

# Preparation of BaTiO<sub>3</sub> Thick Film by an Interfacial Polymerization Method

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**Abstract** BaTiO<sub>3</sub> thick film by an interfacial polymerization method was prepared at the liquid/liquid interface between benzyl alcohol saturated solution with the basic catalyst [diethyl amine (NH<sub>2</sub>Et<sub>2</sub>) or triethylamine (NEt<sub>3</sub>)], and the water dissolved with TiO<sub>2</sub> and Ba(CH<sub>3</sub>COO)<sub>2</sub>. The film thickness increased gradually with an increase in diethyl amine(NH<sub>2</sub>Et<sub>2</sub>) or triethylamine(NEt<sub>3</sub>) volume and the reaction time. The homogeneity of BaTiO<sub>3</sub> thick film after sintered at 600°C was confirmed by EPMA analysis, which showed that both of Ba and Ti element were homogeneously distributed on the surface as well as in the perpendicular direction of the film. The thickness of BaTiO<sub>3</sub> film obtained by this process was 8.75 μm.

**Key words** BaTiO<sub>3</sub> thick film, Polymerization method, Liquid/liquid interface, Basic catalyst.

## 1. Introduction

In recent, the development of thin film technique has been remarkable and it has supported the semiconductor integrated circuit industry which is a center of frontier microelectronic industry revolution. A thin film is different from an usual bulk object in that it is extremely thin in one direction. Accordingly, the unique physical properties related to this shape are expected.<sup>1-3)</sup> The epitaxial thin film is well-known as such a representative example. In general, an oriented thin film can be easily obtained by matching the lattice constant of thin film to that of a substrate precisely.

The thin film manufacturing processes are classified as the vacuum system and the non-vacuum one on a large scale. There are sputtering method, CVD (Chemical Vaporization Deposit) and MBE (Molecular Beam Epitaxy) method in the vacuum systems, while, in the non-vacuum systems, there are plating, anodic oxidation, dip-coating and LB (Langmuir Blodgett) method.

The thin film below 1 mm is generally manufactured in the vacuum systems, which make it possible to control precisely the composition in the perpendicular direction to the substrate. In other words, the vacuum systems are preferable to fabricating the oriented thin film. However,

there are some drawbacks in that those equipments need a large space and they are too expensive. For the non-vacuum systems, the other processes besides LB method are easy to make a little thick film, whereas they have many difficulties in controlling the orientation direction. Moreover, all of these processes must need a substrate.

Meanwhile, BaTiO<sub>3</sub> material is widely used as a condenser, a piezoelectric component and/or a pyro-electric device in the electronic industry fields.<sup>1-3)</sup> For the BaTiO<sub>3</sub> thin film, it is normally manufactured in compliance with MOCVD method (Metal Organic Chemical Vapor Deposition method).<sup>4-6)</sup> This process uses the organic metal reagent with high purity as the raw materials. It evaporates concurrently with a carrier gas such as the rectified hydrogen gas and decomposes thermally at the gas state. The metal or poly-crystalline film grows through this process. However, because each raw material used in this technique has spontaneous combustion property and toxicity, users must be very careful to treat those reagents. And it also costs highly and it's too difficulty to make the film up to the 10 mm thickness.

In recent, we have developed the process which used the liquid/liquid interface as the reaction field and successfully made the thick film of amorphous SiO<sub>2</sub> and the oriented metal oxide such as ZnO.<sup>7)</sup> Here, the basic catalyst was used because it was preferable to the 3 dimensional network formation of gel as well-known in a

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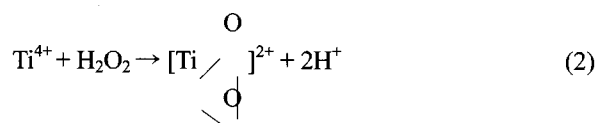
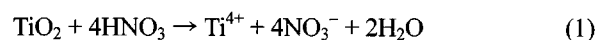
sol-gel process.<sup>8)</sup> This process has the features that it is relatively cheap and possible to prepare the thick film metal oxide easily. In this work, we tried to fabricate the BaTiO<sub>3</sub> thick film by using the interfacial polymerization method which may overcome the drawbacks of the traditional film manufacturing methods. And also the processing conditions which made it possible to fabricate the BaTiO<sub>3</sub> thick film were investigated.

## 2. Experimental Procedures

The reagents used in this experiment are barium acetate (Ba(CH<sub>3</sub>COO)<sub>2</sub>; Kitsuda Chemical Co., Japan), amorphous titania (TiO<sub>2</sub>; Wako Purity Chemical Co., Japan), benzyl alcohol (Kanto Chemical Co., Japan), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>; Tokai Denka Kyougyo Co., Japan), nitric acid (HNO<sub>3</sub>; Kanto Chemical Co., Japan), 1-butanol (C<sub>4</sub>H<sub>9</sub>OH; Kanto Chemical Co., Japan), di-ethyl amine (NH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>; Kanto Chemical Co., Japan) and tri-ethyl amine (NH(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>; Kanto Chemical Co., Japan).

Fig. 1 shows the experimental apparatus. The scheme is as follows. The reaction parts consisted of three layers, that is, the lower layer, the middle layer, and the upper one. In the lower layer, NHEt<sub>2</sub> (di-ethylamine) or NEt<sub>3</sub> (tri-ethylamine) in the range of 0-25 mL was poured into the saturated water solution of benzyl alcohol (300 mL). For preparing the middle layer, HNO<sub>3</sub> in the range of 10-30 mL and 80 mL of H<sub>2</sub>O<sub>2</sub> was added to 640 mL of the distilled water containing 0.7988 g of TiO<sub>2</sub>. Subsequently, 2.5543 g of barium acetate (Ba(CH<sub>3</sub>COO)<sub>2</sub>) was added to this

solution. Total quantity of the solution in the middle layer was 200 mL. Herein, amorphous TiO<sub>2</sub> fine powder reacts with H<sub>2</sub>O<sub>2</sub> under the acidic environment such as the HNO<sub>3</sub> solution and completely dissolves as the following reaction equations.<sup>9)</sup>



Meanwhile, in order to prevent Ba<sup>2+</sup> ion from reacting with CO<sub>2</sub> in the air, the upper layer containing 1-butanol was laid on the middle layer.

After keeping the apparatus at room temperature for the desired reaction period, the solution of the lower layer is slowly drained from it. In the event, BaTiO<sub>3</sub> thick film formed between the lower and the middle layer, and it was laid on the glass substrate, dried at 80°C and sintered at various temperatures.

X-ray diffraction meter (Rigaku Denki RINT 2500) was used to determine the crystal phase of the film formed at liquid/liquid interface. (Measurement condition: The Ni-filtrated Cu-Kα radiation was used, the voltage was 40 kV, the electric current was 80 mA, and the measurement range was 2θ = 5-105 degree.). IR spectra were measured by FT-IR spectrometer (Perkin-Elmer, Model 1760-X) using a diffuse reflection method. The sample for IR measurement was diluted by 20 times with KBr. The line analysis of the thick film's section was carried out by EPMA (Electron Probe Micro Analyzer, Nihonn Denshi, Model JXM-8600 M; the accelerating voltage was 10 kV and the spot size was 3 μm φ.). ICP equipment (Shimatsu Manufacture, Model ICP-1000) was used for the analysis of Ba/Ti mole ratio in the film. The sample was diluted by 10 times after the BaTiO<sub>3</sub> film dissolved into HNO<sub>3</sub>. TG-DTA analysis was carried out by TAS-300 thermal analysis system (Rigaku Denki) in order to investigate how the organic component in the BaTiO<sub>3</sub> as-prepared film decomposed. (Measurement condition; Heating rate was 10°/minute, the measurement range was 20-1000°C, and the amount of the sample was about 10 mg).

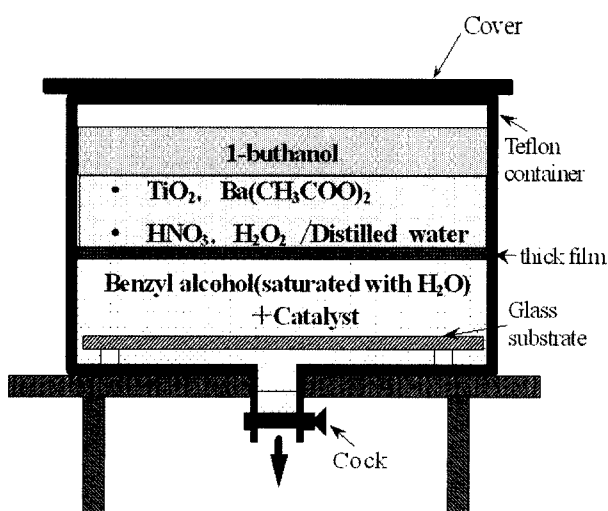


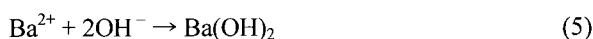
Fig. 1. A cross section of experimental apparatus.

## 3. Results and discussions

The factors to influence on the film formation yield Fig. 2 shows the results of the film formation yield (in

gram) according to the reaction time, herein the quantity of the basic catalyst  $\text{NHEt}_2$  and  $\text{NEt}_3$  was fixed at 15 mL. Up to 4 hours of the reaction time, both of  $\text{NHEt}_2$  and  $\text{NEt}_3$  increased the formation yield, but it almost saturated as the reaction time prolonged over 4 hours.

The film actually begins to form at the liquid/liquid interface, wherein  $\text{Ti}^{4+}$  and/or  $\text{Ba}^{2+}$  ion in the middle layer react with the  $\text{OH}^-$  ion in the lower layer. (See the following (3)-(5) equations.)



At the initial stage of the film formation,  $\text{Ti}^{4+}$ ,  $\text{Ba}^{2+}$ , and  $\text{OH}^-$ , respectively, diffuses into the liquid/liquid interface by the rate-controlling reaction. As the film thickens over 4 hours of the reaction time, the diffusion rate of  $\text{OH}^-$  ion into the film may confine the rate-controlling reaction. Eventually, the formation yield for the  $\text{NHEt}_2$  addition is higher than that for  $\text{NEt}_3$ . The reason is because its basicity (pKa) is higher in this reaction system.

Fig. 3 demonstrates the film formation yield depending on the amount of the basic catalyst when the quantity of  $\text{HNO}_3$  was fixed at 20 mL. At 5 mL of each basic catalyst, the film almost never formed on the liquid/liquid interface irrespective of using any basic catalyst. This results from that a series of reactions in the equation (3)-(5) didn't occur because the amount of the basic catalyst and the resulting  $\text{OH}^-$  at the liquid/liquid interface was too little. However, the film begun to form at the liquid/liquid interface as the amount of the basic catalyst

exceeded over 10 mL. And the yield also increased as the amount of the basic catalyst increased. In conclusion, the film formation needs to incorporate the basic catalyst over 10 mL. Meanwhile, seeing the fig. 3, the film formation yield for the  $\text{NHEt}_2$  catalyst is higher comparing to that for  $\text{NEt}_3$ . This is ascribed to the higher pKa value of  $\text{NHEt}_2$  than that of  $\text{NEt}_3$ . When the amount of  $\text{NHEt}_2$  exceeded over 15 mL, the film formation yield nearly didn't change. This resulted from that the pH value of the solution didn't change even though the addition of  $\text{NHEt}_2$  was beyond 15 mL.

The factors to influence on the Ba/Ti mole ratio in the as-prepared film

When the reaction time was kept as 24 hours and the amount of the basic catalyst was fixed at 15 mL, the Ba/Ti mole ratio in the as-prepared film depending on the quantity of  $\text{HNO}_3$  is shown in the Fig. 4. In the figure, the Ba/Ti mole ratio shows higher value than the designed mole ratio ( $\text{Ba/Ti} = 1.0$ ) at 10 mL of  $\text{HNO}_3$  regardless of the kinds of the catalyst. This phenomenon occurs from the result that the quantity of  $\text{HNO}_3$  addition was relatively little and the resulting  $\text{Ba(OH)}_2$  formed largely. Also, this means that the Ba/Ti mole ratio in the as-prepared film using  $\text{NHEt}_2$  was higher than that of  $\text{NEt}_3$  case. Over 20 mL of  $\text{HNO}_3$ , the Ba/Ti mole ratio was 1.2 for  $\text{NHEt}_2$  catalyst, while this value decreased as the amount of  $\text{HNO}_3$  to  $\text{NEt}_3$  catalyst increased. In general, it is well-known that a  $\text{Ba}^{2+}$  ion hardly precipitates if the pH value of the solution is too low. Therefore, when the amount of  $\text{HNO}_3$  addition exceeded over 20 mL and  $\text{NEt}_3$  was used as the basic catalyst, the precipitation of  $\text{Ba(OH)}_2$  nearly didn't occur.

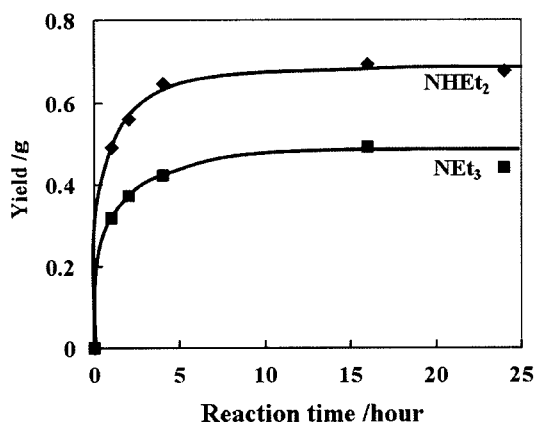


Fig. 2. Film formation yield depending on the reaction time ( $\text{HNO}_3$ : 20 mL, Catalyst: 15 mL).

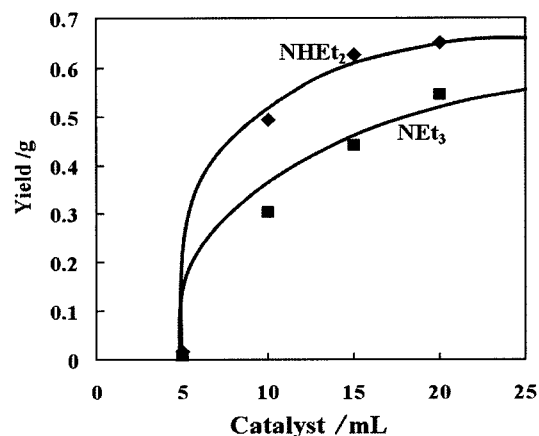


Fig. 3. Film formation yield according to the catalyst content ( $\text{HNO}_3$ : 20 mL, Reaction time: 24 h).

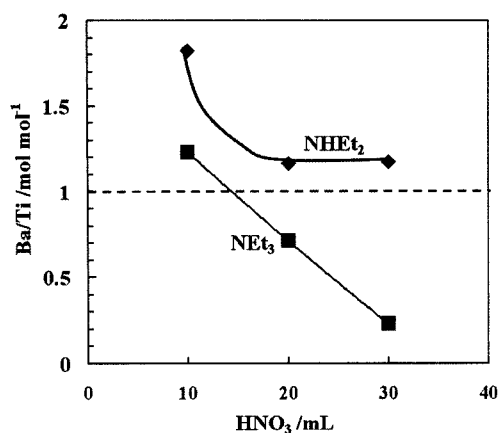


Fig. 4. Ba/Ti mole ratio in the as-prepared film according to HNO<sub>3</sub> content (Catalyst : 15 m, Reaction time : 24 h).

From these results, the film, in which the Ba/Ti mole ratio was about 1.0, could be prepared when the amount of HNO<sub>3</sub> was kept at 20 mL irrespective of using any basic catalyst in this reaction.

Fig. 5 shows the Ba/Ti mole ratio in the film according to the reaction time when the amount of HNO<sub>3</sub> addition and the basic catalyst were fixed at 20 mL and 15 mL, respectively. For the NHEt<sub>2</sub> catalyst, the Ba/Ti mole ratio in the film converged to the constant value, that is, around 1.18 regardless of the reaction time. For the NEt<sub>3</sub> catalyst, the value decreased gradually as the reaction time prolonged. After 24 hours, it converged to 0.7. As described from the equation (3) to the equation (5), the film formation by this interfacial polymerization method needs the consumption of OH<sup>-</sup> ions. Herein, before and after the film formation, the concentration change of OH<sup>-</sup> ion in the lower layer seemed to be little because of the high basicity of NHEt<sub>2</sub> catalyst. In the mean time, for the NEt<sub>3</sub> catalyst with lower basicity, the precipitating amount of Ba(OH)<sub>2</sub> relatively would lessen as the reaction time prolongs. The solubility of Ti<sup>4+</sup> and Ba<sup>2+</sup> ions in the solution decreases as the pH increases. At pH ≈ 4, Ti<sup>4+</sup> ions completely subside.<sup>10)</sup> Meanwhile, the solubility of Ba<sup>2+</sup> ions is found to be over 10<sup>-2</sup> M even at pH = 12.<sup>11)</sup> Therefore, at the initial stage of the film formation, both of Ti<sup>4+</sup> and Ba<sup>2+</sup> ions for NEt<sub>3</sub> catalyst reacts at the same concentration. However, as the reaction time advances, the basicity of the solution decreases. This reason is ascribed to that Ti<sup>4+</sup> ion ahead of Ba<sup>2+</sup> ions reacted firstly. In conclusion, it was revealed that the Ba/Ti mole ratio in the film decreased gradually as prolonging the reaction time.

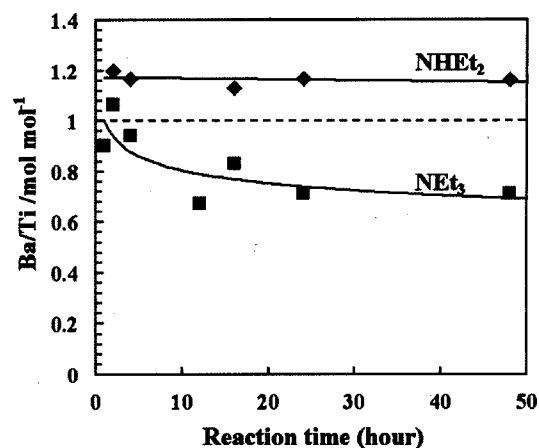


Fig. 5. Ba/Ti mole ratio in the as-prepared film depending on the reaction time (HNO<sub>3</sub> : 20 mL, Catalyst : 15 mL).

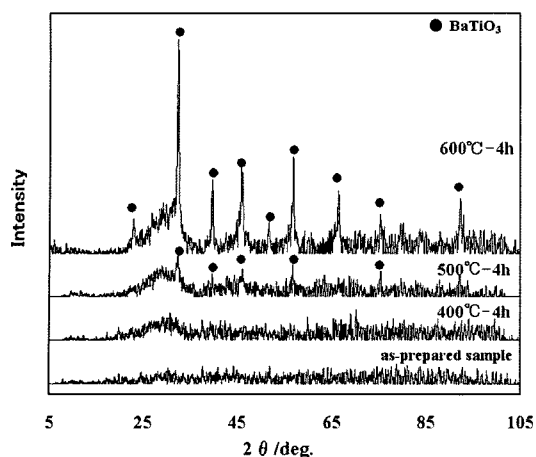
#### The characterization of the BaTiO<sub>3</sub> thick film

The X-ray diffraction patterns of the film heat-treated at the various temperatures, which film was prepared through 24 hours reaction time when the amount of the NHEt<sub>2</sub> catalyst and HNO<sub>3</sub> was kept at 15 mL and 20 mL, respectively, are shown in the Fig. 6 and 7. As shown in the fig. 6, the XRD pattern for the film prepared by using NEt<sub>3</sub> shows the haloes up to 400°C. The diffraction peaks assigned to the BaTiO<sub>3</sub> crystal phase appears slightly at 500°C, and the intensity strengthens at 600°C. Therefore, the film is amorphous until 400°C, the crystallization begins at 500°C and the crystal growth occurs at 600°C. Meanwhile, for the film using NHEt<sub>2</sub> catalyst, the peaks attributed to BaTiO<sub>3</sub> crystal phase already appears at 400°C. Concurrently, a few of small peaks assigned to BaCO<sub>3</sub> are observed. As described in the equation of (6) and (7), BaCO<sub>3</sub> originates from the fact that BaO reacted with a part of CO<sub>2</sub> exhausted from the combustion of the acetic acid remaining after the hydrolysis. For the film heat-treated at 600°C, the only BaTiO<sub>3</sub> peaks are observed.

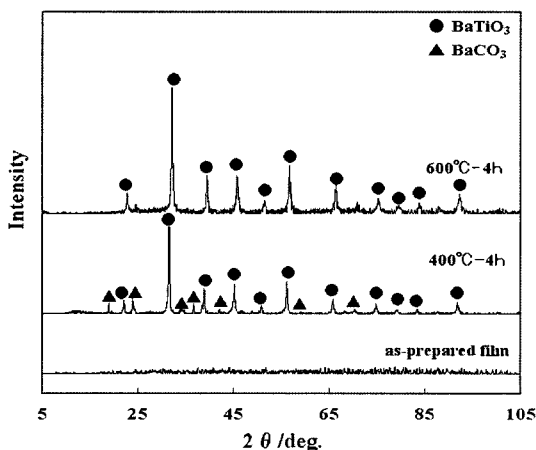


From the results that BaTiO<sub>3</sub> crystal precipitates at the lower temperature in the film by using NHEt<sub>2</sub> catalyst, the composition distribution seems to be homogeneous in the film.

Fig. 8 shows the FT-IR spectra of the film fabricated under the same conditions as aforementioned in fig. 6 and 7. In this figure, the absorption peak around 1400 cm<sup>-1</sup> observed in the as-prepared film without heat-treatment is

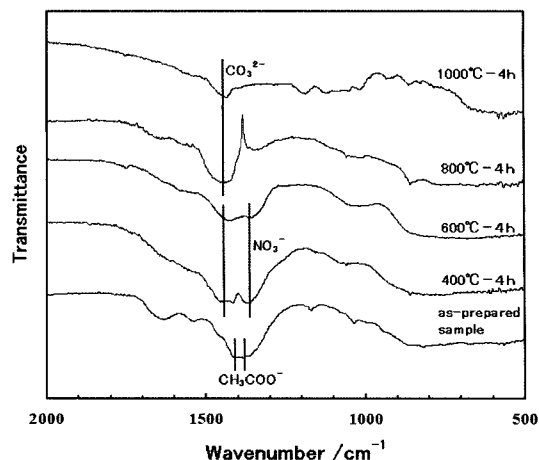


**Fig. 6.** XRD patterns of as-prepared and heat-treated samples using  $\text{NEt}_3$  catalyst ( $\text{NEt}_3$ : 15 mL,  $\text{HNO}_3$ : 20 mL, Reaction time: 24 h).



**Fig. 7.** XRD patterns of as-prepared and heat-treated samples using  $\text{NHEt}_2$  catalyst ( $\text{NHEt}_2$ : 15 mL,  $\text{HNO}_3$ : 20 mL, Reaction time: 24 h).

assigned to the functional group of the acetic acid. The absorption peaks around  $1450\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$  belong to the nitric acid. The  $1450\text{ cm}^{-1}$  peak of these peaks is attributed to the carbonic acid. This means that both of the acetic acid and the nitric acid remain in the as-prepared film. However, the functional group of the acetic acid disappeared when it was heat-treated at  $400^\circ\text{C}$ , but that of the nitric acid remained still. The peak based on the nitric acid weakened at  $600^\circ\text{C}$ , and disappeared at  $800^\circ\text{C}$ . Alternatively, a peak based on the carbonic acid showed up noticeably. This peak is hard to be interpreted from FT-IR spectra below  $800^\circ\text{C}$  because it was overlapped by that of the nitric acid. Meanwhile, from the XRD results of  $400^\circ\text{C}$  in fig. 7, the carbonic acid already would occur in the film. The small peak based on the carbonic acid was



**Fig. 8.** FT-IR spectra of as-prepared and heat-treated samples using  $\text{NHEt}_2$  catalyst ( $\text{NHEt}_2$ : 15 mL,  $\text{HNO}_3$ : 20 mL, Reaction time: 24 h).

observed in the film even though it was heat-treated at  $1000^\circ\text{C}$ . In other words, a little amount of  $\text{BaCO}_3$  would remain even though almost of it was decomposed by the heat-treatment at  $600^\circ\text{C}$ .

Fig. 9 demonstrates The TG-DTA analysis results of the film heat-treated at the various temperatures, which film was also prepared through 24 hours reaction time when the amount of  $\text{NHEt}_2$  and  $\text{HNO}_3$  was fixed at 15 mL and 20 mL, respectively. Considering the TG-DTA results corresponding to the aforementioned FT-IR spectra, the weight loss and the exothermic peak around at  $200^\circ\text{C}$  occurred due to the combustion of the functional group of the acetic acid salts. Around  $570^\circ\text{C}$ , the endothermic peak accompanied by the weight loss was attributed to the decomposition of the nitric acid. The dissociation of carbonic acid and its weight loss seemed to occur around  $700^\circ\text{C}$ . Totally, the weight loss of the sample heat-treated up to  $800^\circ\text{C}$  was 48%. From the results of TG-DTA analysis and if the film formation yield is 50% under the reaction condition as aforementioned in fig. 2, the film with  $8.5\ \mu\text{m}$  in thickness can be evaluated to be fabricated by this method. Here, the theoretical density of  $\text{BaTiO}_3$  is assumed to be  $6.68\ \text{g/cm}^3$ .

Fig. 10 shows the EPMA line analysis results of the film prepared under the same reaction condition as described in fig. 9. From the figure, it is clear that the signal intensity attributed to Ba and Ti increases as that of Si based on the glass substrate gradually decreases. The Ba/Ti mole ratio converges on the nearly constant value in the direction perpendicular to the substrate even though it slightly deviates near the substrate. Here, the thickness of

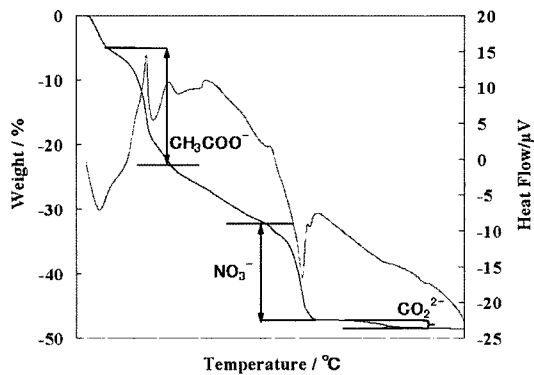


Fig. 9. TG-DTA curves of as-prepared samples using NHEt<sub>2</sub> catalyst (NHEt<sub>2</sub> : 15 mL, HNO<sub>3</sub> : 20 mL, Reaction time : 24 h).

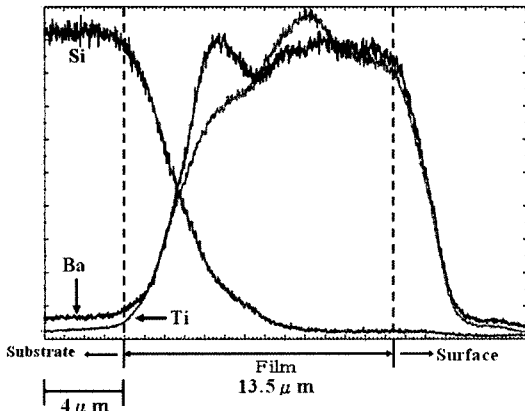


Fig. 10. EPMA line analysis for the cross section of the as-prepared film using NHEt<sub>2</sub> catalyst (NHEt<sub>2</sub> : 15 mL, HNO<sub>3</sub> : 20 mL, Reaction time : 24 h).

the as-prepared film was found to be 13.5 μm.

The EPMA line analysis results of the thick film heat-treated for 4 hours at 600°C is given in Fig. 11. In the figure, the Ba/Ti mole ratio in the direction perpendicular to the substrate is almost at constant like the as-prepared

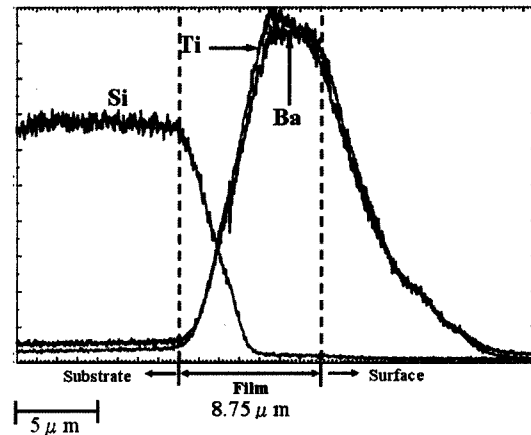


Fig. 11. EPMA line analysis for the cross section of the heat-treated BaTiO<sub>3</sub> film using NHEt<sub>2</sub> catalyst at 600°C (NHEt<sub>2</sub> : 15 mL, HNO<sub>3</sub> : 20 mL, Reaction time : 24 h).

sample, and the thickness of the BaTiO<sub>3</sub> film after sintering is found to be 8.75 μm. Therefore, considering that the film thickness becomes to half by sintering, the porosity is expected to be as below 5% because the evaluated film thickness is 8.5 μm.

Fig. 12 demonstrates the X-ray photo image by EPMA of the same sample in Fig. 11. The white points in the photo on the left side indicate Ba elements and the others on the right represent Ti elements. In both, it is clear that Ba and Ti atoms didn't segregate and homogeneously localized at the surface of the film. In conclusion, both of Ba and Ti elements are likely to be distributed homogeneously on the surface including the perpendicular direction of the film and the resulting homogeneity of this film is well accomplished in this work.

#### 4. Conclusions

BaTiO<sub>3</sub> thick film was successfully fabricated by the

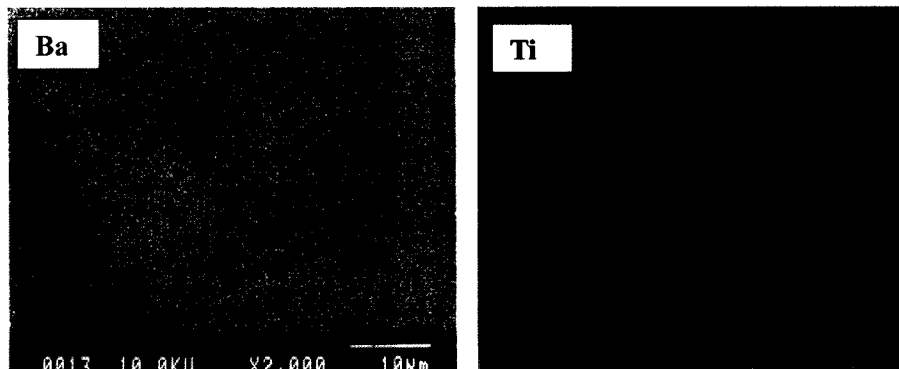


Fig. 12. Characteristic X-ray images of the surface of the heat-treated BaTiO<sub>3</sub> film using NHEt<sub>2</sub> catalyst at 600°C (NHEt<sub>2</sub> : 15 mL, HNO<sub>3</sub> : 20 mL, Reaction time : 24 h).

interfacial polymerization process using the titania oxide ( $\text{TiO}_2$ ) and the barium acetate ( $\text{Ba}(\text{CH}_3\text{COO})_2$ ) as the raw materials. The thick film, the Ba/Ti mole ratio of which was around 1.18, was obtained under the conditions that the reaction time was 24 hours and 15 mL of  $\text{NH}_4\text{Et}_2$  when the basic catalyst was laid in the lower layer and 20 mL of  $\text{HNO}_3$  was added to the middle layer in the apparatus. The thickness of the as-prepared film was found to be  $13.5\ \mu\text{m}$  and the Ba/Ti mole ratio in the direction perpendicular to the substrate was almost at constant. By the heat-treatment of as-prepared film at  $600^\circ\text{C}$ , the thickness of the crystalline  $\text{BaTiO}_3$  film became to  $8.75\ \mu\text{m}$  and the porosity was below 5%. The homogeneity of the sintered  $\text{BaTiO}_3$  film was confirmed by EPMA analysis, which showed that both of Ba and Ti element were homogeneously well-distributed at the surface including the perpendicular direction of the film.

## References

1. A. I. Kingon and S. K. Streiffer, *Current Opinion in Solid State & Materials Science*, **4**(1), 39 (1999).
2. J. Schwarzkopf and R. Fornari, *Progress in Crystal Growth and Characterization of Materials*, **52**(3), 159 (2006)
3. T. Asamaki, *Introduction to the fabrication of thin films*, Nikkan kogyoshinnbunn-sha (1984) (in Japanese).
4. T. Chiba, K. Itoh and O. Matsumoto, *Thin Solid Films*, **300**(1), 6 (1997).
5. Z. Jianming, W. Hong, W. Ming, S. Suxia, W. Zuo and L. Chenglu, *Journal of Physics D, Applied Physics*, **31**(19), 2416 (1998).
6. *Fundamental knowledge of advanced materials*, Ed. by Society of Materials Science, Japan (1991) (in Japanese).
7. M. Yamane, M. Iwasaki and S. Ito, *Ceramic Transactions*, **81**, 113 (1998).
8. S. Saka, *The science of sol-gel process*, Chapter 9, Published by Agne Shouhusya (1998) (in Japanese)
9. G. Munuera, A. R. Gonzalez-Elipse, A. Fernandez, P. Malet and J. P. Espinos, *J. Chem. Soc. Faraday Trans.*, **1**, **85**(6), 1279 (1989).
10. C. F. Bass Jr., and R. E. Mesmer, *The hydrolysis of cations*, Krieger Publishing Company, 147 (1976).
11. *Experiments in inorganic qualitative analysis*, Ed. by Kyoto University, Kyoritushuppan, (1994) (in Japanese).