

Microstructure and electrical properties of BaTiO₃ thin films by modified CSD

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0.3 M BaTiO₃ (BT) precursor solution was prepared by the modified CSD, in which partially hydrolyzed Ti-alkoxide and Ba precursor solution was reacted in iced water bath to prepare the highly polymerized BT precursor solution. The BT precursor solution was spin-coated on a Pt/Ti/SiO₂/Si substrate with and without (100)-oriented LaNiO₃ (LNO) thin film electrode. In addition, effect of the pre-annealing at 600°C in O₂ atmosphere was elucidated by measuring the electrical properties of the resulting BT thin films deposited by the different annealing process. The results clearly indicated that the 600°C pre-annealing and the LNO thin film electrode are effective to enhance the electrical properties of the resultant BT thin films from the precursor solution by the partial hydrolysis method.

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1. Introduction

Ferroelectric materials have been investigated for their wide range of applications, such as nonvolatile memories,¹⁾ dynamic random access memories, and ceramic capacitors. BaTiO₃ (BT) exhibits high dielectric permittivity, low dielectric loss and is widely used for Multi-Layer Ceramic Capacitors (MLCC).²⁾

Recently, downsizing and/or higher capacitance are the trend in the next generation MLCC as well as the lower cost. Therefore, development of high quality BT thin films by a cost effective method is essential. BT thin films have been prepared by different methods such as sputtering,^{3,4)} pulsed laser deposition (PLD),⁵⁾ and chemical solution deposition (CSD).⁶⁻⁸⁾ Among them, CSD technique offers quite a few advantages such as low deposition cost, ease of preparation and stoichiometry control as well as the ease of deposition over the large area. To deposit the good ferroelectric and dielectric thin films with a CSD, we should prepare the good precursor solutions with higher polymerization degree and homogeneity. Therefore in this study, BT precursor solution was prepared by the modified CSD to elucidate the effect of the molecular design by the partial hydrolysis.⁹⁾ In this study, BT precursor solution was prepared by the modified CSD to elucidate the effect of the molecular design by the partial hydrolysis on the microstructure and electrical properties of the resulting BT thin films. In addition, annealing process was optimized based on the decomposition behavior of the molecular-designed precursor.

2. Experimental

2.1 Preparation of the precursor solution

Barium metal (Nacalai Tesque, Inc.) and Ti isopropoxide [Ti(OC₃H₇)₄] (Kanto Chemical Co., Inc.) was used as starting reagents for BT precursor solution. 2-methoxyethanol (Kanto Chemical Co., Inc.) was used as a solvent. Acetic acid (Kanto

Chemical Co., Inc.) was used as a chelating reagent. 0.3 M BT precursor solution was prepared by the modified CSD. Ba metal and 2-methoxyethanol were refluxed for 2 h. at 125°C to prepare the Ba precursor solution. On the other hand, Ti-isopropoxide and 2-methoxyethanol were refluxed for 2 h. at 125°C to prepare the Ti precursor solution. Then the acetic acid ($R_A = [\text{CH}_3\text{COOH}]/[\text{Ti}(\text{OR})_4] = 1.5$) and distilled water ($R_W = [\text{H}_2\text{O}]/[\text{Ti}(\text{OR})_4] = 1.0$) were added in the Ti precursor solution and stirred for 4 h. at room temperature for the partial hydrolysis to increase the polymerization degree. Ba and Ti precursor solutions were mixed and reacted for 6 h. in an iced water bath to prepare the highly polymerized BT precursor solution.

2.2 Film deposition

A Pt/Ti/SiO₂/Si (Taiyo Yuden Co., Ltd.) was used as a substrate (the substrate will be stated as Pt/Si hereafter). Lanthanum nitrate and nickel acetate were used as raw materials for the LNO precursor solution. 2-methoxyethanol and 2-aminoethanol mixed solution was used as a solvent. Details of the LNO precursor solution preparation are described in the previous papers.^{10,11)} The LNO precursor solution was spin-coated and dried at 150°C for 10 min. on the Pt/ Si substrate. After pre-annealing at 350°C for 10 min to remove residual organics, LNO precursor films were annealed by Rapid Thermal Annealing (RTA) at 700°C for 5 min with heating rate of 200°C/min. The LNO film was deposited twice in order to increase the LNO film thickness until about 100 nm. BT precursor solution was spin-coated and dried at 150°C for 10 min. on the Pt/ Si substrate with and without (100)-oriented LaNiO₃ (LNO) thin film electrode. After the pre-annealing at 420°C for 10 min., the BT precursor films were annealed by RTA at 750°C for 5 min. in O₂ atmosphere with heating rate of 200°C/min. In some cases, the pre-annealing at 600°C for 15 min. in O₂ atmosphere was introduced before the final annealing at 750°C to elucidate the effect of the pre-annealing on the electrical properties of the resulting BT thin films deposited by the different annealing process. BT film deposition were repeated 6 times.

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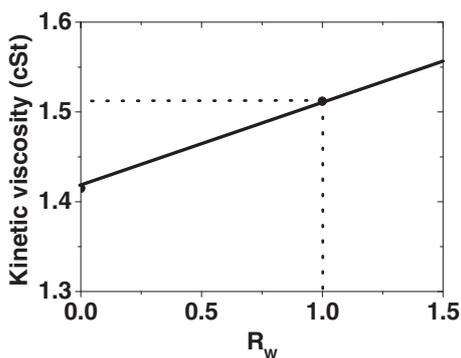


Fig. 1. Extant of polymerization of the Ti alkoxide.

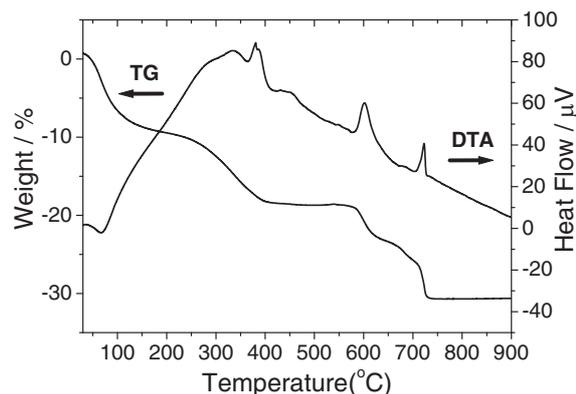


Fig. 2. TG-DTA curves for 0.3 M BT xerogel precursor.

2.3 Characterization

The structure and crystal orientation of the BT thin films were characterized by X-ray diffraction (XRD) (D8 ADVANCE, Bruker AXS K.K.). Surface structure was observed by Atomic Force Microscope (AFM, SPI3800N, SII NanoTechnology Inc.). Cross-sectional microstructures were observed by a Field-Emission type Scanning Electron Microscope (FE-SEM, JSM-7001F, JEOL. Ltd.). Film thickness was estimated from the FE-SEM images. Dielectric constants were measured with an impedance analyzer (4194A, Hewlett-Packard Japan, Ltd.). Ferroelectric properties were measured with a ferroelectric test system (FCE-1, TOYO Corporation).

3. Results and discussion

3.1 Polymerization degree of Ti-alkoxide prepared by partial hydrolysis

Figure 1 shows change in the viscosity for the Ti precursor solutions with and without partial hydrolysis as a function of the amount of the hydrolysis water (R_w) added. The addition of the distilled water to the chelated Ti-alkoxide resulted in the increase in the kinetic viscosity of the Ti-precursor solutions without any precipitates. This indicated that the highly polymerized precursor solution was obtained by the partial hydrolysis method. However, large amount of the hydrolysis water more than $R_w > 2.0$ led to the local hydrolysis and following poly-condensation of the Ti-alkoxide to form precipitates before the reaction with a Ba-precursor solution, therefore, we chose the partial hydrolysis condition of $R_a = 1.5$ and $R_w = 1.0$.

3.2 Decomposition behavior of precursor

Figure 2 shows thermo gravimetry and differential thermal analysis (TG-DTA) curves for 0.3 M BT precursor powder deposited by drying the precursor solution at 150°C. The total weight loss of xerogel was approximately 30%, and the total decomposition process can be divided into four distinct steps. The first weight loss appeared approximately in the range from 50 to 150°C was corresponding to the evaporation of water and the organic solvents. The second weight loss appeared at approximately 300–400°C with the exothermic peaks of the DTA curve, corresponding to the decomposition of the residual organics. The third weight loss appeared at approximately 600°C with a sharp peak of the DTA curve, which was due to the decomposition of residual organics. The last weight loss appeared at approximately 700°C with a sharp exothermic peak of the DTA curve was ascribed to the crystallization because weight loss ended approximately 700°C.

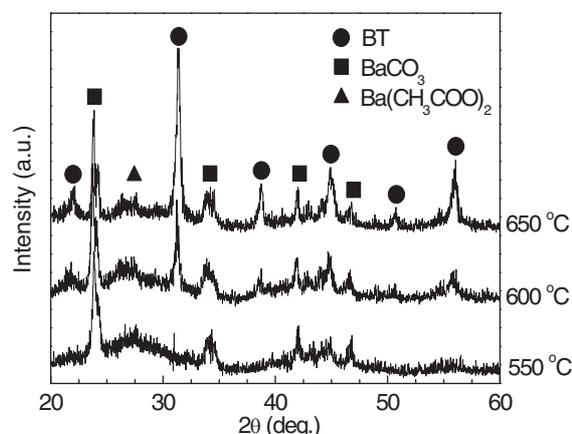


Fig. 3. X-ray diffraction patterns for the BT powders obtained from 0.3 M BT xerogel precursor calcined at different annealing temperature.

Figure 3 shows XRD patterns for BT powders obtained from 0.3 M BT xerogel precursor calcined in the temperature range from 550 to 650°C. It was shown that the BT began to generate above 600°C and barium acetate began to decompose with increasing the calcination temperature. The reason why the barium acetate generated can be considered that a part of acetic acid reacted with barium in the precursor solution. According to the thermal analysis of the xerogel, we chose the heat treatment (pre-annealing) temperature for the BT thin films as 600°C in order to avoid the barium acetate contained in the film.

3.3 Crystallization behavior of BT film

Figure 4 shows XRD patterns for the BT thin films with different stacking structures of BT/Pt/Si and BT/LNO/Pt/Si. BT thin film on the Pt/Si substrate exhibited random orientation, whereas the BT thin films on the LNO/Pt/Si substrate exhibited (100) & (001) orientation. High tendency for (100) & (001) orientation, i.e. *c*- & *a*-orientation, of the BT films on the LNO seeding layer was obviously indicated by calculated degree of orientation by the following equation (see also **Table 1**).

$$\text{Degree of film orientation} = \frac{I_{(hkl)}}{I_{(001)(100)} + I_{(110)(101)} + I_{(111)}}$$

As shown in the Table 1, the BT film with 600°C pre-annealing exhibited higher *c*- & *a*-axes orientation degree (91.1%) than that without pre-annealing (69.0%) although both are prepared on the same LNO layers.

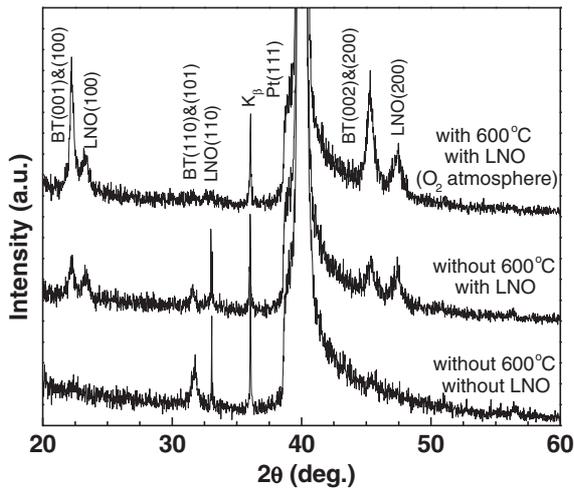


Fig. 4. X-ray diffraction patterns for the BT thin films.

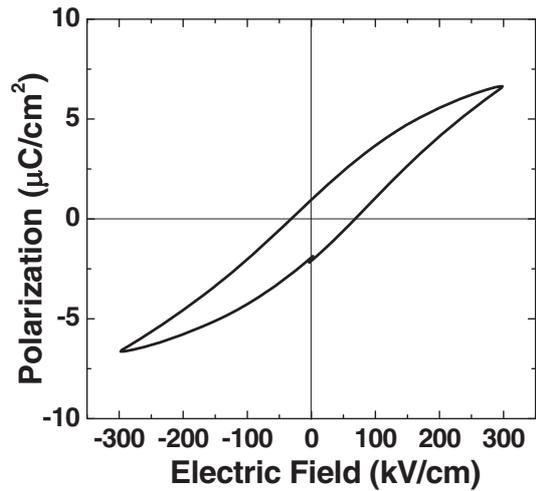


Fig. 6. Hysteresis curves of the BT thin films with the LNO seeding layer and 600°C pre-annealing.

Table 1. Degree of c- & a-axes orientation of BT thin films with and without 600°C pre-annealing

	Without 600°C pre-annealing, with LNO	With 600°C pre-annealing, with LNO
Degree of c- & a-axes orientation	69.0	91.1

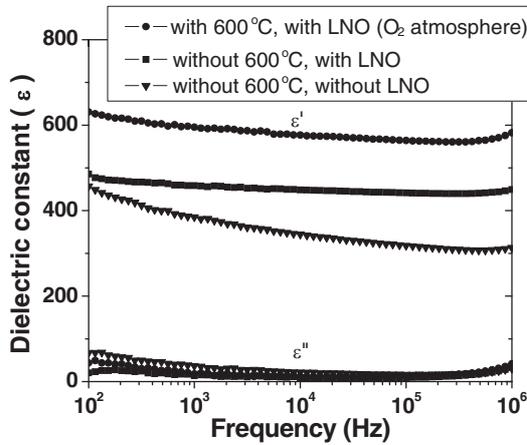


Fig. 5. Dielectric constant and dielectric loss of the BT thin films as a function of frequency.

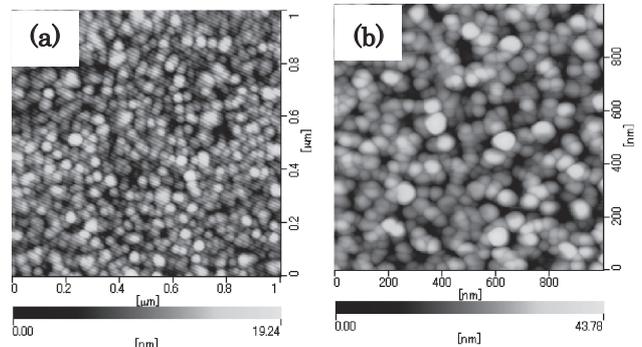


Fig. 7. DFM images of the BT thin films: (a) without 600°C pre-annealing and (b) with 600°C pre-annealing.

3.4 Electrical properties

We also confirmed the effect of the LNO seeding layer and the 600°C pre-annealing on the electrical properties of the resultant BT thin films on different substrate structures. **Figure 5** shows dielectric constant and loss tangent for the resultant BT/Pt/Si and BT/LNO/Pt/Si thin films. BT thin films with LNO seeding layer and 600°C pre-annealing exhibited higher dielectric constant than those films without 600°C. This suggested that the 600°C pre-annealing was considerably effective to improve the electrical properties of the BT thin films obtained from the molecular-designed precursor solution using partial hydrolysis method. On the other hand, dielectric loss for the resulting BT thin films exhibited the effect of the LNO seeding layer. BT thin films on the LNO/Pt/Si substrate showed low dielectric loss of

3%, whereas that for the BT thin film on the Pt/Si substrate was 11%. All these results suggested that the BT thin film deposited on the LNO/Pt/Si with 600°C pre-annealing was an optimum synthesis condition which led better electrical properties. The hysteresis curve for the film deposited by the optimum condition showed the obvious ferroelectric hysteresis loop (see **Fig. 6**). These results clearly indicated that both of the 600°C pre-annealing and the LNO seeding layer were crucially important to enhance the electrical properties of the resultant BT thin films obtained from the precursor solution by the partial hydrolysis method.

3.5 Microstructures

Figure 7 shows the surface microstructure of BT thin films on a LNO/Pt/Si substrate with or without 600°C pre-annealing. These films showed almost smooth and crack free surface morphologies, although porous regions were existed in some parts of the films. It can be considered that these porous regions were formed when the residual organics were burned out. It is worth to note that the grain size for the BT thin film on the LNO/Pt/Si with 600°C pre-annealing was larger than that for the BT thin film without pre-annealing. This indicated that the 600°C pre-annealing enhanced the grain growth of the BT thin films. **Figure 8** shows the cross-sectional microstructure for the BT thin films on the LNO/Pt/Si substrate with or without

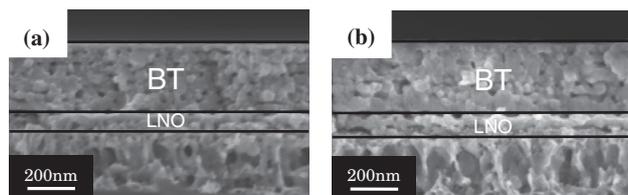


Fig. 8. SEM micrographs of the cross section of the BT thin films: (a) without 600°C pre-annealing and (b) with 600°C pre-annealing. Both of the BT films thicknesses were about 300 nm.

600°C pre-annealing. The FE-SEM images indicated both of the BT films thicknesses were about 300 nm. The FE-SEM images also showed some pores seen in both of the LNO thin film electrode and BT thin films. In the case of LNO thin film, we intentionally designed the molecular structure of it to form some pores in the film by the large side chain groups burned out during the annealing in order to relax the thermal tensile stress subjected from the Si substrate. On the other hand, the BT precursor was recognized as highly polymerized and it should form the dense microstructure in contrast to the resultant microstructures. In the present stage, the reason for the pores generated in the BT film was not clearly explained, however, the residual organics might be one of the reason because 600°C pre-annealing could reduce the pores in the BT thin film which resulted in relatively dense microstructure as shown in Fig. 8(b) and relatively higher dielectric constant. It can be said that the BT film with high electric properties was obtained by preparing highly polymerized BT precursor solutions and performing appropriate heat-treatment from the microstructure observation.

4. Conclusions

The highly polymerized BT precursor solutions were successfully prepared by the partial hydrolysis method. BT precursor

solution was spin-coated on a Pt/Ti/SiO₂/Si substrate with and without (100)-oriented LaNiO₃ (LNO) thin film electrode. In addition, effect of the pre-annealing at 600°C in O₂ atmosphere on the microstructure of the resulting BT thin films was elucidated by measuring the electrical properties of the BT thin films. These results clearly indicated that the appropriate heat-treatment and the LNO thin film electrode were effective to improve the microstructure and to enhance the electrical properties of the resultant BT thin films from the precursor solution by the partial hydrolysis method. It was essential to optimize the annealing process for the further improvement of the electrical properties of BT thin films from the molecular-designed precursor solution by the partial hydrolysis.

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