

Atmosphere Effects in Low Temperature Pyrolysis of Chemical Solution Derived Pb(Zr,Ti)O₃ Films

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Pb(Zr,Ti)O₃ (Pb:Zr:Ti=1:0.52:0.48) thin films were prepared on single crystal MgO(100) substrates by dipping-pyrolysis process using a solution of constituent metal naphthenates as starting materials. The solution was spin-coated onto substrate and the precursor films were pyrolyzed at 200°C in air or at 200°C in argon for 1, 2, 5 and 24 h, followed by final heat treatment at 750°C. For all the films, highly (*h*00)/(00*l*)-oriented Pb(Zr,Ti)O₃ thin films with smooth surfaces and crack-free were obtained, whereas thin film pyrolyzed in air for 24 h exhibited polycrystalline character. According to the pole-figure analysis, epitaxy of the product films was found to depend on pyrolysis atmosphere.

Key words : Pb(Zr,Ti)O₃, MgO, Dipping-pyrolysis process, Polycrystalline, Epitaxy

I. Introduction

In recent years, there has been an increasing interest in technical usage of ferroelectric thin films in electronic devices such as memories and sensors. Many of these applications require films with low defect density. Epitaxial Pb(Zr,Ti)O₃ (PZT) films have been successfully deposited by sputtering,¹⁾ sol-gel,²⁾ pulsed laser ablation³⁾ and metalorganic chemical vapor deposition (MOCVD).^{4,5)}

Unfortunately, the quality of the PZT films prepared by chemical solution method such as sol-gel and dipping-pyrolysis (DP) process often did not meet the standards of device engineering, since partial cracks and rosette-like grains were easily observed in product film owing to the vaporization of organic compounds during pyrolysis and heat treatment.

Using the X-ray diffraction (XRD) pole-figure analysis (β scanning), and asymmetric ω - 2θ scans (reciprocal space mapping), we have examined the detailed microstructure of the PZT thin films on Nb-doped SrTiO₃ (100)⁶⁾ and MgO(100)⁷⁾ prepared by DP process for the first time. Pole-figure analysis indicates that the films are indeed epitaxial.

DP process consists of the following two heating stages; pyrolysis at 200°~500°C and final heating at 500°~1000°C. Pyrolysis is the process for pyrolytic conversion of metal organic acid salts into metal oxides, while the final heat treatment is the process of solid-state reaction among the constituent oxides. In the previous studies⁷⁾ on DP process, pyrolysis has been mostly carried out in the atmosphere of air, however, the present authors have suspected if the film might be excessively or locally heated up to the high temperature, such as 700°~800°C since the decomposed organic component during the pyrolysis

should be rapidly burnt in the oxidizing atmosphere. This case may cause the random nucleation and heterogeneous crystal growth, then disturb the high epitaxy. Thus, comparison between oxidizing atmosphere (air) and non-oxidizing atmosphere was considered to be important in order to achieve homogeneous nucleation giving the high epitaxy.

To make a comparison with the result of our previous report^{6,7)} in which pyrolysis was performed in air, in this work, we put a particular emphasis on examining the effect of atmosphere during the pyrolysis processes on the epitaxy of the film. According to the thermal analysis on Pb-, Zr- and Ti-naphthenate mixed solution, pyrolysis begins at 200°C and completes below 500°C. In this work, therefore, pyrolysis temperature was fixed at 200°C and holding time was varied in order to clearly investigate the effect of atmosphere.

II. Experimental

The experimental procedure and the reagents used in this study were reported previously.⁷⁾ Briefly, the spin-on solution was prepared from lead-, zirconium-, and titanium-naphthenates dissolved in toluene in a concentration corresponding to 35.2 mg metal/ml solution. Excess Pb (5 mol%) was added to the solution to compensate for PbO loss occurring during the heat treatments of the PZT films.

The solution was spin-coated onto the cleaned MgO substrate (10 mm × 10 mm × 0.5 mm³) for 10 sec at 4000 rpm. The coated films were dried at 110°C for 30 min in air and as denoted in Table 1. The following two pyrolysis atmospheres were adopted in pre-firing: i) pyrolysis at 200°C in air for 1, 2, 5 or 24 h, and ii) pyrolysis at 200°C in argon for 1, 2, 5 or 24 h, respectively. The

Table 1. Denotation of Films Prepared.

Pyrolysis condition (at 200°C)		
Time (h)	air	argon
1	A1	B1
2	A2	B2
5	A3	B3
24	A4	B4

* In all the samples, final heat-treated condition was fixed at 750°C for 30 min in air.

spin coating and pyrolysis were repeated five times to adjust the thickness of the precursor films. The films were subsequently heat-treated at the final temperature of 750°C for 30 min in air by directly inserting the samples into a preheated furnace, then rapidly cooled to room

temperature.

The thickness of the product films was 0.4~0.6 μm, confirmed by both the measurement of weight gain and the observation of fracture cross section of the films with a scanning electron microscope (SEM). Crystallinity and in-plane alignment of the product films were analyzed by XRD θ -2 θ scans and X-ray pole-figure analysis (β scanning) (MAC Science, MXP^{SA}) using CuK α radiation by Schulz reflection method. Residual carbon was observed by SEM with energy dispersive X-ray spectroscopy (EDS) (JED-2100) equipped with an ultra thin-film window (UTW) type X-ray detector. Surface morphology was observed by SEM.

III. Results and discussion

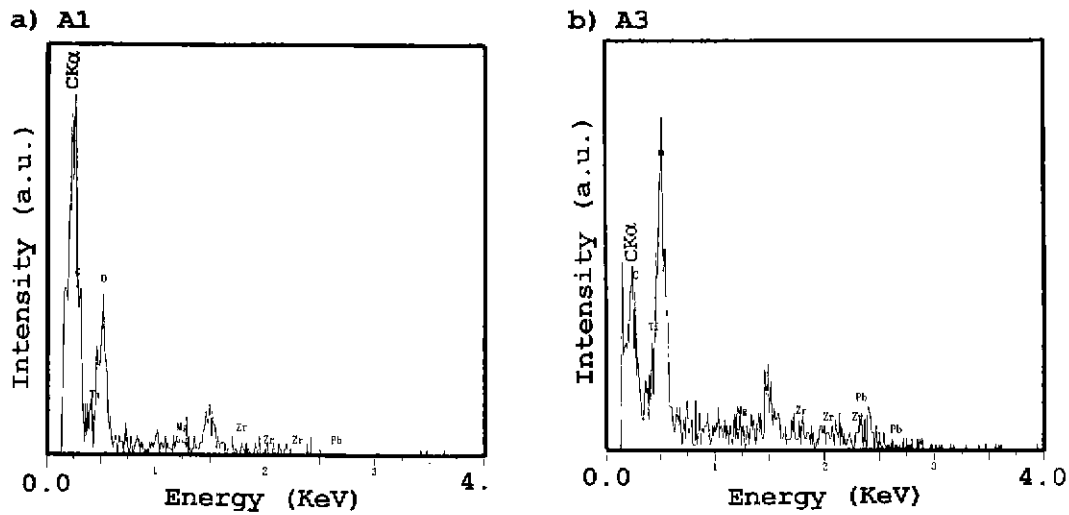


Fig. 1. EDS spectra of precursor films pyrolyzed at 200°C for 1 h in air (a) and at 200°C for 5 h in air (b), respectively.

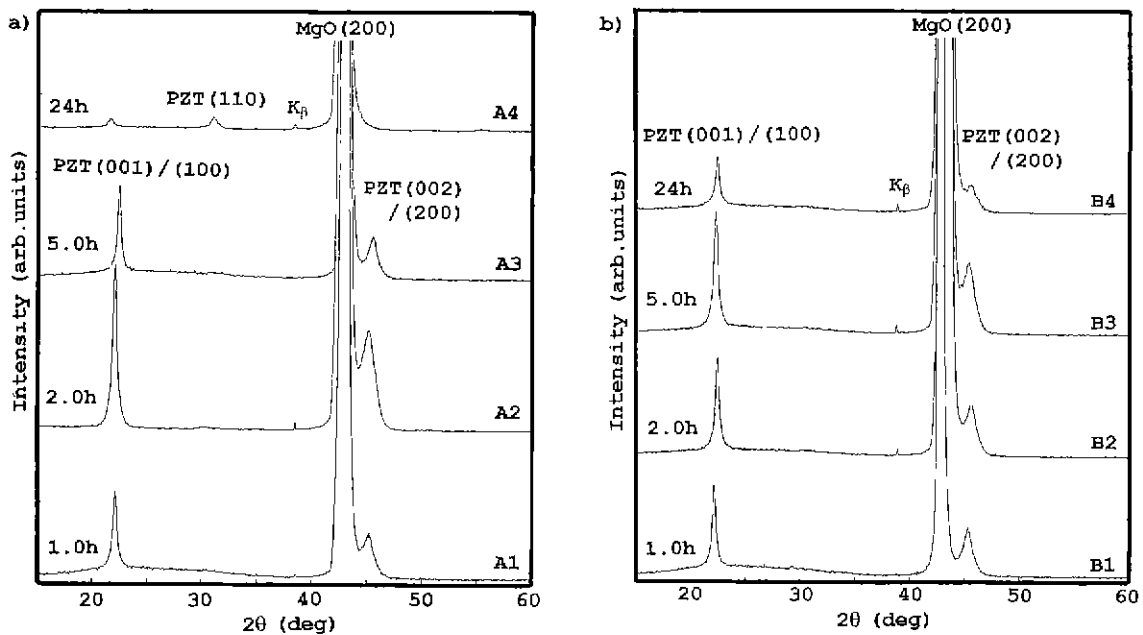


Fig. 2. XRD θ -2 θ scans of PZT films A1-A4 (a) and B1-B4 (b), respectively.

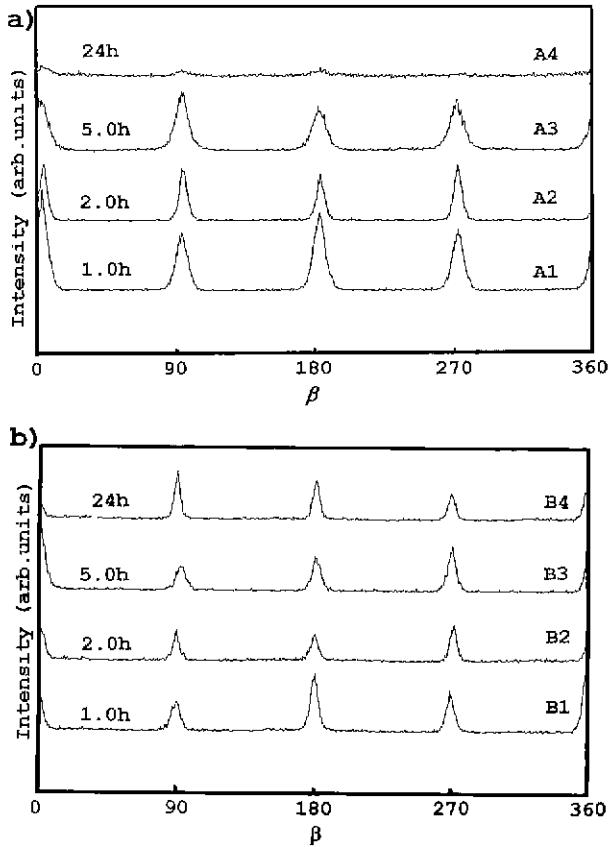


Fig. 3. Line profiles of β scans of PZT(110)/(101) reflection for PZT films on MgO(100).

Residual carbon content in the precursor films was investigated by EDS. Figures 1 (a) and (b) show EDS spectra of the films pyrolyzed at 200°C in air for 1 h and

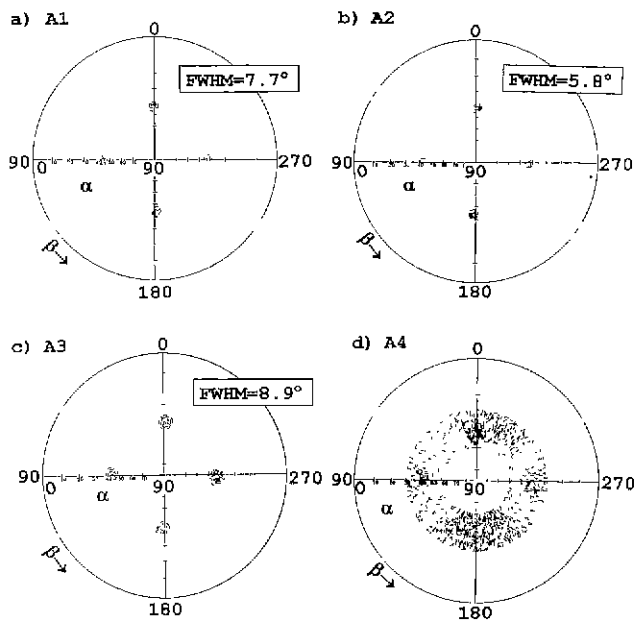


Fig. 4. X-ray pole figures of PZT(110)/(101) reflection for PZT films A1-A4 on MgO(100).

at 200°C in air for 5 h, respectively. Comparing these two spectra, an apparent large peak of C-K α was recognized in Fig. 1 (a). Furthermore, precursor films pyrolyzed for 1 h contained a larger amount of carbon than those pyrolyzed for 5 h from the results of Figs. 1 (a) and (b).

Figures 2 (a) and (b) show the XRD patterns of PZT thin films pyrolyzed in air and in argon for different pyrolysis time. Obviously, (h00)/(00l)-oriented single perovskite phase was formed and the reflections of other phases such as pyrochlore or PZT(110) (tetragonal indices) were not recognized. This means that the films are highly oriented since the PZT(110) is the strongest peak of powder diffraction pattern, in all the samples except the film A4. The pattern of the film A4 indicates that the film is polycrystalline. The longer pyrolysis time gives the higher peak intensity for the films A1 and A2.

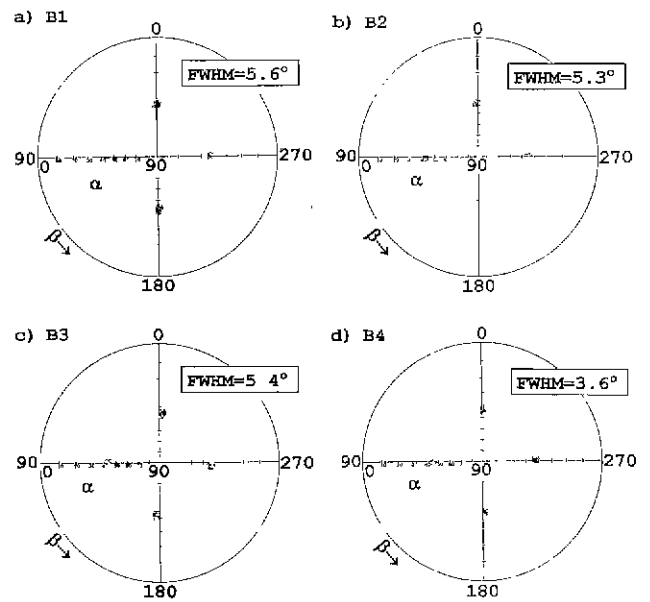


Fig. 5. X-ray pole figures of PZT(110)/(101) reflection for PZT films B1-B4 on MgO(100).

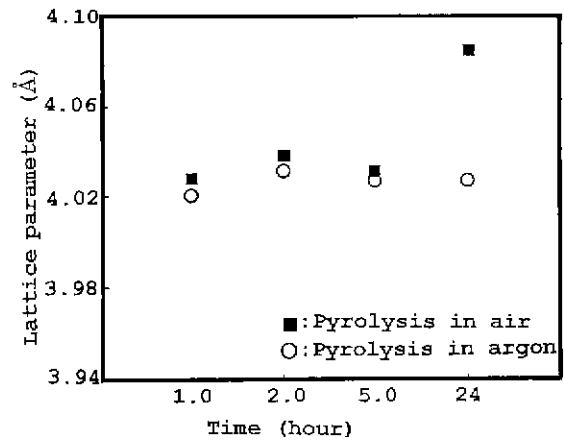


Fig. 6. Lattice parameters (d) of PZT films prepared.

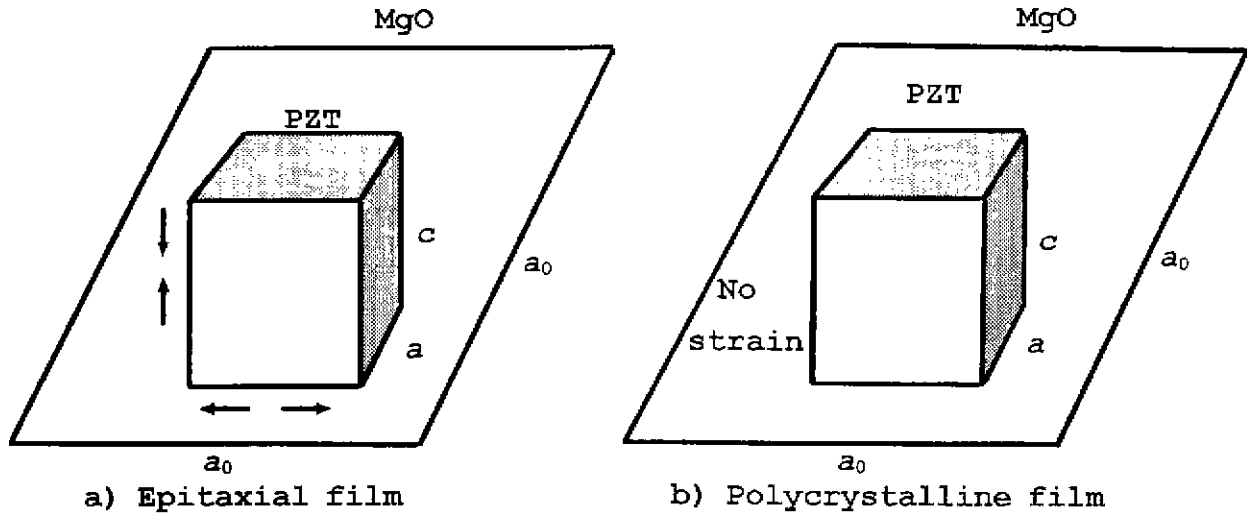


Fig. 7. Schematic of grain growth of epitaxial PZT films (a) and polycrystalline PZT films (b) on MgO, respectively. The arrows indicate the direction of stress.

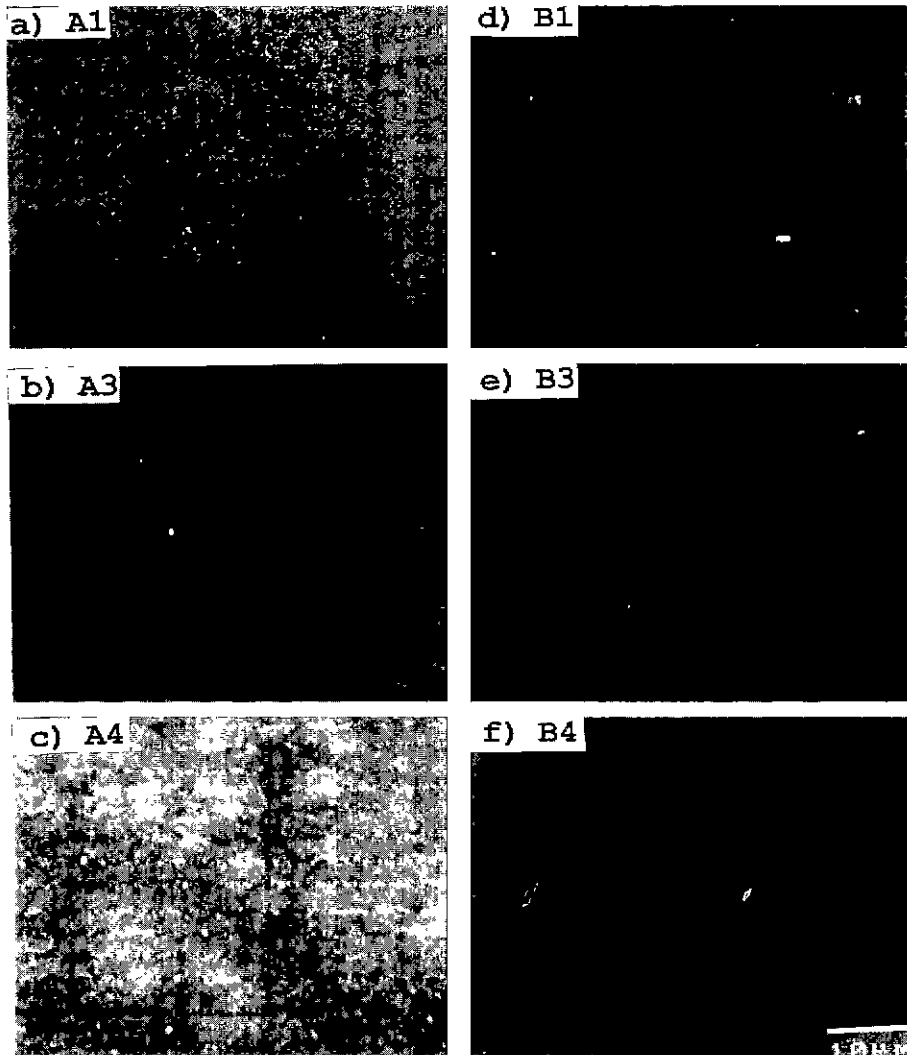


Fig. 8. SEM photographs of the free surfaces of PZT films on MgO(100).

In contrast, for the films A3 and A4, (*h*00)/(00*l*)-oriented peak intensity became smaller when the pyrolysis time became longer. As shown in Fig. 2 (b), the film B4 pyrolyzed for 24 h in argon exhibits lower peak intensities than those of films pyrolyzed for a shorter time, but it is still (*h*00)/(00*l*)-oriented.

As a result, it can be considered that the presence of oxygen affects the orientation of the product films. The higher oxygen content in the pyrolysis environment can facilitate the oxidation of organics during the long time treatment and inhibit the orientation as shown in the film A4. Using the pole-figure analysis described later, this effect is more clearly confirmed.

To investigate the in-plane alignment of these films, XRD pole-figure analysis was performed. Figures 3 (a) and (b) and Figs. 4 and 5 show the β scans and resultant pole-figures of PZT(110)/(101) reflection for these films. After setting 2θ at 31.61° which corresponds to PZT(110) reflection, each film was rotated from $\beta=0^\circ$ to 360° at tilted angles between $\alpha=30^\circ$ to 60° . Highly oriented PZT films gave four sharp peaks. The β angles of these peaks were 45° -misoriented to MgO(111) reflection for each film, whereas no distinct spots or rings were obtained in the film A4. This means that these PZT films have grown epitaxially with *c*- or *a*-axis perpendicular to the substrate surface. The full widths at half-maximum (FWHMs) of the spots along the β direction decreased with increasing pyrolysis time, for the films pyrolyzed in argon. The film B4 exhibited the lowest FWHM, i. e., 3.6° . This means that the longer pyrolysis time in argon gives the better epitaxy of the product films. Moreover, the FWHM of the films pyrolyzed in air becomes greater than those for the films pyrolyzed in argon. Therefore, from the above results, we can confirm that, in pyrolysis, the presence of O₂ affect the epitaxy of PZT on MgO.

We also examined the lattice parameters of the films prepared. Using the (200) reflection of MgO substrate as an internal standard, we estimated the lattice parameters (d_{\perp}) of the product films as shown in Fig. 6. The d_{\perp} -values of the epitaxial films are far closer to the *a*-axis parameter of tetragonal PZT ($a_0=0.4036$ nm) than c_0 (0.4146 nm) [a_0 and c_0 are the values at morphotropic phase boundary (MPB)]. Thus, as shown in Fig. 7 (a), *a*-axis orientation can be reasonably considered to take place in the present films based on the following reason; compressive film stress, primarily due to the expansive stress parallel to the substrate surface, causes the small d_{\perp} -value almost agree with a_0 . On the other hand, $d_{\perp}=0.4085$ nm for the film A4 is considerably larger than that of others. Since the film A4 is polycrystalline, the d_{\perp} -length is assumed not to be affected by the MgO substrate, as shown in Fig. 7 (b).

SEM photographs of the free surfaces for films are shown in Fig. 8. Rosette-like grains up to ~ 5 μ m in size

were easily observed on the free surface of the film A4 [Fig. 8 (c)]. On the contrary, the film B4 gave remarkably smooth surfaces at the same magnification as shown in Fig. 8 (f).

In this study, we can conclude that pyrolysis in argon improves epitaxy of the product films and homogeneity of surface morphology.

IV. Conclusion

We have demonstrated that fabrication of PZT thin films using Pb-, Zr- and Ti-naphthenates as starting materials is feasible. The effect of atmosphere during the pyrolysis processes on the crystallinity and epitaxy of the film was discussed. For all the samples except the film pyrolyzed in air for 24 h, PZT films with smooth surfaces exhibited (*h*00)/(00*l*) orientation. Pyrolysis at low temperature (200°C) in a non-oxidizing atmosphere (argon) was found to be most important to obtain the epitaxy of the product film.

References

1. R. Takayama and Y. Tomita, "Preparation of Epitaxial Pb(Zr,Ti)_{1-x}O₃ Thin Films and Their Crystallographic, Piezoelectric and Ferroelectric Properties," *J. Appl. Phys.*, **65**(4), 1666-1670 (1989).
2. K. Nashimoto and S. Nakamura, "Preparation and Characterization of Sol-Gel Derived Epitaxial and Oriented Pb(Zr_{0.62}Ti_{0.48})O₃ Thin Films," *Jpn. J. Appl. Phys.*, **33**, 5147-5150 (1994).
3. S. H. Ling, Y. S. Tang, W. S. Au and H. K. Wong, "Epitaxial Growth of Pb(Zr,Ti)O₃ Films on MgAl₂O₄ by Pulsed Laser Deposition," *Appl. Phys. Lett.*, **62**(15), 1757-1759 (1993).
4. M. Shimizu and T. Shiosaki, "Growth and Characterization of Pb-based Ferroelectric Oxide Thin Films by MOCVD"; pp. 129-138 in *Treatise on Epitaxial Oxide Thin Films*, Vol. 401, Epitaxial Oxide Thin Films II, Edited by J. S. Speck, D. K. Fork, R. M. Wolf and T. Shiosaki, Materials Research Society, Pittsburgh, 1996.
5. M. de Keijser, J. F. M. Cillessen, R. B. F. Janssen, A. E. M. De Veirman and D. M. de Leeuw, "Structural and Electrical Characterization of Heteroepitaxial Lead Zirconate Titanate Thin Films," *J. Appl. Phys.*, **79**(1), 393-402 (1996).
6. K. S. Hwang, T. Manabe, I. Yamaguchi, T. Kumagai and S. Mizuta, "Preparation of Epitaxial Pb(Zr,Ti)O₃ Thin Films on Nb-doped SrTiO₃(100) Substrates by Dipping-Pyrolysis Process," *Jpn. J. Appl. Phys.*, **36**, 5221-5225 (1997).
7. K. S. Hwang, T. Manabe, I. Yamaguchi, S. Mizuta and T. Kumagai, "Preparation of Epitaxial Pb(Zr,Ti)O₃ Thin Films on MgO(100) Substrates by Dipping-Pyrolysis Process," *J. Ceram. Soc. Jpn.*, **105**(11), 952-956 (1997).