Transactions of the Materials Research Society of Japan 29 [8] 3435-3438 (2004)

$Pb(Zr,Ti)O_3$ Thin Films Grown on Seeding Layer with Electric Field-Assisted Annealing

Hiroshi Nakayama[1,2], Shigeru Suzuki[1], Shouichi Miyahara[3], Desheng Fu[4] and Hisao Suzuki[5]

[1]Graduate School of Science and Technology, Shizuoka University, 3-5-1 Johoku, Hamamatsu 432-8561, Japan
Fax: 81-53-478-1157, e-mail: tchsuzu@ipc.shizuoka.ac.jp

[2]Fuji Industrial Research Institute of Shizuoka Prefecture, 2590-1 Obuchi, Fuji 417-8550, Japan
Fax: 81-545-35-5195, e-mail: nakayama@f-iri.pref.shizuoka.jp

[3]Shizuoka Industrial Research Institute of Shizuoka Prefecture, 2078 Makigaya, Shizuoka 421-1298, Japan
Fax: 81-54-278-3066, e-mail: miyahara@s-iri.pref.shizuoka.jp

[4]National Institute of Advanced Industrial Science and Technology, 2266-98 Anagahora, Shimoshidami, Moriyama-ku, Nagoya 463-8560, Japan
Fax: 81-52-736-7236, e-mail: Desheng-fu@aist.go.jp

[5]Departmennt of Materials Science, Shizuoka University, 3-5-1 Johoku, Hamamatsu 432-8561, Japan
Fax: 81-53-478-1157, e-mail: tchsuzu@ipc.shizuoka.ac.jp

$Pb(Zr_{0.5},Ti_{0.5})O_3$ thin films were grown on PZT seeding layer with an electric-field-assisted annealing (EFA-A) through Chemical Solution Deposition (CSD). After PZT seeding layer was deposited with an EFA-A onto $Pt/Ti/SiO_2/Si$ substrate, PZT layers were deposited on PZT seeding layers by rapid thermal annealing without an electric field. PZT layers deposited without an electric field healed cracks formed in PZT seeding layer during EFA-A. For the PZT film grown on PZT seeding layer with an EFA-A, the XRD intensities of (001)&(100) planes effectively increased. The remanent polarization (P_r) for the PZT film deposited with an EFA-A exhibited higher P_r than that for the film deposited without an EFA-A. The P_r value for the film deposited without an EFA-A was 17.9 $\mu C/cm^2$. On the other hand, the P_r value for the film deposited with an EFA-A at 10 kV/cm exhibited 23.8 $\mu C/cm^2$. In addition, the PZT film deposited with an EFA-A at 10 kV/cm also exhibited a larger effective d_{33} value of 372 pC/N in comparison with the film deposited without an EFA-A.

Key words: PZT, thin film, CSD, electric-field-assisted annealing, orientation

1. INTRODUCTION

Lead zirconate titanate ($Pb(Zr,Ti)O_3$:PZT) thin films have high potential for ferroelectric random access memories, microactuators and infrared sensors because of their excellent ferroelectric, piezoelectric and pyroelectric properties.[1-2] In order to deposit PZT films, various techniques have been used, such as CSD, sputtering, and metal organic chemical vapor deposition (MOCVD). Among these techniques, CSD technique is advantageous for producing PZT films due to its simplicity, easy control of homogeneous composition and film thickness for large substrates, and low processing temperature, as compared with other techniques.[3-5]

Electrical properties of PZT films are strongly dependent on the crystal orientation. Therefore, it is very important to control orientation of their films. The (001)-oriented tetragonal PZT film and (111)- oriented rhombohedral PZT film are expected to show good electrical properties. There are many reports on the orientaion control of PZT films.[6-9] Epitaxial PZT films with different orientations have been grown on single crystal substrates of MgO and $SrTiO_3$.[10,11] However, highly c-axis oriented PZT films deposited on silicon substrates are required for electronic devices. It has been reported that a tetragonal PZT should have large Pr value and d_{33} along [001] direction after the theoretical calculation.[12] Therefore, it is very important to prepare the (001)- oriented epitaxially grown PZT films on silicon substrates.

In our previous work, we investigated the novel method of Electric-Field-Assisted Annealing (EFA-A) to control orientation of PZT thin films on $Pt/Ti/SiO_2/Si$ substrates through CSD. EFA-A is the method of applying an electric field to thin film during annealing. Tetragonal PZT thin films were deposited with an EFA-A for every layer. The XRD intensities of (001)&(100) planes in the films deposited with an EFA-A increased and that of the (111) plane decreased. However, electrical properties of the PZT films deposited with an EFA-A could not be measured because many cracks existed in the surface of the films. In order to obtain insulated PZT films, only the last PZT layer was deposited without an electric field (infiltration process), and the electrical properties of the resultant films could be measured. However, the ferroelectricity did not improve effectively because residual cracks still existed in the surface of the films.

In this work, an EFA-A was applied only to the first PZT seeding layer of a same composition. The PZT film

was deposited on seeding layer by rapid thermal annealing (RTA) without an electric field to investigate the relation between crystal orientation, microstructures and electrical properties of the resultant films.

2. EXPERIMENTAL

The precursor solution of $Pb(Zr_{0.5},Ti_{0.5})O_3$ was prepared from lead acetate trihydrate $[Pb(CH_3COO)_2 \cdot 3H_2O]$, zirconium n-propoxide $[Zr(OC_3H_7)_4]$ and titanium iso-propoxide $[Ti((CH_3)_2CHO)_4]$. Lead acetate trihydrate was dehydrated and then dissolved in absolute ethanol by refluxing with NH_3 flow to obtain Pb-precursor solution. After that, titanium iso-propoxide and zirconium n-propoxide were mixed with a Pb-precursor solution to form a PZT precursor solution. Acetylacetone was used to stabilize the precursor solution.

Figure 1 shows the stacking structure for the PZT films grown on PZT seeding layer with an EFA-A. At first, PZT seeding layer was deposited onto $Pt/Ti/SiO_2/Si$ substrate by a spin-coating. The deposited film was dried at 115°C for 10 min to remove water, pyrolyzed at 350°C for 10 min to remove residual organics and then finally annealed at 650°C for 2 h in air with an electric field to develop a PZT seeding layer with preferred orientation. Electric field was generated between platinum plate and bottom electrode by direct current voltage. Platinum plate was a positive terminal and bottom electrode was a negative terminal. Distance between platinum plate and bottom electrode was set at 0.5 mm. PZT layer was deposited on PZT seeding layer by a spin-coating. After drying at 115°C for 10 min and pyrolysis at 350°C for 10 min, the films were annealed at 650℃ for 5 min by rapid thermal annealing (RTA) without an electric field. The deposition of PZT layers by RTA was performed several times to form a film 1 μm-thick. The crystal structure in the thin film was identified by an X-ray diffraction (XRD). The microstructure was observed by a scanning electron microscope (SEM). In order to evaluate electrical properties, gold top electrodes with an area of 2 by 2 mm were deposited on the film. The dielectric property was measured with an impedance analyzer (HP 4284A). The polarization (P-E) hysteresis loops were measured with a ferroelectric test system (Radiant; RT-6000S). The piezoelectric property was measured by a continuous charge integration technique. Static force (2.05 N) was applied normal to the film and the stress-induced polarization was recorded with a charge integrator. Details of the piezoelectric measurement have been described elsewhere.[13-15]

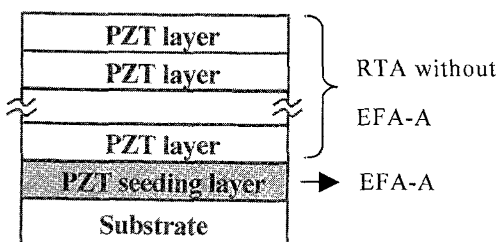

Fig. 1. The stacking structure for the PZT films grown on PZT seeding layer with an EFA-A.

3. RESULTS AND DISCUSSIONS

Figure 2 shows X-ray diffraction patterns for the PZT thin films grown on PZT seeding layers with (10 kV/cm) and without (0 kV/cm) EFA-A. Both of the films exhibited perovskite single phase. For the PZT film deposited without EFA-A, the XRD intensities of (001)&(100) planes were relatively low and that of the (111) plane was relatively high. On the other hand, the XRD intensities of (001)&(100) planes in the film deposited with an EFA-A at 10 kV/cm increased. The degree of orientation calculated from the XRD intensities are listed in Table I. For the PZT film deposited without an EFA-A, the degree of (001)&(100) orientations was calculated to be 31.2%. On the other hand, PZT film deposited with an EFA-A at 10kV/cm exhibited the preferred orientation of 69.2% in the [001]&[100] directions. These results suggest that EFA-A is an effective method to obtain a tetragonal PZT film with preferred orientation of [001]&[100] directions and PZT layers deposited by RTA were epitaxially grown on PZT seeding layer.

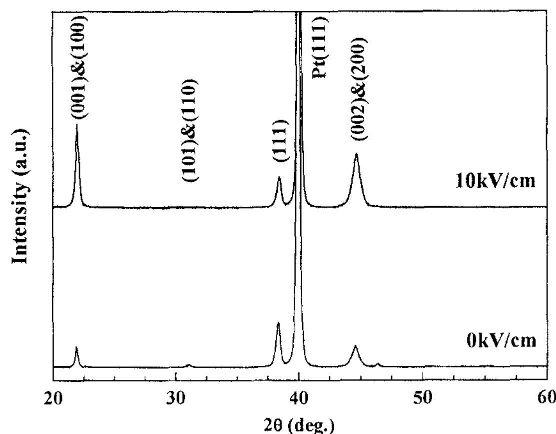

Fig. 2. X-ray diffraction patterns for the PZT thin films grown on PZT seeding layers with (10 kV/cm) and without (0 kV/cm) EFA-A.

Table I. The degree of orientation calculated from the XRD intensities.

Intensities of electric field (kV/cm)	Relative intensities of planes (%)		
	(001)&(100)	(101)&(110)	(111)
0	31.2	2.1	66.7
10	69.2	–	30.8

Figure 3 shows the SEM image of the surface morphology for the PZT seeding layer deposited with an EFA-A at 10 kV/cm. Cracks were observed on the surface of the PZT seeding layer. These cracks were formed during EFA-A. Figure 4 shows the SEM image of the surface morphology for the PZT thin film grown on PZT seeding layer with an EFA-A at 10 kV/cm. Cracks were not observed on the surface of the PZT film. These results indicated that PZT layers deposited without an electric field healed cracks formed in PZT seeding layer during EFA-A.

Figure 5 shows frequency dependences of the

dielectric constants for the PZT thin films grown on PZT seeding layers with (10 kV/cm) and without (0 kV/cm) EFA-A. The dielectric constant of the film grown on seeding layer with an EFA-A at 10 kV/cm decreased compared with that of the film deposited without an EFA-A. The dielectric constants at 1 kHz for the PZT films deposited on the PZT seeding layers with and without EFA-A were 888 and 1135, respectively. The dielectric constant of the (001)-oriented PZT film is known to be smaller than that of the (100)-oriented PZT film. Therefore, the decrease in the dielectric constant suggests that grains with c-axis orientation in the PZT film were increased by an EFA-A.

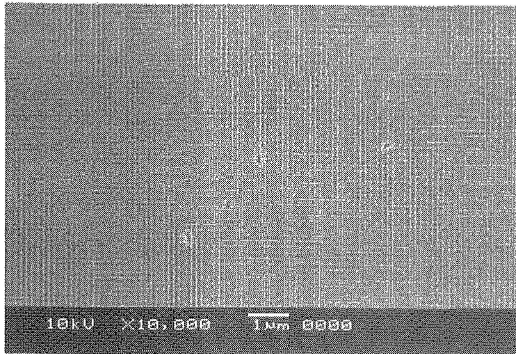

Fig. 3. SEM image of the surface morphology for the PZT seeding layer deposited with an EFA-A at 10 kV/cm.

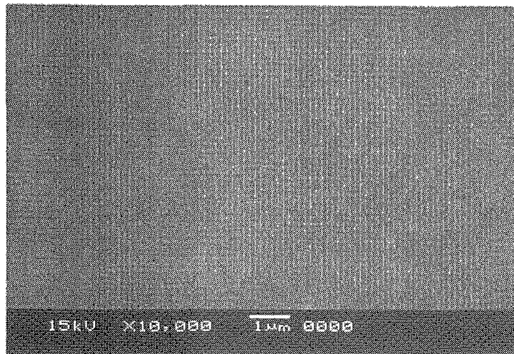

Fig. 4. SEM image of the surface morphology for the PZT thin film grown on PZT seeding layer with an EFA-A at 10 kV/cm.

Figure 6 shows P-E hysteresis loops for the PZT thin films grown on PZT seeding layers with (10 kV/cm) and without (0 kV/cm) EFA-A. The remanent polarization (Pr) for the PZT film deposited with an EFA-A exhibited higher Pr than that for the film deposited without an EFA-A. The Pr value for the PZT film on the PZT seeding layer without an EFA-A was 17.9 $\mu C/cm^2$. On the other hand, the Pr value for the PZT film deposited on the PZT seeding layer with an EFA-A at 10kV/cm exhibited 23.8 $\mu C/cm^2$. The higher Pr value suggests that grains with c-axis orientation in the PZT film were increased by an EFA-A.

Piezoelectric response of the film was also investigated by measuring the stress-induced charge

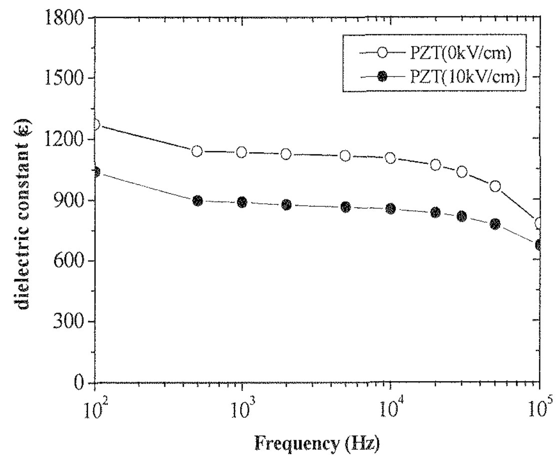

Fig.5. Frequency dependences of the dielectric constants for the PZT thin films grown on PZT seeding layers with (10 kV/cm) and without (0 kV/cm) EFA-A.

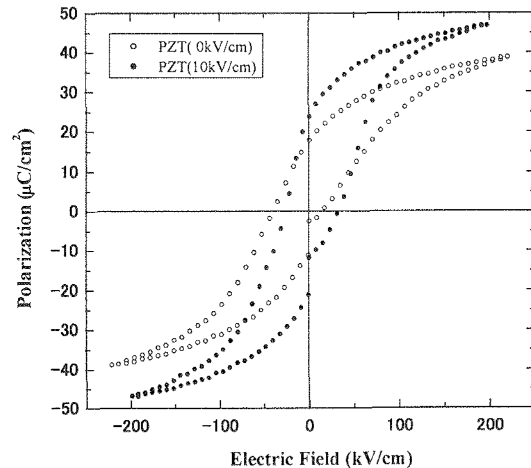

Fig. 6. P-E hysteresis loops for the PZT thin films grown on PZT seeding layers with (10 kV/cm) and without (0 kV/cm) EFA-A.

with a continuous charge integration. We found that the response function of the PZT can be described very well by the following equation,[13-15]

$$d_{33}(t) = d_{33}^{intri} + d_{33}^{relax}(1 - e^{-(t/\tau)^n}) \quad t>0. \qquad (1)$$

Here, the first term d_{33}^{intri} represents the contribution from the intrinsic response due to the rapid coupling of polarization to the unit cell distortion, and the second term d_{33}^{relax} originates from the relaxation effect due to the slow domain wall motion in multidomain materials. Table. II lists the values of d_{33}^{intri} and d_{33}^{relax} in eq. (1) obtained from the fits for the PZT films grown on PZT seeding layers with (10 kV/cm) and without (0 kV/cm) EFA-A. The intrinsic value of d_{33} for the PZT film deposited without an EFA-A was 302 pC/N, whereas the intrinsic value of d_{33} for the PZT film deposited with an EFA-A at 10kV/cm reached appreciably large value of about 372 pC/N. For (001)&(100)-oriented film, only c-axis domains along the stress direction respond to the

application of a stress. Therefore, these results indicated that the degree of (001) orientation for the PZT film was increased by an EFA-A. The contribution of the relaxation for the PZT films grown on PZT seeding layers with and without EFA-A was estimated to be 8.0% and 30.4% of the total piezoelectric response, respectively. This relaxation is due to the domain wall motion. When a normal force is applied to the PZT film, the 180° domains should not influence the relaxation. On the other hand, the non-180° domains will reorient toward the direction of the applied force. Therefore, the contribution of the relaxation for the PZT film grown on PZT seeding layer with an EFA-A is considered to be lower than that for the PZT film deposited without an EFA-A.

Table II. The values of d_{33}^{intri} and d_{33}^{relax} in eq. (1) obtained from the fits for the PZT thin films grown on PZT seeding layers with (10 kV/cm) and without (0 kV/cm) EFA-A.

Intensities of electric field (kV/cm)	d_{33}^{intri} (pC/N)	d_{33}^{relax} (pC/N)	$\frac{d_{33}^{relax}}{d_{33}^{intri}+d_{33}^{relax}}$ (%)
0	302	92	30.4
10	372	30	8.0

4. SUMMARY

We investigated the influence of PZT seeding layer with an EFA-A on the electrical properties of the tetragonal $Pb(Zr_{0.5},Ti_{0.5})O_3$ thin film. PZT thin film was grown on PZT seeding layer deposited with an EFA-A through CSD. PZT layers, which were deposited on the PZT seeding layer without an electric field, healed cracks formed in the PZT seeding layer during EFA-A. The XRD intensities of (001)&(100) planes in the PZT film were increased by an EFA-A. The PZT film deposited with an EFA-A exhibited a higher Pr value compared with the PZT film deposited without an EFA-A. Additionally, the PZT film deposited with an EFA-A exhibited excellent piezoelectricity. These results suggested that grains with c-axis orientation in PZT seeding layer were increased by an EFA-A and PZT film deposited by RTA was epitaxially grown on PZT seeding layer. It was concluded from these results that PZT seeding layer deposited by an EFA-A effectively increased the degree of c-axis orientation to enhance the electrical properties of the resultant PZT thin film.

5. REFERENCES

[1] J. F. Scott and C. A. Paz de Araujo, *Science*, **246**, 1400-05 (1989).
[2] P. Muralt, *J. Micromech. Microeng.*, **10**, 136-46 (2000).
[3] K. Maki, N. Soyama, K. Nagamine, S. Mori, and K. Ogi, *Jpn. J. Appl. Phys.*, **40**, 5533-38 (2001).
[4] H. Suzuki, M. B. Othman, K. Murakami, S. Kaneko, and T. Hayashi, *Jpn. J. Appl. Phys.*, **35**, 4896-99 (1996).
[5] K. Ishikawa, K. Sakura, D. S. Fu, S. Yamada, H. Suzuki, and T. Hayashi, *Jpn. J. Appl. Phys.*, **37**, 5128-31 (1998).
[6] H. Suzuki, Y. Kondo, S. Kaneko and T. Hayashi, *Mater. Res. Soc. Symp. Proc.*, **596**, 241-46 (2000).
[7] H. Suzuki, S. Kaneko, K. Murakami, and T. Hayashi, *Jpn. J. Appl. Phys.*, **36**, 5803-07 (1997).
[8] D. V. Taylor and D. Damjanovic, *Appl. Phys. Lett.*, **76**, 1615-17 (2000).
[9] S. Y. Chen and C. L. Sun, *Appl. Phys. Lett.*, **90**, 2970-74 (2001).
[10] I. Kanno, S. Fujii, T. Kamada and R. Takayama, *Appl. Phys. Lett.*, **70**, 1378-80 (1997).
[11] K. Nagashima, M. Aratani and H. Funakubo: *Appl. Phys. Lett.*, **89**, 4517-22 (2001).
[12] X. Du, U. Belegundu and K. Uchino, *Appl. Phys. Lett.*, **72**, 2421-23 (1998).
[13] D. S. Fu, H. Suzuki, T. Ogawa, and K. Ishikawa, *Appl. Phys. Lett.*, **80**, 3572 -74(2002).
[14] D. S. Fu, K. Ishikawa, Y. Yoshimi, and H. Suzuki, *Jpn. J. Appl. Phys.*, **41**, L580-82 (2002).
[15] D. S. Fu, K. Ishikawa, M. Minakata, and H. Suzuki, *Jpn. J. Appl. Phys.*, **40**, 5683-86 (2001).

(Received October 8, 2003; Accepted March 12, 2004)