Low-Temperature Preparation of Hydrothermal Lead Zirconate Titanate Thin Films

Kyung Won Seo[†] and Hyun Goo Kong

School of Chemical Engineering & Biotechnology, Ajou Univ., Suwon 442-749, Korea
(Received 8 March 2000 • accepted 29 May 2000)

Abstract—In preparing lead zirconate titanate thin films under hydrothermal conditions, we investigated the effects of concentrations of nutrient and mineralizer, reaction time and reaction temperature on crystallinity, grain size and shape. Experiments were performed in the ranges of 0.1-1.0 M Pb(NO_3)$_2$, and 0-6.0 M KOH with varying reaction time from 0 to 48 hours at 60-200 °C. In the experiment, lead zirconate titanate thin film of homogeneous crystalline grain was obtained through a 24 hour reaction with 0.4 M Pb(NO_3)$_2$ and 5.0 M KOH at 140 °C. The thickness of the film was 0.9-1.6 µm, and it exhibited a saturation polarization (Ps) of 18.3 µC/cm², remnant polarization (Pr) of 7.4 µC/cm² and coercive field (Ec) of 0.41 kV/cm. The dielectric constant and loss (δ) measured at 1 kHz were approximately 1020 and 0.15, respectively.

Key words: Lead Zirconate Titanate, Thin Films, Hydrothermal Conditions, Polarization, Dielectric Constant

INTRODUCTION

Recently, lead zirconate titanate thin films have been widely investigated for their applications in DRAM (dynamic random access memory) or NVRAM (non-volatile random access memory) because of their high values of dielectric constant (ε), remnant polarization (Pr) and Curie point [Park et al., 1995]. Reaction conditions for preparing lead zirconate titanate thin films have been studied because the properties of thin films strongly depend on reaction conditions such as ratios of Zr and Ti, annealing temperature and reaction time [Schwartz et al., 1997; Yi et al., 1984]. A variety of techniques such as sol-gel [Aoki et al., 1993], sputtering [Park et al., 1998] and chemical vapor deposition (CVD) [Kim et al., 1996] have been used to fabricate thin films. But these methods bring about undesirable chemical phenomena such as stoichiometric change of the film composition due to the loss of Pb component during the reaction and annealing process at high temperatures [Wang et al., 1999]. Therefore, when PZT thin film is fabricated using sol-gel or sputtering methods, an excess amount of Pb is required [Amanuma et al., 1993]. On the other hand, when the hydrothermal synthetic method is introduced for thin film fabrication, films of homogeneous and uniform grain size having high crystallinity can be prepared directly from feed stock solution without a high temperature calcination step [Seo and Kong, 1999; Kajiyoshi et al., 1991]. Hydrothermal synthesis has been recognized as a wet-chemistry technique that produces complex inorganic oxide powders in supercritical state and/or sub-critical state [Seo and Oh, 2000; Jung and Seo, 1997].

In this study, the effects of process parameters such as nutrient concentration, mineralizer concentration, reaction time and reaction temperature on crystallinity, grain size, grain shape and physical property of hydrothermally prepared lead zirconate titanate thin films for DRAM or NVRAM applications were investigated.

EXPERIMENTAL

Pb(NO_3)$_2$ solution (0.1-0.5 M) was put into an autoclave with the addition of a mineralizer, KOH. Mineralizer was added to increase the solubility of the feedstock, which results in a decrease in the required reaction temperature for crystal formation. The mole ratio of Pb/Zr/Ti in reactant solution was 1.0/0.52/0.48. Then a Ti-metal substrate was put into the mixed solution. The autoclave had a 500 ml working volume. The volume of the feedstock remained constant throughout the experiment. The range of reaction time was 0 to 48 hours, that of reaction temperature was 60 to 200 °C and that of the mineralizer concentrations was 0 to 6.0 M. After the autoclave apparatus cooled down, the product was washed consecutively with de-ionized water, acetic acid and ethanol, and again with de-ionized water to remove impurities. The chemicals used in this procedure were extra pure reagent grade [Seo and Kong, 1999]. The experimental procedures are schematically shown in Fig. 1.

In the experiment, Ti-metal substrate of 99% purity was cleansed with acetone, methanol and de-ionized water consecutively, then etched with hydrofluoric acid in order to remove the oxide layer, and rinsed again with de-ionized water.

To determine the degree of relative crystallinity of the products, the synthetic film was analyzed by X-ray diffractometer (XRD: MXP3, Mac Science Co.) using a monochromatic CuK$_\alpha$ radiation, 40 kV, 30 mA in the range of 20-60°. The surface roughness, morphology, microstructure and cross-section of the film were observed using a scanning electron microscope (SEM: JSM-840A, JEOL) and an atomic force microscope (AFM: PARK, Scientific instrument LS). The film composition and its depth profile were measured by auger electron spectroscopy (AES: PERKIN-ELMER, PHI-670). The thickness of the thin film was measured by the mechanical stylus profilometer (Tensor, P-10). To measure electrical properties of the thin film, Au was deposited on the film surface as a top electrode. The dot size was 200 µm in diameter. The remnant polarization (Pr) and coercive field (Ec) were determined

---

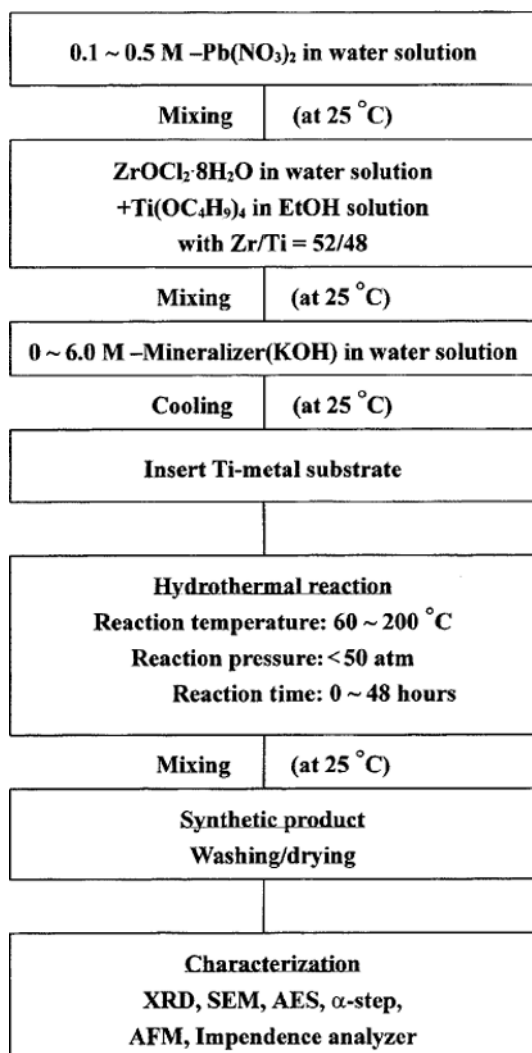[†]To whom correspondence should be addressed.
E-mail: kwseoi@madang.ajou.ac.kr

Fig. 1. Experimental procedures.

Fig. 2. XRD patterns of product thin films prepared with various Pb(NO₃)₂ concentrations and 5.0 M KOH from a 24 hour reaction at 140 °C.

Fig. 3. SEM photographs of PZT thin film prepared with various Pb(NO₃)₂ concentrations and 5.0 M KOH from a 24 hour reaction at 140 °C (A: 0.2 M, B: 0.4 M).

from P-E hysteresis loops measured by a ferroelectric tester (RT-66A, Radiant Technologies, Inc.).

RESULTS AND DISCUSSION

1. Effect of Nutrient Concentration

Fig. 2 shows XRD patterns of PZT thin films formed on Ti-metal substrate in 24 hour reactions when different concentrations of nutrient were used with 5.0 M KOH at 140 °C. The mole ratios of the PZT solution were Pb/Zr/Ti=1.00/0.52/0.48. As shown in this figure, the peaks of crystalline PZT appeared at the concentration of Pb(NO₃)₂ over 0.25 M.

Fig. 3 shows SEM micrographs of Pb(NO₃)₂ thin films formed from a 24 hour reaction when (A) 0.2 M and (B) 0.4 M of Pb (NO₃)₂ were used with 5.0 M KOH at 140 °C. When the concentration of nutrient was low, as shown in Fig. 3(A), only amorphous PZT grains were set on the film surface. However, when the concentration of nutrient Pb(NO₃)₂ increased to 0.4 M, as shown in Fig. 3(B), crystal film of small, regular and compact grains (about 800 nm) was formed. We can confirm from these figures that PZT thin film with more regular and compact crystalline grains can be
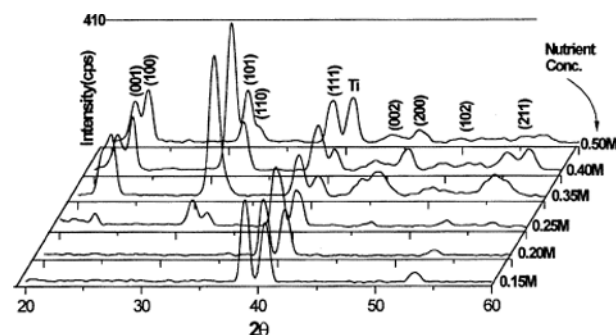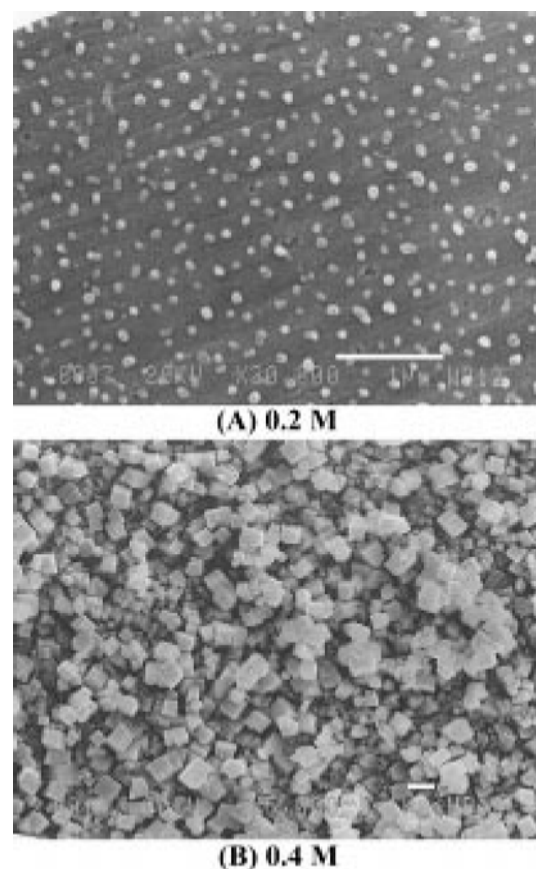
fabricated as the nutrient concentrations are increased.

Fig. 4 shows an SEM micrograph of the PZT thin film cross-section prepared from a 24 hour reaction at 140 °C when 0.4 M Pb(NO₃)₂ was used with 5.0 M KOH. As we can see in this figure, the Ti-metal layer and PZT layer are clearly distinguished. The thickness of the PZT layer was about 1.3 μm.

2. Effect of Mineralizer Concentration

Fig. 5 shows XRD patterns of PZT thin films formed from a 24 hour reaction when different concentrations of mineralizer were used with 0.4 M Pb(NO₃)₂ at 140 °C. Peaks of PZT crystallites did not appear when the concentration of mineralizer (KOH) was be-
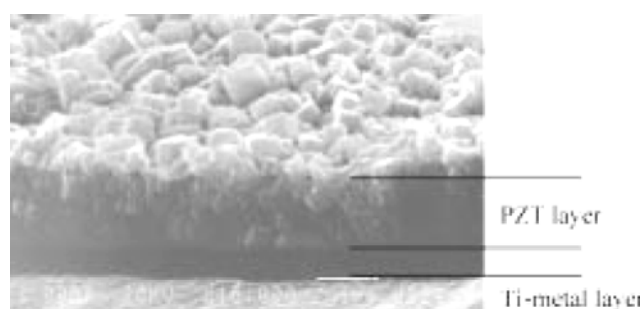
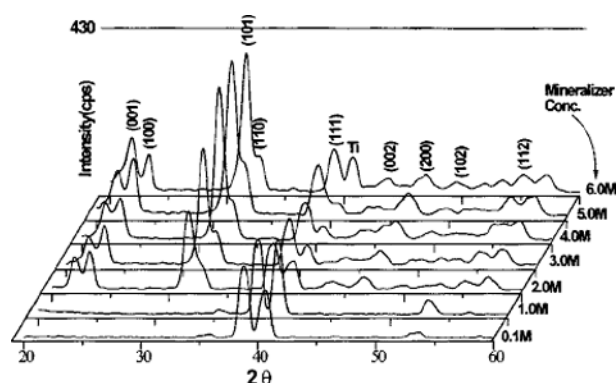Fig. 4. SEM micrograph of PZT thin film cross-section with 0.4 M Pb(NO₃)₂ and 5.0 M KOH from a 24 hour reaction at 140 °C.

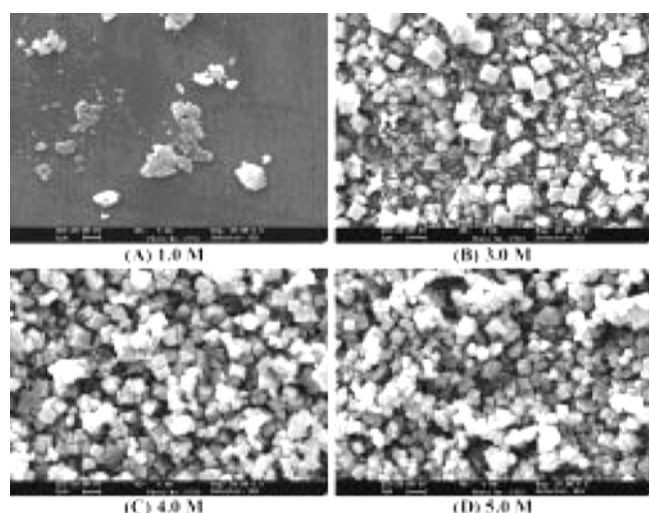Fig. 5. XRD patterns of product thin films prepared with various mineralizer concentrations and 0.4 M Pb(NO₃)₂ from 24 hour reaction at 140 °C.

Fig. 6. SEM micrographs of product thin films prepared with various mineralizer concentrations and 0.4 M Pb(NO₃)₂ from a 24 hour reaction at 140 °C (A: 1.0 M, B: 3.0 M, C: 4.0 M, D: 5.0 M).

low 0.1 M, but were seen when the concentration of mineralizer was over 2.0 M.

Fig. 6 shows SEM micrographs of PZT thin films formed from a 24 hour reaction when (A) 1.0 M, (B) 3.0 M, (C) 4.0 M and (D) 5.0 M of mineralizer (KOH) were used with 0.4 M Pb(NO₃)₂ at
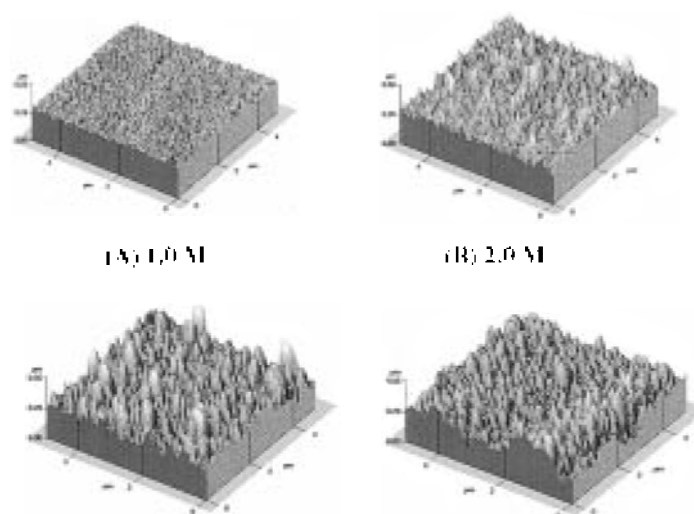

Fig. 7. AFM micrographs of product thin films for different mineralizer concentrations with 0.4 M Pb(NO₃)₂ from a 24 hour reaction at 140 °C (A: 1.0 M, B: 2.0 M, C: 4.0 M, D: 5.0 M).

140 °C. As we can see in these micrographs, amorphous PZT grains were partly formed on the surface of Ti-metal substrate when the concentration of mineralizer was 1.0 M. And, as the concentration of mineralizer increased, smaller and more compact PZT grains were formed. The sizes of PZT grains shown in these figures are about (B) 100-1,000 nm, (C) 600 nm and (D) 400-600 nm. From this result we can say that the relative supersaturation of the reactant solution increases as the concentration of mineralizer increases, and therefore, the nucleation rate becomes relatively faster than the growth rate, and the number of crystal grains increases, but the size decreases.

Fig. 7 shows AFM micrographs of PZT thin films formed from a 24 hour reaction when different concentrations of mineralizer (KOH) were used with 0.4 M Pb(NO₃)₂ at 140 °C. The surface of the PZT thin films roughened as the concentration of mineralizer increased. However, when the concentration of mineralizer was over 5.0 M, the roughness of the PZT thin films decreased. This result was due to the fact that re-dissolution of crystallites by the strong alkali solution increased as the concentration of mineralizer increased. Therefore, the optimum amount of mineralizer should
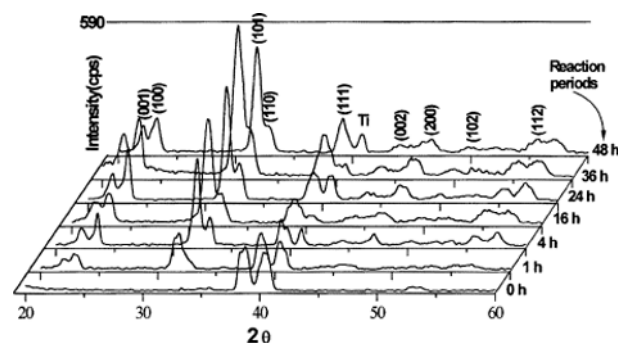

Fig. 8. XRD patterns of product thin films prepared for different reaction times with 0.4 M Pb(NO₃)₂ and 5.0 M KOH at 140 °C.
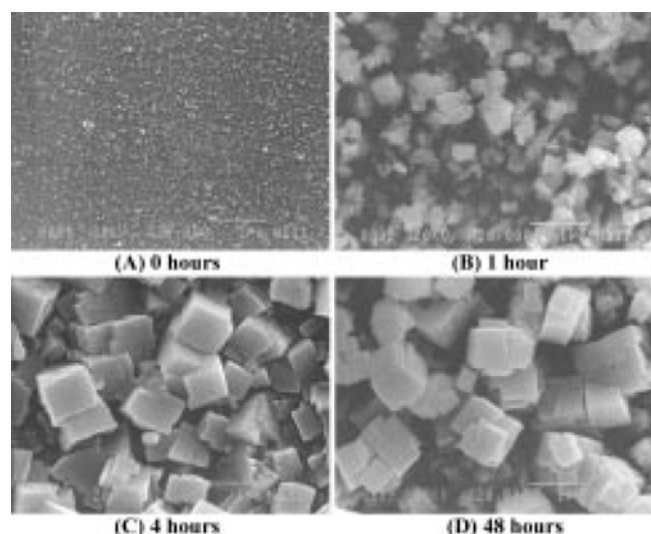
Fig. 9. SEM micrographs of product thin films prepared for different reaction times with 0.4 M Pb(NO₃)₂ and 5.0 M KOH at 140 °C (A: 0 hour, B: 1 hour, C: 4 hours, D: 48 hours).

Fig. 11. SEM micrographs of product thin films prepared at different reaction temperatures with 0.4 M Pb(NO₃)₂ and 5.0 M KOH from a 24 hour reaction (A: 120 °C, B: 140 °C, C: 160 °C, D: 180 °C).

be used for the best fabrication of thin films under hydrothermal conditions [Seo and Kong, 1999].

3. Effect of Reaction Times

Fig. 8 shows XRD patterns of PZT thin films formed on Ti-metal substrate at 140 °C with different reaction times when 0.4 M Pb(NO₃)₂ and 5.0 M KOH were used. As shown in the figure, the crystallinity of the PZT thin film was enhanced as the reaction time increased.

Fig. 9 shows SEM micrographs of these PZT thin films. PZT thin films of homogeneous crystal grains were obtained with reaction times of 4 hours or more. The crystalline grains on the film surface became more compact and clearly distinguished as the reaction time increased. The size of the PZT crystal grains shown in Fig. 9(C) ranged from 600 to 800 Å and in Fig. 9(D) from 400 to 700 Å.

4. Effect of Reaction Temperature

Fig. 10 shows XRD patterns of PZT thin films formed at different reaction temperatures from a 24 hour reaction when 0.4 M Pb(NO₃)₂ and 5.0 M KOH were used. The PZT crystallite peaks

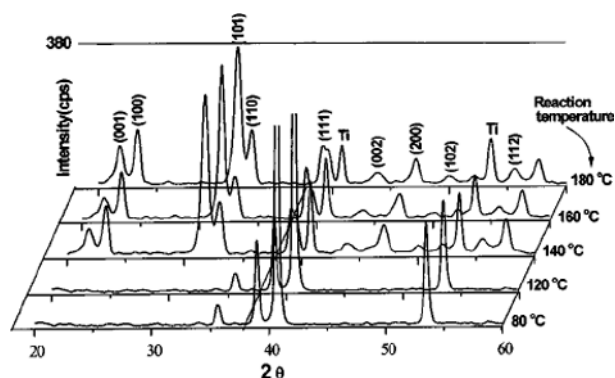of perovskite structure ($2\theta=22°$, $31°$, $45°$ and $55°$) appeared at reaction temperatures over 140 °C.

Fig. 11 shows SEM micrographs of PZT thin films formed from a 24 hour reaction when 0.4 M Pb(NO₃)₂ was used with 5.0 M of mineralizer (KOH) at different reaction temperatures. As the reaction temperature increased, as we can see in Fig. 11(B), (C) and (D), smaller and more compact PZT grains were formed at the surface of the thin film. The sizes of the PZT grains are about (B) 500 nm, (C) 450 nm and (D) 400 nm. It is expected that the grain size distribution becomes narrower as the reaction temperature increases due to an increase in the rate of the nuclei formation reaction [Seo and Kong, 1999].

Fig. 12 shows the relation between film thickness and reaction temperature. The thickness of PZT thin films was about 0.9-1.6 μm at 140-170 °C. As we can see in the figure, the thickness of PZT thin films increased gradually up to 170 °C. However, when the reaction temperature was raised to over 170 °C, the film thickness decreased drastically. Therefore, we can say that the depend-

Fig. 10. XRD patterns of product thin films prepared at different reaction temperatures with 0.4 M Pb(NO₃)₂ and 5.0 M KOH from a 24 hour reaction.

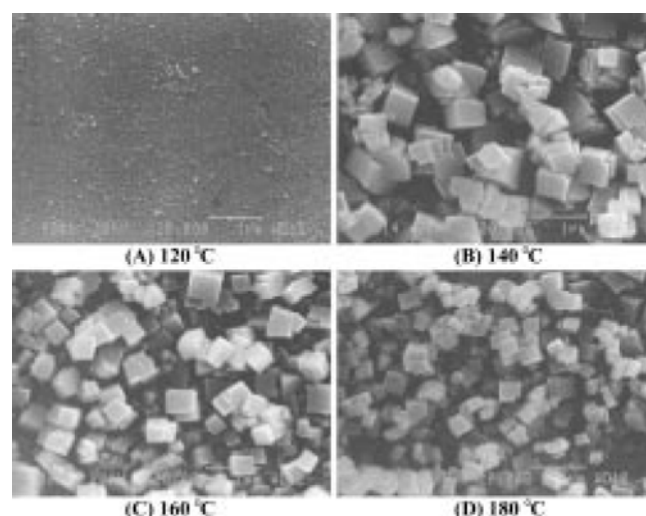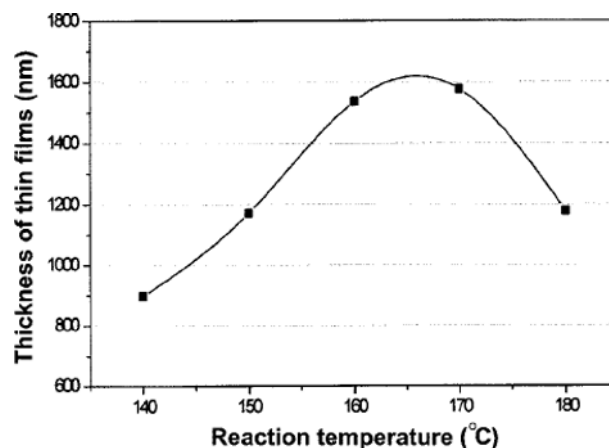Fig. 12. Relation between film thickness and reaction temperature.

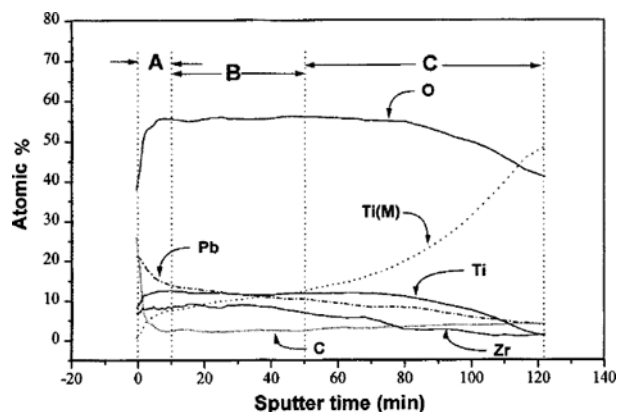**Fig. 13. AES depth profile of PZT thin film prepared with 0.4 M Pb(NO₃)₂ and 5.0 M KOH from a 24 hour reaction at 140 °C.**

ency of film thickness on the reaction temperature is significant.

5. Electrical Properties

Fig. 13 shows the AES depth profiles of Pb, Zr, Ti, O and C in the PZT thin film from the surface up to the titanium layer, which was prepared at 140 °C from a 24 hour reaction using 0.4 M Pb(NO₃)₂ and 5.0 M KOH. The zirconium and titanium signals followed each other throughout the film, decreasing slowly as the titanium metal was reached (in region 'C'). The amount of carbon was greatest at the film surface (in region 'A') due to the presence of absorbed carbon caused by atmospheric contamination. Only a trace amount of carbon was detected inside the film. Fig. 13 shows that an interdiffusion of Pb into a Ti bottom electrode was observed for the PZT thin film (in region 'C'). From this result we can say that the nonstoichiometric perovskite PZT layer was formed at the layer nearest the bottom electrode.

Fig. 14 shows a P-E hysteresis loop of a prepared PZT thin film that was measured by a Sawyer-Tower circuit. Au-top electrodes (200 μm in diameter) were evaporated at room temperature. Spontaneous polarization (Ps), remnant polarization (Pr) and coercive field (Ec) were about 18.3 μC/cm², 7.4 μC/cm² and 0.41 kV/cm, respectively. But the P-E hysteresis loop could not be measured at

high voltage, since the nonstoichiometric perovskite PZT layer was formed at the layer nearest the bottom electrode by an interdiffusion of Pb. Therefore, the perovskite PZT grains were not formed near the bottom electrode. Dielectric constants and dielectric loss (δ) of the thin film, which were measured at 1 kHz, were approximately 1020 and 0.15, respectively, at the room temperature.

CONCLUSION

Experiments were performed to investigate the effect of the reaction parameters, such as concentration of nutrient, mineralizer, reaction time and reaction temperature on PZT thin film fabrication under hydrothermal conditions. The results are summarized as follows:

1. When the concentration of nutrient, Pb(NO₃)₂, increased over 0.4 M, crystal film of small, regular and compact grains (about 800 nm) was formed.

2. As the concentration of mineralizer increased, smaller and the more compact PZT grains were formed.

3. PZT thin films of homogeneous crystal grains were obtained with reaction times of 4 hours or more when 0.4 M of Pb(NO₃)₂ was used with 5.0 M KOH.

4. As the reaction temperature increased to over 140 °C, smaller and more compact PZT grains were formed at the surface of the thin film. And the thickness of PZT thin films was about 0.9-1.6 μm at 140-170 °C.

5. Spontaneous polarization (Ps), remnant polarization (Pr) and coercive field (Ec) were about 18.3 μC/cm², 7.4 μC/cm² and 0.41 kV/cm, respectively. Dielectric constants and dielectric loss (δ) of the thin film, which were measured at 1 kHz, were approximately 1020 and 0.15, respectively, at room temperature.

REFERENCES

Amanuma, K., Mori, T., Hase, T., Sakuma, T., Ochi, A. and Miyasaka, Y., "Ferroelectric Properties of Sol-Gel Derived Pb(Zr, Ti)O₃ Thin Films," *Jpn. J. Appl. Phys.*, **32**(1), 4150 (1993).

Aoki, K., Fukuda, Y. and Nishimura, A., "Preparation of <100>-oriented Lead-Zirconate-Titanate Films by Sol-Gel Technique," *Jpn. J. Appl. Phys.*, **32**(1), 4147 (1993).

Jung, S. T. and Seo, K. W., "Studies on Characteristics of Hydrothermal Conditions in Preparing PZT Powders: Effect of Reaction Temperature, Mineralizer and Reaction Time," *HWAHAK KONGHAK*, **35**, 520 (1997).

Kajiyoshi, K., Ishizawa, N. and Yoshimura, M., "Preparation of Tetragonal Barium Titanate Thin Films on Titanium Metal Substrate by Hydrothermal Method," *J. Am. Ceram. Soc.*, **74**(2), 369 (1991).

Kim, Y. M., Lee, W. J. and Kim, H. G., "Deposition of PZT Films by MOCVD at Low Temperature and Their Charge in Properties with Annealing Temperature and Zr/Ti Ratio," *Thin Solid Films*, **279**, 140 (1996).
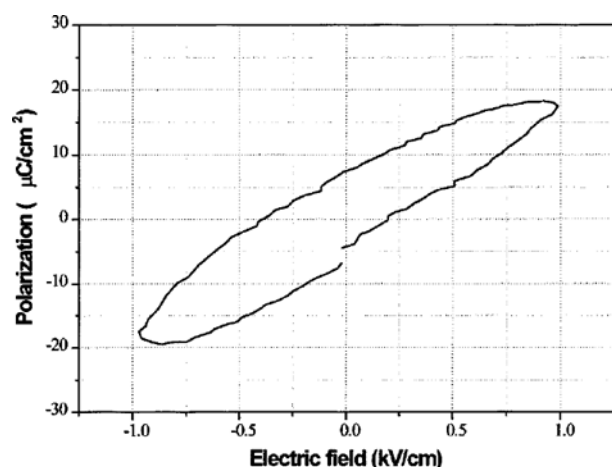

Fig. 14. P-E hysteresis loop of PZT thin film prepared with 0.4 M Pb(NO₃)₂ and 5.0 M KOH from a 24 hour reaction at 140 °C.

Park, H. H., Jin, I. S., Kim, D. H. and Kim, T. S., "Effect of Excess Pb and O Content the Ferroelectric Properties of Sputter Deposited Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$/Pt System," *Thin Solid Films*, **332**, 300 (1998).

Park, S. H., Kim, D. J., Streiffer, S. K. and Kingon, A. I., "Preparation and Ferroelectric Properties of Mixed Composition Layered Lead Zirconate Titanate Thin Films for Nonvolatile Memory Applications," *J. Mater. Res.*, **14**(6), 2476 (1995).

Schwartz, R. W., Voigt, J. A. and Tuttle, B. A., "Comments on the Effects of Solution Precursor Characteristics and Thermal Processing Conditions on the Crystallization Behavior of Sol-Gel Derived Lead Zirconate Titanate Thin Films," *J. Mater. Res.*, **12**(2), 144 (1997).

Seo, K. W. and Kong, H. G., "Hydrothermal Preparation of BaTiO$_3$ Thin Film," *Korean J. Chem. Eng.*, Submitted (1999).

Seo, K. W. and Oh, J. K., "Interpretation of Hydrothermal Crystallization of Fine BaTiO$_3$ Powders," *Korean J. Chem. Eng.*, **17**, 47 (2000).

Wang, Z., Maeda, R. and Kikuchi, K., "Effect of Pb Content on Electric Properties of Sol-Gel Derived Lead Zirconate Titanate Thin Films Prepared by Three-Step Heat-Treatment Process," *Jpn. J. Appl. Phys.*, **38**(1), 5342 (1999).

Yi, G., Wu, Z. and Sayer, M., "Preparation of Pb(Zr, Ti)O$_3$ Thin Films by Sol Gel Processing: Electrical, Optical, and Electro-Optic Properties," *J. Appl. Phys.*, **64**(5), 2717 (1984).