired at 650°C. The thin film that was pyrolyzed at 400°C indicated a (100) dominant oriented texture as shown in Fig. 2 (a). On the other hand, when the pyrolysis temperature increased to 520°C, the thin film showed a (111) dominant orientated texture as shown in Fig. 2 (b). Therefore, it can be seen that the texture orientation changed abruptly from the (100) to (111) with increasing the pyrolysis temperature from 400°C to 520°C. Fig. 3 shows

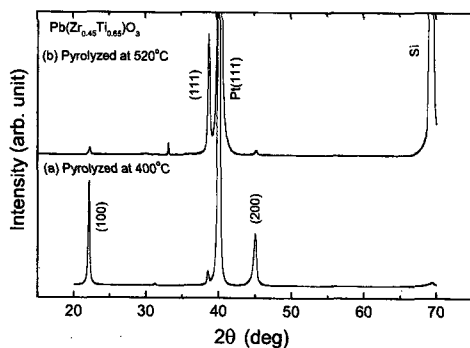


Fig. 2 X-ray diffraction patterns of PZT thin films for $x=0.45$.

the result of XRD analysis of the PZT thin film for $x=0.53$ fired at 700°C. When the pyrolysis process was performed at 450°C, the texture of the thin film showed the (100) preferred orientation. However, the thin film pyrolyzed at 510°C showed the (111) dominant orientated texture. The result of XRD analysis of the PZT thin film for $x=0.6$ fired at 650°C is shown in Fig. 4. It can be seen that the (100) preferred orientation was formed for 400°C and the (111) preferred orientation formed for 450°C. These results suggest that the (100) texture predominates lower than 450°C and the (111) texture predominates higher than 450°C in the pyrolysis process. Therefore, a nucleation of the PZT on a surface of the (111) oriented Pt layer seems to be related to the texture orientation of the PZT.

From these X-ray diffraction patterns, a lattice constant of PZT thin films was calculated using the (100), (111) and (200) peaks. Fig. 5 shows the relationship between the lattice constant and Zr content of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films. The crystal structure of the thin films was determined tetragonal for $x=0.45$ and 0.53, and rhombohedral for $x=0.6$. With increasing Zr content, value of *c* axis decreased and that of *a* axis increased. This tendency of the lattice constant for the PZT thin film was consistent to the reported data [7].

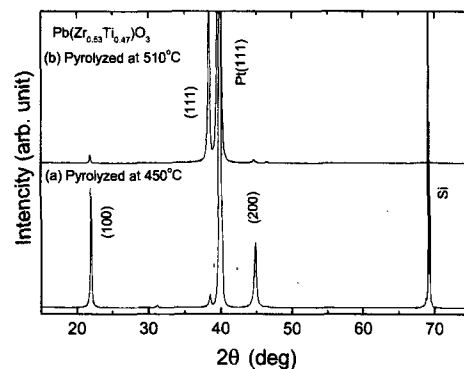


Fig. 3 X-ray diffraction patterns of PZT thin films for $x=0.53$.

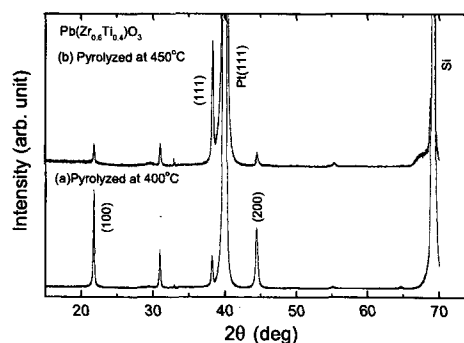


Fig. 4 X-ray diffraction patterns of PZT thin films for $x=0.6$.

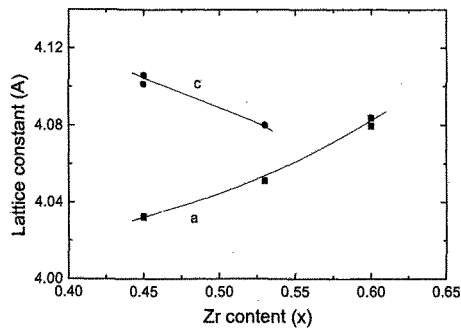


Fig. 5 Lattice constant of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films.

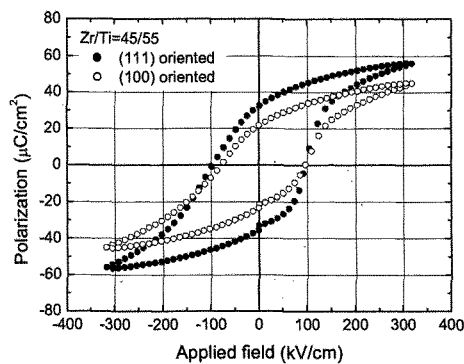


Fig. 6 P - E hysteresis curves of the (100) and (111) oriented PZT thin films for tetragonal phase, $\text{Zr}/\text{Ti}=45/55$.

Therefore, it appears that the Zr/Ti rate and crystal structure do not affect the texture orientation of the PZT thin films. This suggests that pyrolysis temperature is an important factor to control the PZT thin film texture using the CSD process.

The P - E hysteresis curves of the predominantly (100) and (111) oriented PZT thin films for tetragonal phase, $\text{Zr}/\text{Ti}=45/55$, are indicated in Fig. 6. The (111) dominant orientated film showed high value of the remnant polarization

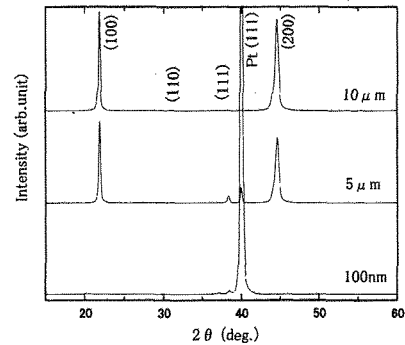


Fig. 7 X-ray diffraction patterns of PZT thick film with increasing the film thickness.

(P_r) compared to the (100) dominant oriented film. A polarization axis of the tetragonal PZT is a [001] direction and an angle between the [001] and [111] direction is smaller than that between the [001] and [100], so that the P_r of the (111) preferred film appears to be higher than that of the (100) preferred film. These values were $P_r=20\mu\text{C}/\text{cm}^2$ for (100) preferred orientation and $P_r=31\mu\text{C}/\text{cm}^2$ for (111) preferred orientation.

3.2 Preparation of PZT thick film

Figure 7 shows X-ray diffraction patterns of the PZT film with increasing the film thickness. All patterns show a well-defined perovskite structure except for the Pt (111) peak. When the film thickness was 100nm, the PZT film showed a (111) preferred orientation. With increasing the film thickness, however, peak intensity of the (100) and (200) planes increase, and it is difficult to distinguish (110), (111) and Pt(111) peaks for 10-mm-thick PZT film. This tendency is consistent with reported data [9].

Figure 8 shows SEM micrographs of the PZT thick film for (a) a surface and (b) a cross-section. These micrographs indicate that a surface of the PZT thick film is flat. Furthermore, grains and grain boundaries were not clear from the top and cross-section view. In the case of thick films prepared by powders like screen-printing, the surface is not so flat and many pores are seen in

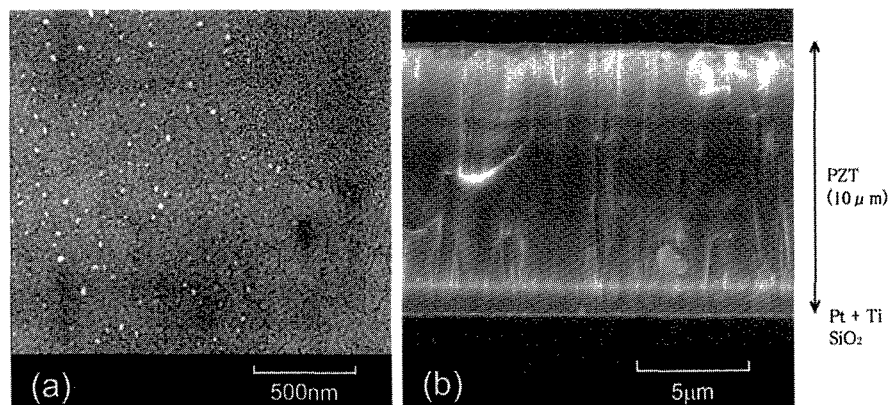


Fig. 8 SEM micrographs of 10- μm -thick PZT film fired at 700 $^{\circ}\text{C}$, (a) surface, (b) cross-section.

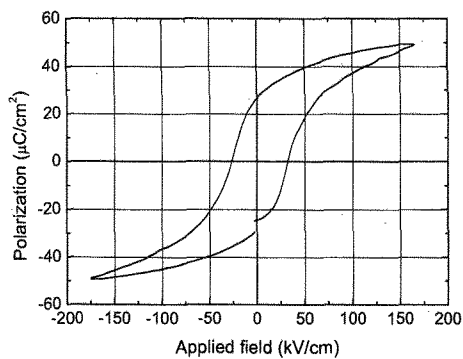


Fig. 9 *P-E* hysteresis curve of 10- μm -thick PZT film.

cross-section because of low sintered density [1, 13]. On the other hand, large grains and layers are often observed in cross-section of sol-gel derived PZT thick films [9, 17]. However, the prepared PZT thick film seems to be dense and layers caused by coating process cannot be seen.

The dielectric constant (ϵ_r) calculated from the PZT thick film capacitance was $\epsilon_r=1453$, and the dissipation factor ($\tan\delta$) was $\tan\delta=0.039$, respectively. The dielectric properties are considered to be better, higher ϵ_r and lower $\tan\delta$, than reported PZT thick films [12, 13]. Figure 9 shows *P-E* hysteresis curve of the PZT thick film measured at ± 175 kV/cm. The shape of the hysteresis curve is well saturated in spite of a relatively low applied field. The values of the remnant polarization (P_r) and the coercive field (E_c) were about $P_r=25$ $\mu\text{C}/\text{cm}^2$ and $E_c=30$ kV/cm, respectively. The value of P_r is relatively higher than that of screen-printed PZT thick films [12], but the value is lower than that of bulk PZT ceramics. This reason seems to be the difference of the polarization direction, [001], from the texture-oriented direction, [100] as shown in Fig. 6. On the other hand, the value of E_c is comparable to that of bulk PZT ceramics, and it is relatively low compared with that of the reported PZT thick films [13, 14].

4. CONCLUSIONS

Texture controlled $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, $x=0.45$, 0.53 and 0.6, thin films were fabricated onto Pt (111)/Ti/SiO₂/Si substrate. When the thin films were pyrolyzed between 400°C and 520°C, the (100) or (111) dominant texture could be formed. However, crystal structure and Zr content of PZT did not affect the texture orientation. In the case of the texture oriented tetragonal film, the remnant polarization of the (111) dominant oriented film was higher than that of the (100) dominant oriented film. Moreover, the thick PZT film preparation process was investigated, and crack free 10- μm -thick $\text{Pb}_{1.1}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ films were successfully fabricated. The prepared PZT thick films showed (100) preferred orientation. A flat surface and dense microstructure was observed. Prepared PZT thick film show

comparable electrical properties to the bulk PZT ceramics. The dielectric constant, dissipation factor, remnant polarization and coercive field were $\epsilon_r=1453$, $\tan\delta=0.039$, $P_r=25$ $\mu\text{C}/\text{cm}^2$ and $E_c=30$ kV/cm, respectively.

REFERENCES

- [1] H. D. Chen, K. R. Udayakumar, L. E. Cross, J. J. Bernstein, and L. C. Niles, *J. Appl. Phys.*, **77**, 3349-3353 (1995).
- [2] S. Wakabayashi, M. Sakata, H. Goto, M. Takeuchi, and T. Yada, *Jpn. J. Appl. Phys.*, **35**, 5012-5014 (1996).
- [3] K. Aoki, Y. Fukuda, K. Numata and A. Nishimura, *Jpn. J. Appl. Phys.*, **33**, Part1, No. 9B, 5155-5158 (1994).
- [4] K. G. Brooks, I. M. Reaney, R. Klissurska, Y. Huang, L. Bursill and N. Setter, *J. Mater. Res.*, **9**, 2540-2553 (1994).
- [5] M. Adachi, T. Matsuzaki, T. Yamada, T. Shiosaki and A. Kawabata, *Jpn. J. Appl. Phys.*, **26**, 550-553 (1987).
- [6] R. Takayama and Y. Tomita, *J. Appl. Phys.*, **65**, 1666-1670 (1989).
- [7] Y. Sakashita, T. Ono, H. Segawa, K. Tominaga and M. Okada, *J. Appl. Phys.*, **69**, 8352-8357 (1991).
- [8] D. Kim, T. Y. Kim, J. K. Lee, W. Tao and S. B. Desu, *Mat. Res. Soc. Symp. Proc.*, **433**, 213-224 (1996).
- [9] H. D. Chen, K. R. Udayakumar, C. J. Gaskey, L. E. Cross, J. J. Bernstein, and L. C. Niles, *J. Am. Ceram. Soc.*, **79**, 2189-2192 (1996).
- [10] I. Kanno, S. Fujii, T. Kamada, and R. Takayama, *Appl. Phys. Lett.*, **70**, 1378-1380 (1997).
- [11] Y. Ohba, M. Miyauchi, T. Tsurumi, and M. Daimon, *Jpn. J. Appl. Phys.*, **32**, 4095-4098 (1993).
- [12] Y. Jeon, J. Chung, and K. No, *J. Electroceramics*, **4**, 195-199 (2000).
- [13] T. Tsurumi, S. Ozawa, G. Abe, N. Ohashi, S. Wada, and M. Yamane, *Jpn. J. Appl. Phys.*, **39**, 5604-5608 (2000).
- [14] M. Lebedev, J. Akedo and Y. Akiyama, *Jpn. J. Appl. Phys.*, **39**, 5600-5603 (2000).
- [15] Y. Akiyama, K. Yamanaka, E. Fujisawa, and Y. Kowata, *Jpn. J. Appl. Phys.*, **38**, 5524-5527 (1999).
- [16] T. Iijima, N. Sanada, K. Hiyama, H. Tsuboi, and M. Okada in *Ferroelectric Thin Films VIII*, edited by R. W. Schwartz, P. C. McIntyre, Y. Miyasaka, S. R. Summerfelt, and D. Wouters, (Mater. Res. Soc. **596**, Pittsburgh, PA, 2000) pp. 223-228.
- [17] K. Brooks, D. Damjanovic, A. Kholkin, I. Reaney, N. Setter, P. Luginbuhl, G. A. Racine, N. F. De Rooji, and A. Saaman, *Integrated Ferroelectrics*, **8**, 13-23 (1995).

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