

## Hydrothermal Preparation of BaTiO<sub>3</sub> Thin Films

Kyung Won Seo<sup>†</sup> and Hyun Goo Kong

School of Chemical Engineering & Biotechnology, Ajou Univ., Suwon 442-749, Korea

(Received 5 October 1999 • accepted 14 March 2000)

**Abstract**—In preparing BaTiO<sub>3</sub> thin films under hydrothermal conditions, the effects of concentrations of nutrient and mineralizer, and reaction time on crystallinity, grain size, surface roughness, and film thickness were investigated. Experiments were performed in the ranges of 0.1–1.5 M BaCl<sub>2</sub> · 2H<sub>2</sub>O or Ba(OH)<sub>2</sub> · 8H<sub>2</sub>O and 0–1.5 M KOH with varying reaction time from 0.16 to 8 hours at 140 °C. Bimodal dispersion of crystalline grains on the surface of BaTiO<sub>3</sub> thin films was predicted through nucleation and crystal growth reaction. As the concentrations of nutrient and/or mineralizer increased, grain size of the thin film became smaller, but more uniform and compact. When 0.4 M Ba(OH)<sub>2</sub> · 8H<sub>2</sub>O was used with 1.0 M KOH, a reaction time longer than 4 hours was required in order to fabricate BaTiO<sub>3</sub> thin films.

Key words: Hydrothermal, BaTiO<sub>3</sub>, Thin Film, Bimodal Dispersion

### INTRODUCTION

BaTiO<sub>3</sub> ceramic has been used in capacitors, thermistors and sensors because of its high piezoelectricity, good PTCR (Positive Temperature Coefficient in Resistivity) characteristics and high dielectric constant (about 8,000), especially close to the Curie point (120 °C) [Smart and Moore, 1995]. Even at room temperature, the dielectric constant of BaTiO<sub>3</sub> is about 1,000–2,000, which is still higher than that of other materials. To maximize the above-mentioned properties such as permittivity, piezoelectricity and PTCR characteristics, the volumetric efficiency of BaTiO<sub>3</sub> should be improved. A recommended technique for enhancing volumetric efficiency is to fabricate thin films.

A variety of techniques such as sol-gel [Matsuda et al., 1993], sputtering [Craven et al., 1998] and chemical vapor deposition (CVD) [Funakubo et al., 1997] have been used to fabricate thin films. But the sol-gel method often brings about undesirable chemical phenomena, such as interdiffusion at the film-substrate interface, inhomogeneous crystallization and selective evaporation, which decrease the electrical properties of the final products [Yoshimura et al., 1989]. Sputtering and CVD methods also have disadvantages such as stoichiometric change of the film composition, unreacted source material remaining in the film, and cracking and/or peeling of the film [Cho and Yoshimura, 1997].

On the other hand, if a hydrothermal synthetic method was introduced for the thin film fabrication, films of homogeneous and uniform grain size having high crystallinity could be prepared directly from feed stock solution without a high temperature calcination step. Hydrothermal synthesis is a wet-chemistry technique that produces complex inorganic oxide powders in supercritical state and/or sub-critical state. By changing the reaction variables such as reaction temperature, reaction pressure, mineralizer concentration and additive concentration, nucleation and/or crystal growth rates can be controlled easily in the hydrothermal process. The

properties of thin films formed by the hydrothermal synthesis strongly depend on the reaction conditions [Lee et al., 1996; Seo and Lee, 1999; Kajiyoshi et al., 1991].

In this study, the effects of process parameters such as nutrient concentration, mineralizer concentration and reaction time on crystallinity, grain size, surface roughness and film thickness during hydrothermal crystallization of BaTiO<sub>3</sub> thin film on Ti-deposited Si(100) wafers were investigated.

### EXPERIMENT

The experimental procedures are schematically shown in Fig. 1. BaCl<sub>2</sub> · 2H<sub>2</sub>O or Ba(OH)<sub>2</sub> · 8H<sub>2</sub>O solution (0.1–1.5 M) was put into an autoclave with addition of mineralizer, KOH. Mineralizer was added to increase the solubility of the feedstock, which results in decreasing the required reaction temperature for crystal formation. Then a Ti-deposited Si(100) wafer was put into the mixed solution. The autoclave had 500 ml of working volume. The volume of the feedstock was kept constant throughout the experiments. The range of reaction time was 0.16 to 8 hours, and that of the mineralizer concentration was 0 to 1.5 M. However, the reaction temperature was fixed at 140 °C throughout this work as recommended in the previous research work [Oh and Seo, 1999].

After the autoclave apparatus cooled down, the product was washed successively with deionized water, acetic acid and ethanol, and again with deionized water to remove impurities. The product was then dried in a freezing dryer. The chemicals used in this work were extra pure reagent grade.

In this experiment, a p-type Si(100) wafer was cleansed with 1,1,2,2-tetrachloroethylene, acetone, methanol and deionized water successively. The Si(100) wafer was etched with hydrofluoric acid in order to remove the oxide layer, and rinsed with deionized water. After the Si(100) wafer was dried under N<sub>2</sub> gas ambient, Ti having thickness of about 1,000 Å was deposited on it by RF-magnetron sputtering to form Ti/SiO<sub>2</sub>/Si(100) on the surface.

To determine the degree of the relative crystallinity of products, the synthetic film was analyzed by X-ray diffractometer (XRD:

<sup>†</sup>To whom correspondence should be addressed.

E-mail: kwseo@madang.ajou.ac.kr

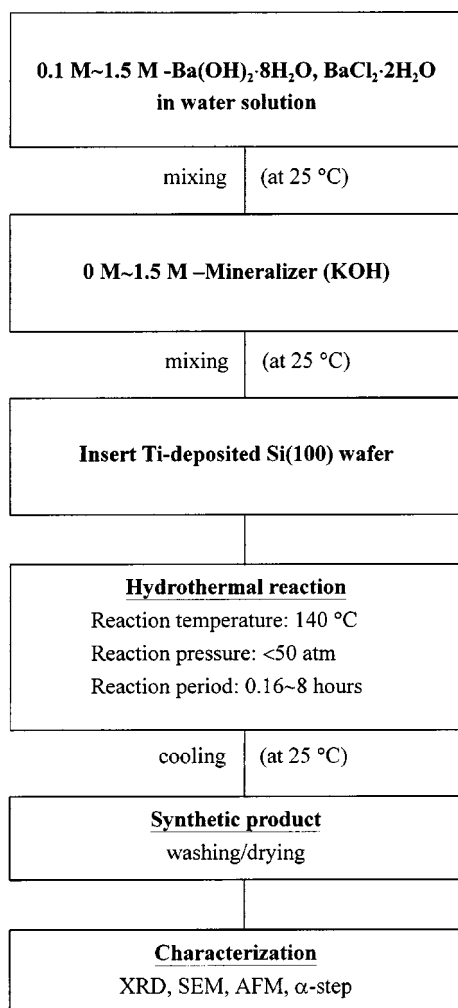


Fig. 1. Experimental procedures.

MXP3, Mac Science Co.) using a monochromatic CuK $\alpha$  radiation, 40 kV, 30 mA in the ranges of 20-70°. Surface roughness and cross-section of the film were observed by using a scanning electron microscope (SEM: JSM-840A, JEOL) and an atomic force microscope (AFM: PARK, Scientific instrument LS). The thickness of thin film was measured by the mechanical stylus profilometer (Tensor, P-10).

## RESULTS AND DISCUSSION

### 1. The Effect of Nutrient Concentration

Fig. 2 shows SEM micrographs of BaTiO<sub>3</sub> thin films formed for two-hour reactions when (A) 0.1 M, (B) 0.2 M, (C) 0.4 M and (D) 1.0 M of Ba(OH)<sub>2</sub> · 8H<sub>2</sub>O were used with 1.0 M KOH at 140 °C. Fig. 3 shows XRD patterns of these BaTiO<sub>3</sub> thin films where the peaks of crystalline BaTiO<sub>3</sub> appeared at the concentrations of Ba(OH)<sub>2</sub> · 8H<sub>2</sub>O over 0.4 M. When the concentration of nutrient was low, as shown in Fig. 2(A), only the amorphous BaTiO<sub>3</sub> grains were set on the film surface. However, when the concentration of nutrient, Ba(OH)<sub>2</sub> · 8H<sub>2</sub>O, increased over 0.4 M [Fig. 2(C) and (D)], crystal film was formed, the grain size of which was small and compact. From this figure, we could predict the bimodal dispersion of crystalline grains on the surface of thin film where the

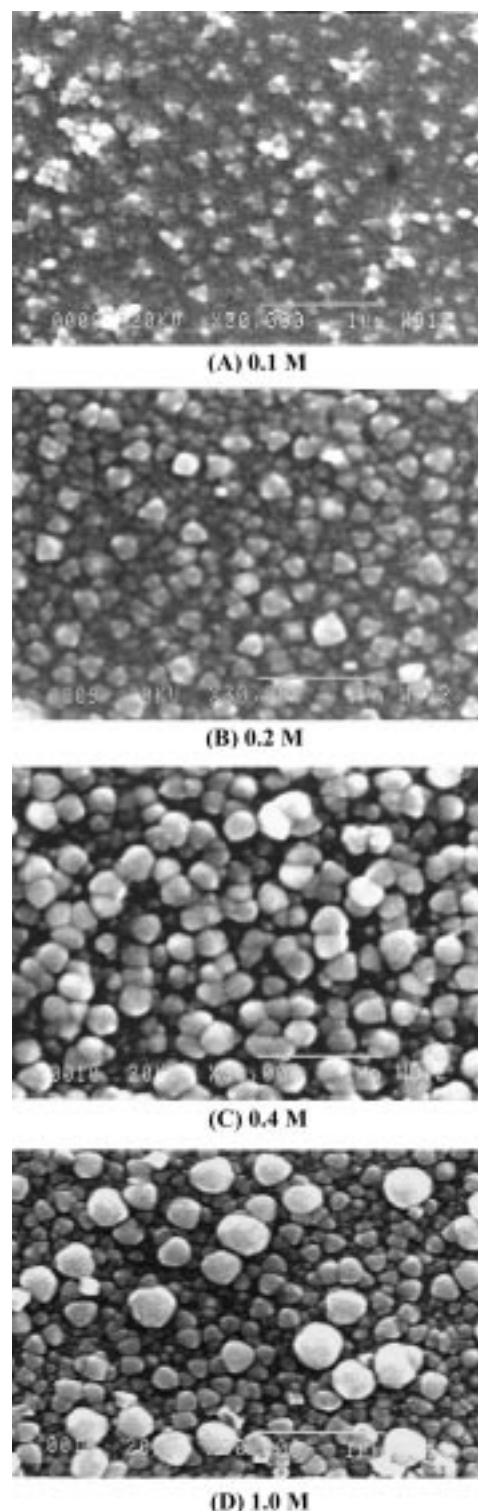


Fig. 2. SEM photographs of product thin film with various concentrations of Ba(OH)<sub>2</sub> · 8H<sub>2</sub>O and 1.0 M KOH for two-hour reactions at 140 °C (A: 0.1 M, B: 0.2 M, C: 0.4 M, D: 1.0 M).

smaller grains (about 1,800 Å) were located on the inner surface, while larger grains (about 3,700 Å) settled on the outer surface. As was mentioned in the previous research work [Seo and Oh, 2000], the crystal formation of BaTiO<sub>3</sub> powders underwent a first order

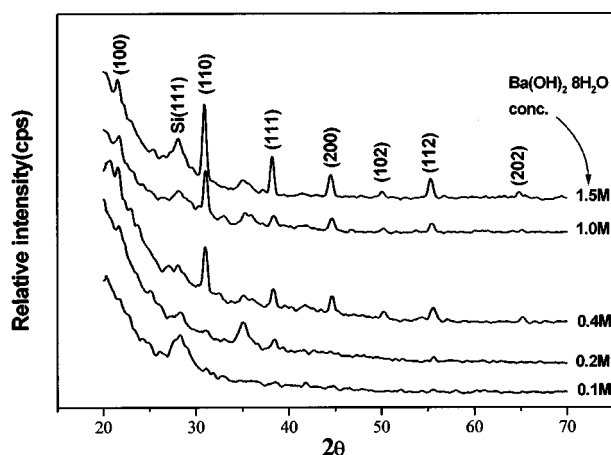


Fig. 3. XRD patterns of product thin films formed with various concentrations of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and 1.0 M KOH for two-hour reactions at 140 °C.

hydrolysis-condensation reaction with phase-boundary transition. Fig. 4 illustrates the crystal-formation mechanism of  $\text{BaTiO}_3$  thin film, the basic idea of which was referred from Basca et al. [Basca et al., 1992].  $\text{Ba}^{2+}$  ions diffuse through the boundary of the  $\text{BaTiO}_3$  crystals formed earlier to the surface of the substrate where Ti is deposited. Therefore, the grains which previously formed through nucleation reaction become larger by crystal growth reaction and are pushed out to the outer surface by small grains which are newly created on the Ti-deposited surface. Therefore, the bimodal dispersion of crystalline grains was obtained.

Fig. 5 shows an SEM micrograph of the  $\text{BaTiO}_3$  thin film cross-section prepared at 140 °C for two-hour reaction when 0.4 M  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  was used with 1.0 M KOH. As shown in this figure, the Si(100) wafer, Ti-deposited layer and  $\text{BaTiO}_3$  layer are clearly distinguished. The thickness of  $\text{BaTiO}_3$  layer was about 3,300 Å.

## 2. The Effect of Mineralizer Concentration

Fig. 6 shows SEM micrographs of  $\text{BaTiO}_3$  thin films formed for two-hour reactions when (A) 0.2 M, (B) 0.5 M, (C) 1.0 M and (D) 1.5 M of mineralizer (KOH) were used with 0.4 M  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  at 140 °C. As we can see in these micrographs,  $\text{BaTiO}_3$  crystals were partly formed on the surface of Ti-deposited Si(100) wafer when the concentration of mineralizer was low. However, as the concentration of mineralizer increased, smaller and more compact

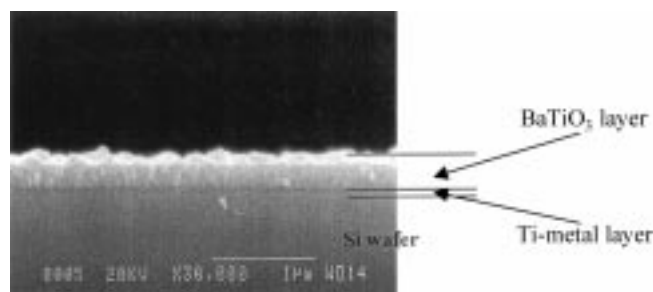


Fig. 5. SEM micrograph of the  $\text{BaTiO}_3$  thin film cross-section with 0.4 M  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and 1.0 M KOH for two-hour reactions at 140 °C.

$\text{BaTiO}_3$  grains were formed. The diameters of  $\text{BaTiO}_3$  grains shown in these micrographs are about (B) 3,800 Å, (C) 2,500 Å and (D) 2,200 Å. This result is due to the fact 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 reduces.

Fig. 7 shows AFM photographs of  $\text{BaTiO}_3$  thin films formed for two-hour reactions when the different concentrations of mineralizer (KOH) were used with 0.4 M  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  at 140 °C. The roughness of product  $\text{BaTiO}_3$  thin film was about  $\pm 41.1$  Å and  $\pm 1,400$  Å, respectively, when (A) 0.2 M and (B) 1.5 M of mineralizer was used. The surface of Ti-deposited Si(100) wafer became roughened as the concentration of mineralizer increased. Therefore, for the better thin film preparation of uniform and homogeneous crystal grains under hydrothermal conditions, an appropriate amount of mineralizer should be used.

## 3. The Effect of Reaction Times

Fig. 8 shows XRD patterns of  $\text{BaTiO}_3$  thin films formed on Ti-deposited Si(100) wafer at 140 °C for different reaction times when 0.4 M  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and 1.0 M KOH were used. As shown in this figure, the crystallinity of  $\text{BaTiO}_3$  thin film was enhanced as the reaction time increased. The  $\text{BaTiO}_3$  thin film of uniform and homogeneous crystal grains was obtained at reaction times greater than two hours. Fig. 9 shows SEM micrographs of these  $\text{BaTiO}_3$  thin films. We can confirm from these micrographs that the crystalline grains became clearly distinguished as the reaction time increased. The diameter of  $\text{BaTiO}_3$  crystal grains shown in these micrographs ranged from 2,100 to 3,700 Å. From these results it

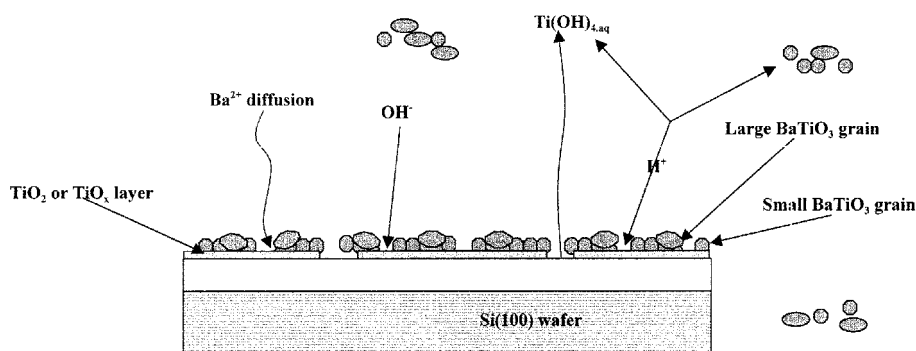


Fig. 4. Deposition scheme of crystal grains for the formation of  $\text{BaTiO}_3$  thin film under hydrothermal conditions.

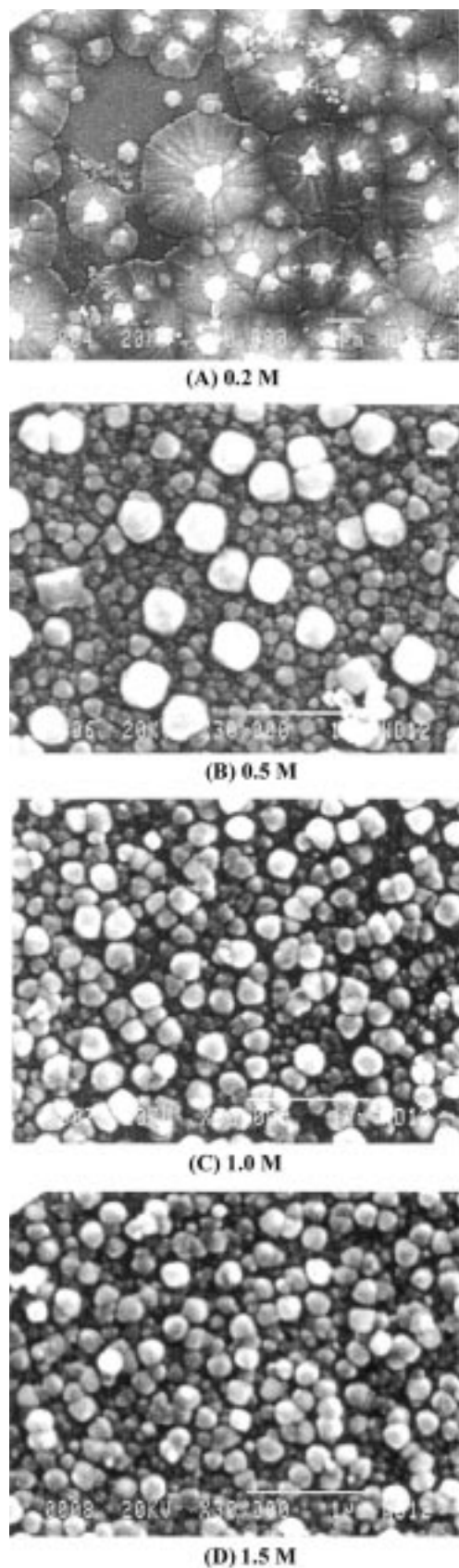


Fig. 6. SEM micrographs of product thin films with various concentrations of mineralizer and 0.4 M BaCl<sub>2</sub> · 2H<sub>2</sub>O for two-hour reactions at 140 °C (A: 0.2 M, B: 0.5 M, C: 1.0 M, D: 1.5 M).

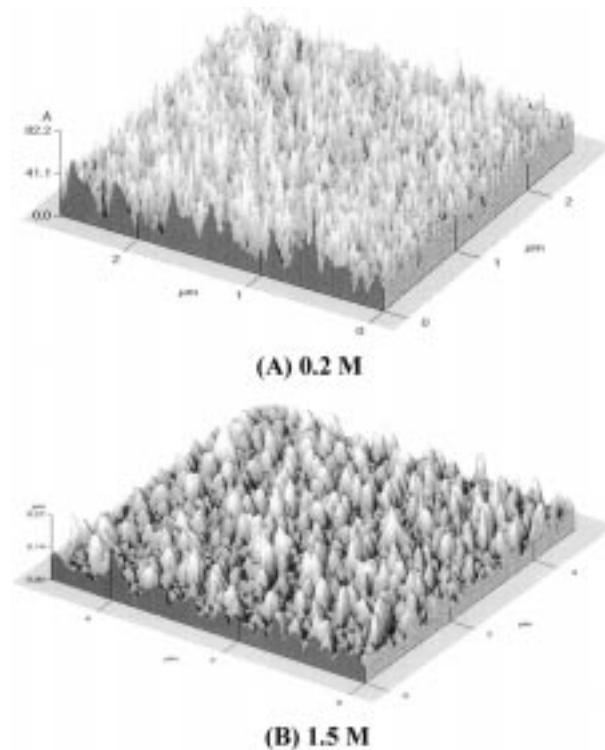


Fig. 7. AFM micrographs of product thin films for different concentrations of mineralizer with 0.4 M BaCl<sub>2</sub> · 2H<sub>2</sub>O for two-hour reactions at 140 °C (A: 0.2 M, B: 1.5 M).

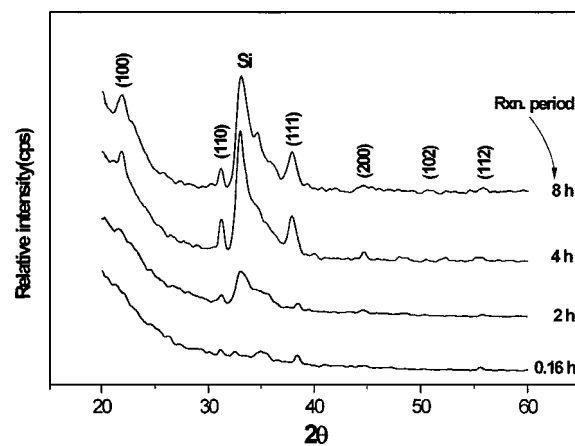
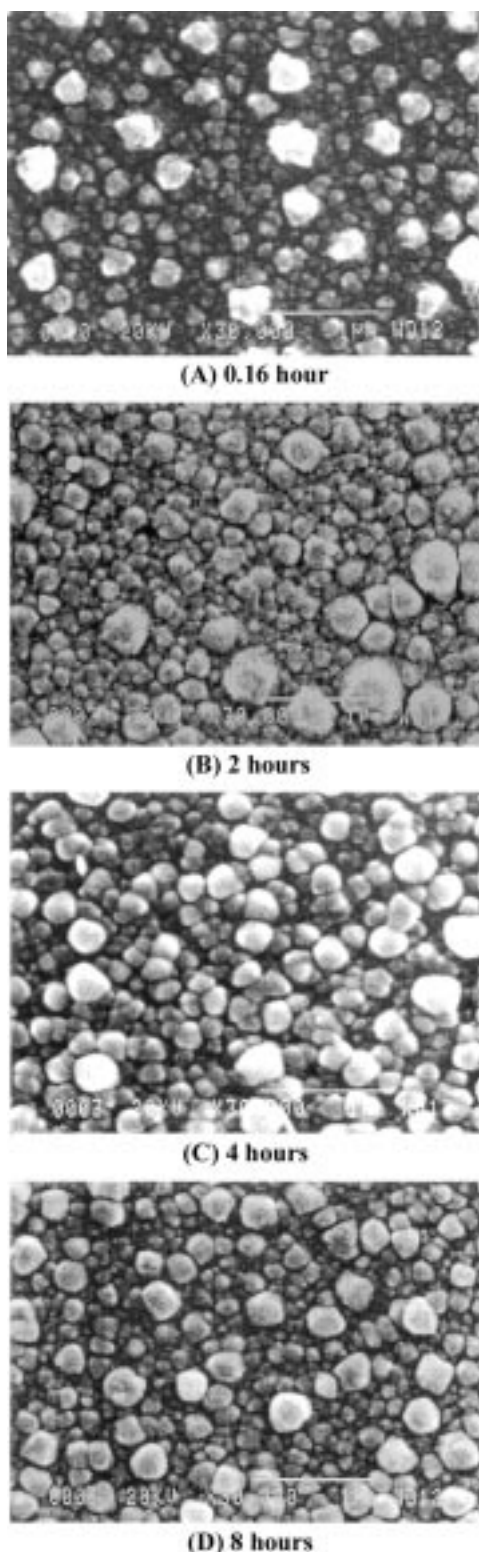


Fig. 8. XRD patterns of product thin films for different reaction times with 0.4 M BaCl<sub>2</sub> · 2H<sub>2</sub>O and 1.0 M KOH at 140 °C.

is concluded that the crystallinity of BaTiO<sub>3</sub> thin films is improved as the reaction time increases because the mass transfer of reactant Ba<sup>2+</sup> and Ti<sup>4+</sup> ions steadily proceeds. However, even if the reaction proceeds for longer than 4 hours, the crystallinity of BaTiO<sub>3</sub> thin film could not be conspicuously improved. Therefore, for the given nutrient (0.4 M BaCl<sub>2</sub> · 2H<sub>2</sub>O) and mineralizer (1.0 M KOH) concentrations at 140 °C, four hours would be enough to prepare BaTiO<sub>3</sub> thin films having uniform and homogenous crystalline grains.

## CONCLUSION



**Fig. 9.** SEM micrographs of product thin films for different reaction times with 0.4 M  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and 1.0 M KOH at 140 °C (A: 0.16 hour, B: 2 hours, C: 4 hours, D: 8 hours).

Experiments were performed to investigate the effect of nutrient and mineralizer concentrations and reaction time on  $\text{BaTiO}_3$  thin film fabrication under hydrothermal conditions. The results

are summarized as follows:

1. Bimodal dispersion of crystalline grains was predicted on the surface of thin films where the smaller grains were located on the inner surface, while larger grains settled on the outer surface.
2. As the concentration of nutrient increased, the grain size of  $\text{BaTiO}_3$  thin film became smaller, but more compact.
3. As the concentration of mineralizer increased, smaller and more compact  $\text{BaTiO}_3$  grains were formed due to the increase in supersaturation of the reactant solution, but the surface roughness increased. Therefore, for better thin film fabrication an appropriate amount of mineralizer has to be used.
4. In order to fabricate  $\text{BaTiO}_3$  thin film of compact and crystalline grains at 140 °C, a reaction for longer than 4 hours should be required when 0.4 M of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  is used with 1.0 M KOH.

## REFERENCES

- Bacsa, R., Ravindranathan, P. and Dougherty, J., "Electrochemical, Hydrothermal, and Electrochemical-hydrothermal Synthesis," *J. Mater. Res.*, **7**(2), 423 (1992).
- Cho, W. S. and Yoshimura, M., "Hydrothermal Synthesis of  $\text{PbTiO}_3$  Films," *J. Mater. Res.*, **12**(3), 833 (1997).
- Craven, M. R., Cranton, W. M., Toal, S. and Reehal, H. S., "Characterization of  $\text{BaTiO}_3$  Thin Films Deposited by RF Magnetron Sputtering for Use in a.c. TFEL Devices," *Semicond. Sci. Technol.*, **13**, 404 (1998).
- Funakubo, H., Nagano, D., Saiki, A. and Inagaki, Y., "Residual Strain and Crystal Structure of  $\text{BaTiO}_3$ - $\text{SrTiO}_3$  Thin Films Prepared by Metal Organic Chemical Vapor Deposition," *Jpn. J. Appl. Phys.*, **36**(1), 5879 (1997).
- Kajiyoshi, K., Ishizawa, N. and Yoshimura, M., "Preparation of Tetragonal Barium Titanate Thin Film on Titanium Metal Substrate by Hydrothermal Method," *J. Am. Ceram. Soc.*, **74**(2), 369 (1991).
- Lee, K. J., Seo, K. W., Yu, H. S. and Mok, Y. I., "The Study on the Effective Factors of Hydrothermal Synthesis in Preparing High Quality Crystalline  $\alpha$ -quartz Powders," *Korean J. Chem. Eng.*, **13**, 489 (1996).
- Matsuda, H., Mizushima, T. and Kuwabara, M., "Low-Temperature Synthesis and Electrical Properties of Semiconducting  $\text{BaTiO}_3$  Ceramics by the Sol-Gel Method with High Concentration Alkoxide Solutions," *J. Ceram. Soc. Jpn.*, **107**(3), 290 (1993).
- Oh, J. K. and Seo, K. W., "Synthesis of Fine Powder for PTC- $\text{BaTiO}_3$ ," *HWAHAK KONGHAK*, **37**, 72 (1999).
- Seo, K. W. and Lee, K. J., "Interpretation of Hydrothermal Crystallization of  $\alpha$ -Quartz Powders," *Powder Technology*, submitted (1999).
- Seo, K. W. and Oh, J. K., "Interpretation of the Hydrothermal Crystallization of Fine  $\text{BaTiO}_3$  Powders," *Korean J. Chem. Eng.*, **17**, 509 (2000).
- Smart, L. and Moore, E., "Solid State Chemistry," Chapman & Hall, London (1995).
- Yoshimura, M., Yoo, S. E., Hayashi, M. and Ishizawa, N., "Preparation of  $\text{BaTiO}_3$  Thin Film by Hydrothermal Electrochemical Method," *Jpn. J. Appl. Phys.*, **28**(11), L2007 (1989).