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Microstructural Control of $BaTiO_3$ Thick Film Fabricated by Utilizing Slide-Off Transfer Printing

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Abstract. Effects of fabrication conditions on the microstructure of thick $BaTiO_3$ films have been investigated by employing slide-off transfer printing technique. Formation of dense films with good adhesive properties was difficult when screen-printing was employed in preparing the slide-off transfer sheets ($BaTiO_3$ green films), irrespective of the kind of solvents used for the slurries. On the other hand, relatively dense films could be fabricated from the slide-off transfer sheet prepared by spin-coating of the slurries consisting of fine $BaTiO_3$ powder (particle size: ca. 0.1 μm), printing oil, and 2-propanol, though cracks formed obviously. Co-addition of large $BaTiO_3$ particles (particle size: ca. 0.5 μm) was very effective for reducing the formation of cracks, and homogenous and dense films could be fabricated by controlling the additive amount of the large particles.

Keywords: barium titanate, thick film, slide-off transfer printing, spin-coating, screen-printing

1. Introduction

Barium titanate ($BaTiO_3$) is one of promising ferroelectric and semiconductive materials applicable to transducers, actuators, capacitors, chemical sensors, and so on [1–3]. In these applications, the material is often utilized in the form of thin or thick films. Thin $BaTiO_3$ films (typical thickness: $<$ ca. 1.0 μm) can be fabricated via various dry and wet processes such as sputtering [4], pulsed laser deposition [5] and sol-gel technique combined with spin-coating [6]. On the other hands, thick $BaTiO_3$ films (>10 μm) are fabricated usually by well-matured ceramic processing such as screen-printing [7, 8] and tape casting [9], employing concentrated slurries of $BaTiO_3$ powder. However, it is difficult in most cases to obtain densely structured thick films by these techniques.

Slide-off transfer printing is one of the most popular techniques to print and decorate underglazes on the surfaces of potteries and porcelains in the field of traditional ceramic industries in large quantities at low cost. The underglaze film obtained is a kind of thick ceramic film. Thus the slide-off transfer printing is of great interest as an alternative method to fabricate thick films of electroceramics. The method may be featured by simple preparation and easy control of the film thickness ($>$ca. 5 μm). In addition it is possible to fabricate the films on either flat or curved surfaces, due to the flexible property of a slide-off transfer sheet as an oxide green sheet. For example, we recently developed highly sensitive and selective semiconductor gas sensors by utilizing this slide-off printing method [10–13]. In this field, the slide-off transfer printing has been proved to be very promising, because porous structure of oxide layers suitable for gas sensing could be constructed easily by adjusting the composition of the oxide slurries and also because different kinds of oxide films could be fabricated in a pile on a substrate. Such a design of porous or hetero-layered structure is very important to control the gas diffusivity and reactivity of target gases inside the

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sensing layers and then to improve the gas sensing properties.

Thus our previous studies have mainly focused on the fabrication of thick and porous oxide films suitable for sensor applications, but the method is also considered to be applicable to fabrication of thick and dense films of other electroceramic materials. In the present study the slide-off transfer printing was applied to thick and dense $BaTiO_3$ films and the preparation conditions were extensively examined to get the films as dense as possible.

2. Experimental

Two kinds of $BaTiO_3$ powders supplied from Sakai Chemical Ind. Co., Ltd., BT-01 (particle size (ps): ca. 0.1 μm in diameter, specific surface area (ssa): ca. 12.7 m^2 g^{-1}) and BT-05 (ps: ca. 0.5 μm in diameter, ssa: ca. 2.3 m^2 g^{-1}), were used after planetary ball-milling in ethanol. Slide-off transfer sheets of $BaTiO_3$ were fabricated by screen-printing or spin-coating, as follows.

(a) *Screen-printing*: $BaTiO_3$ powder was mixed with printing oil (Goo Chemical Co., Ltd., OS-4530) as an organic binder by using a three-roller mill (Degussa Japan Co., Ltd., EXAKT M-35) to give paste stuffs with good homogeneity and viscosity suitable for screen-printing. In some cases, deionized water with ammonium polycarboxylate (Toagosei, Inc., Aron A-6114) as a dispersant and acrylic polymer {Mitsui Chemical, Inc., WA-320 (emulsion type)} as a binder were mixed with the powder by a hybrid mixer (Keyence Corp., HM-500). The paste stuffs were screen-printed using a 100 mesh screen on a mount paper with gum, which was dextrin, soluble in water. Then an organic lacquer (Degussa Japan Co., Ltd., 80450) as a cover coat was screen-printed over the oxide layer using a 26 mesh screen to obtain slide-off transfer sheets.

(b) *Spin-coating*: $BaTiO_3$ powder and printing oil were mixed with an appropriate amount of 2-propanol. The slurry was spin-coated at a speed of 9000 rpm on a mount paper, and then the organic lacquer was further spin-coated on the $BaTiO_3$ green film at the same speed.

Fabrication process of a $BaTiO_3$ thick film by slide-off transfer printing is schematically illustrated in Fig. 1. The slide-off transfer sheet obtained was separated from the mount paper by soaking it in water and was transferred on a silicon substrate, followed by drying at 80°C for 30 min. Thereafter, it was heated at a rate of 1°C min^{-1} and then fired at 1050–1300°C for 2 h in air. Hereafter, the slide-off transfer printing methods employing screen-printing and spin-coating were denoted as SP-STP and SC-STP process, respectively. It was confirmed that all thick films after firing showed single phase of $BaTiO_3$ by X-ray diffraction analysis (XRD, Rigaku, Rint-2200). Morphology of the thick $BaTiO_3$ films was observed by a scanning electron microscope (SEM, Hitachi, S-2250N).

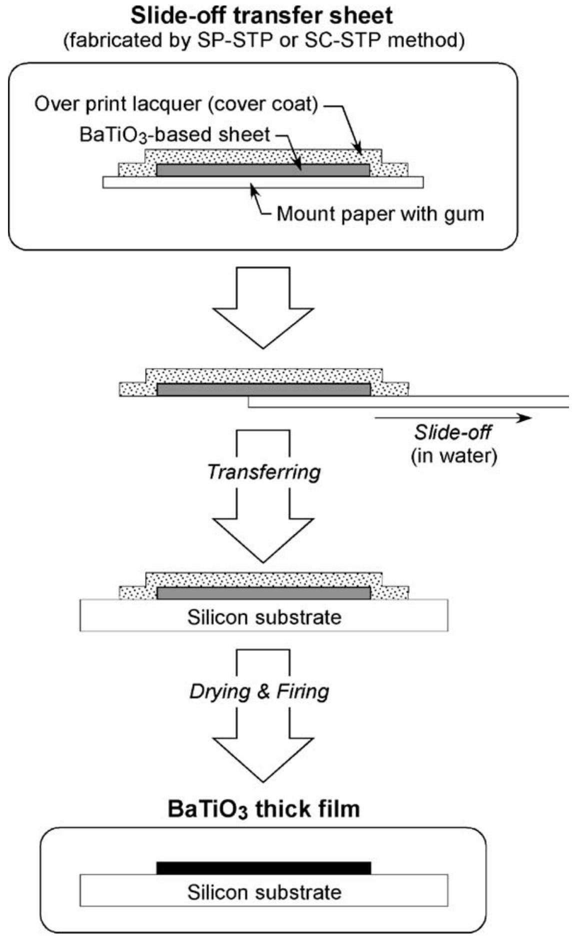

Fig. 1. Fabrication procedure of a $BaTiO_3$ thick film by slide-off transfer printing.

3. Results and Discussion

Thick $BaTiO_3$ films could be fabricated easily after calcination at 1300°C for 2 h by employing the

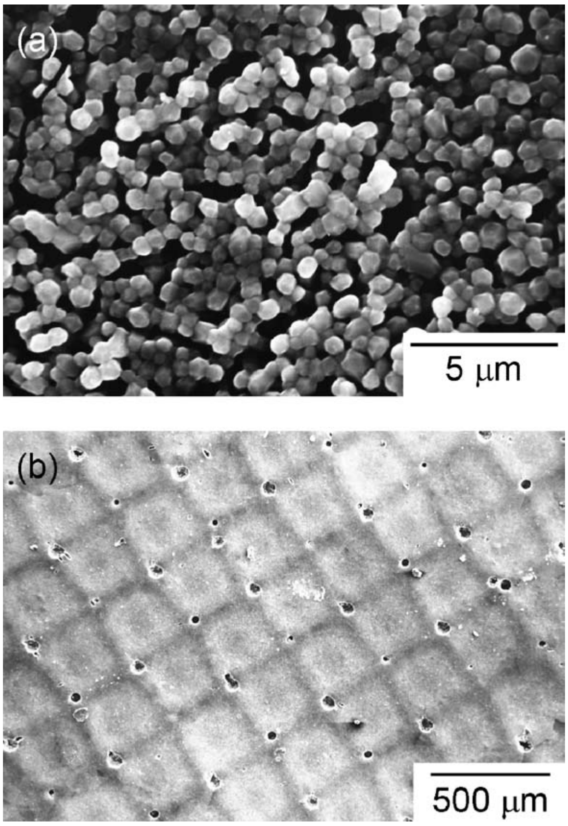

Fig. 2. SEM photographs of a $BaTiO_3$ film fabricated by SP-STP method {BT-01 : printing oil = 2 : 1 (in weight) in slurry} and subsequent calcination at 1300°C for 2 h. (a) High and (b) low magnification.

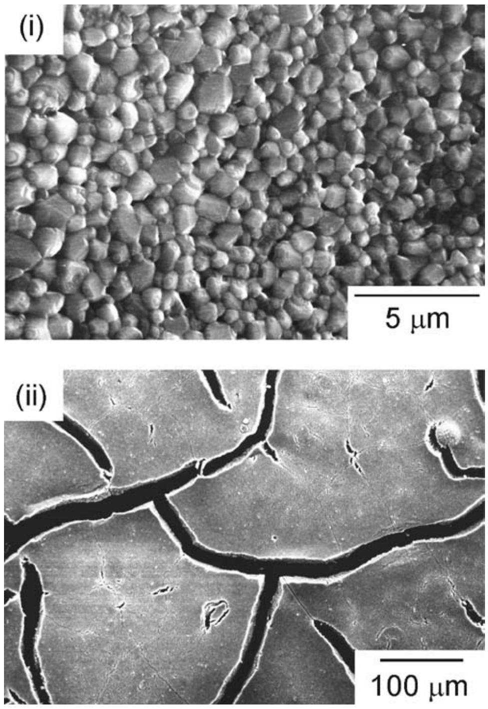

Fig. 3. SEM photographs of the surface of a $BaTiO_3$ film fabricated by (a) SP-STP method {BT-01 : deionized water : ammonium polycarboxylate : acrylic polymer = 74.4 : 22.3 : 1.1 : 2.2 (in weight) in the slurry} and subsequent calcination at 1200°C for 2 h. (a) High and (b) low magnification.

SP-STP process with slurries consisting of different mixing ratios of BT-01 powder and printing oil. The densest film was obtained with the slurry composition of BT-01 : printing oil = 2 : 1 (in weight) under the present conditions. Even at this slurry composition, however, the $BaTiO_3$ film fabricated was still porous, as shown in Fig. 2(a), though BT-01 particles were sintered to each other and then neck-growth was observed clearly. In addition, reticulate parts, which were thinner than the other area and reflected the pattern of 100 mesh screen used for the screen-printing, were obvious at the top view of the film (see Fig. 2(b)), owing to the high viscosity of the slurry used.

To reduce the viscosity as well as to improve a filling ratio of BT-01 particles in a resultant green sheet, deionized water was used as a solvent, instead of the printing oil, along with ammonium polycarboxylate and acrylic polymer in the SP-STP process. The addition of an appropriate amount of deionized water could make the slurry of BT-01 powder suitable for screen-printing. Figure 3 shows SEM photographs of the resultant $BaTiO_3$ thick film after calcination at 1200°C for 2 h. Although no reticulate parts were left behind on the film surface and the BT-01 particles were densely sintered in some parts (see Fig. 3(a)), the film had many large cracks originating from evaporation of water and subsequent large shrinking. The film showed, therefore, poor adhesive properties toward the substrate, as shown in Fig. 3(b). The water-based slurry with almost the same composition as above was also used in the SC-STP process. However, the resultant thick $BaTiO_3$ films after calcination at 1200°C for 2 h showed rather porous structure with many voids, in comparison with the films fabricated by the SP-STP process, as shown in Fig. 4(a), indicating that the filling level of BT-01 particles in the SC-STP process was lower than that in the SP-STP process. In addition, the formation of many large cracks was again observed (see Fig. 4(b)). Thus,

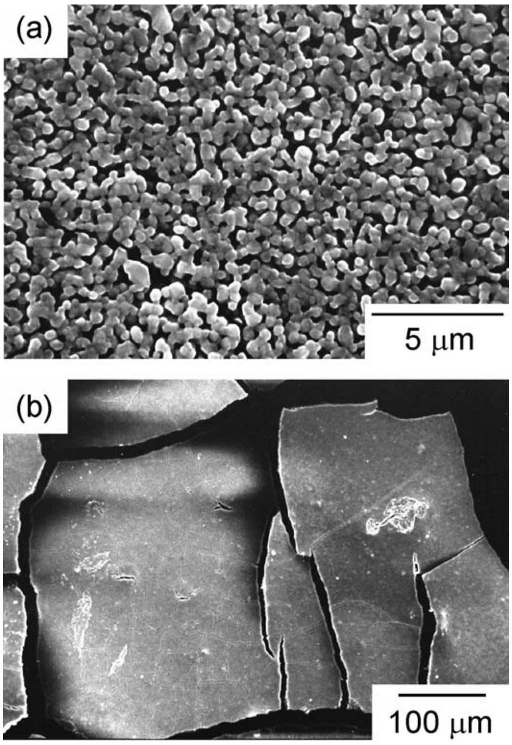

Fig. 4. SEM photographs of the surface of a $BaTiO_3$ film fabricated by SC-STP method {BT-01 : deionized water : ammonium polycarboxylate : acrylic polymer = 78.1 : 19.5 : 1.6 : 0.8 (in weight) in the slurry} and subsequent calcination at 1200°C for 2 h. (a) High and (b) low magnification.

it was found that the water-based slurry was not suitable for fabricating thick and dense $BaTiO_3$ films with good adhesive properties in both process of SP-STP and SC-STP.

In the next step, 2-propanol was used to reduce the viscosity of the slurry consisting of BT-01 powder and printing oil, and then thick $BaTiO_3$ films were fabricated by the SC-STP process. Figure 5 shows SEM photographs of the films thus fabricated with different additive amounts of 2-propanol. All the films fabricated from the slurries containing ca. 41 mass% 2-propanol showed a porous structure along with large voids, as shown in Fig. 5. Sintering of BT-01 particles was promoted clearly at ca. 37 mass% 2-propanol, as shown in Fig. 5(b)(i), but cracks were again formed (see the SEM photograph at lower magnification (Fig. 5(b) (ii))). Further decreases in the amount of 2-propanol resulted in higher viscosity of the slurry, which was unsuitable for the SC-STP process.

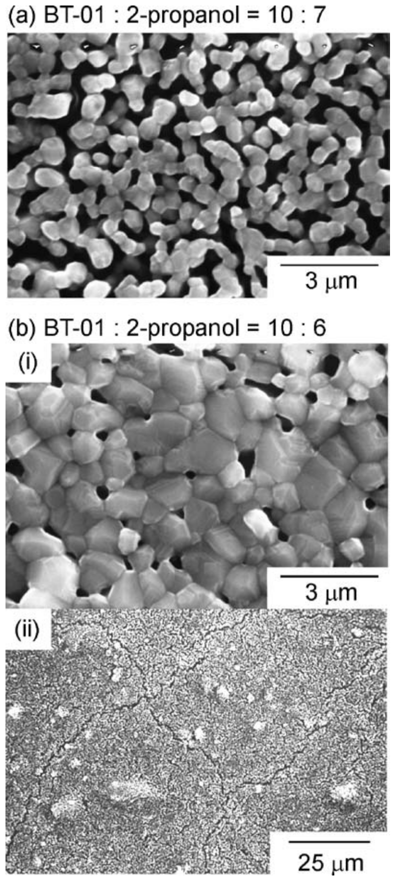

Fig. 5. SEM photographs of the surface of $BaTiO_3$ films fabricated by SC-STP method and subsequent calcination at 1120°C for 2 h. The ratio of components in the slurry (BT-01 : 2-propanol : printing oil) was (a) 10 : 7 : 0.1 and (b) 10 : 6 : 0.1 (in weight). (i) High and (ii) low magnification.

To reduce the shrinkage of the films during calcination, the SC-STP process was conducted by employing a mixture of BT-01 and BT-05 powders with different particle size. Figure 6 shows SEM photographs of the films thus fabricated with several slurry compositions. Although higher contents of BT-05 particles in the slurries resulted in a rather porous structure of the films, as shown in Fig. 6(a), the co-addition of BT-05 powder was found to be effective for reducing the formation of cracks in all the slurry compositions tested (see Fig. 6(b) and (c)). This phenomenon may be ascribed to a relaxation effect of large particles on the sintering among small particles. The most preferable microstructure was achieved with the slurry composition: BT-01: BT-05 : 2-propanol : printing oil = 7 : 3 : 4.2 : 0.1

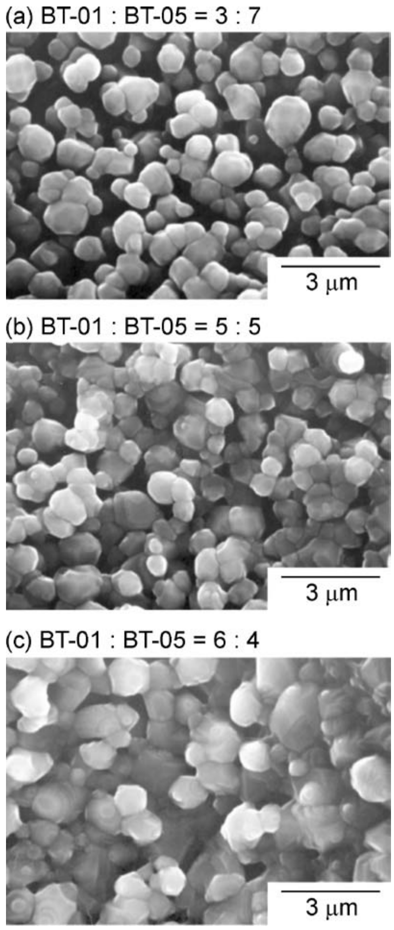

Fig. 6. SEM photographs of the surface of $BaTiO_3$ films fabricated by SC-STP method and subsequent calcination at 1120°C for 2 h. The ratio of components in the slurry (BT-01 : BT-05 : 2-propanol : printing oil) was (a) 3 : 7 : 2.5 : 0.1, (b) 5 : 5 : 3 : 0.1 and (c) 6 : 4 : 3.6 : 0.1 (in weight).

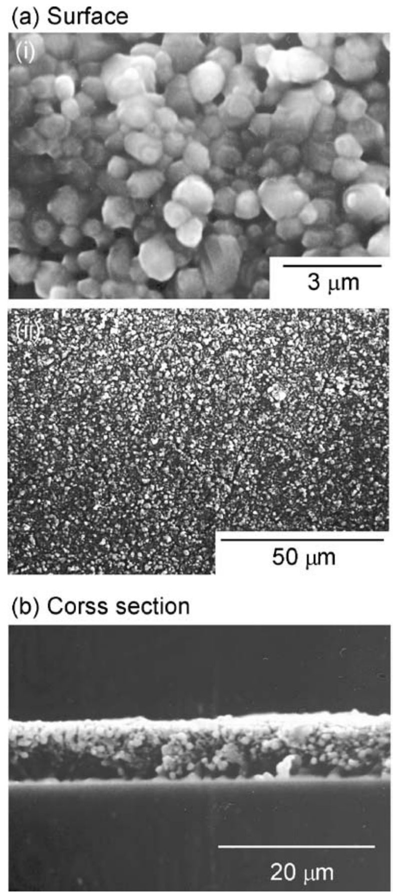

Fig. 7. SEM photographs of (a) the surface and (b) the cross section of $BaTiO_3$ films fabricated by SC-STP method and subsequent calcination at 1120°C for 2 h. The ratio of components in the slurry (BT-01 : BT-05 : 2-propanol : printing oil) was 7 : 3 : 4.2 : 0.1 (in weight). (i) High and (ii) low magnification.

in weight, as shown in Fig. 7. The resultant film was quite homogeneous and dense with no serious cracks (see Fig. 7(a) and (b)). Thickness of the film was also uniform (ca. 9 μm thick) as shown in Fig. 7(c). Thicker films can be fabricated by stacking the slide-off transfer sheets. Ferroelectric and microwave properties of the thick $BaTiO_3$ films fabricated are under investigation.

4. Conclusion

Attempts were made to fabricate dense and thick $BaTiO_3$ films by SP-STP and SC-STP processes. Formation of dense films with good adhesive properties toward a silicon substrate was difficult by the SP-STP process, irrespective of the kind of solvents used for the slurries. On the other hand, relatively dense films could be fabricated by the SC-STP process by employing the slurry consisting of fine $BaTiO_3$ particles (ca. 0.1 μm), printing oil, and 2-propanol. However, cracks were obviously formed by shrinkage during sintering of fine particles. The most preferable microstructure without serious cracks could be achieved with the co-addition of large $BaTiO_3$ particles (ca. 0.5 μm) to the above slurry.

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References

1. J.G. Fagan and R.W. Amarakoon, *Am. Ceram. Soc. Bull.*, **72**, 69 (1993).
2. T. Ishihara, K. Kometani, Y. Mizuhara, and Y. Takita, *Sens. Actuators B*, **5**, 97 (1991).
3. T. Yamamoto, *New Ceramics*, **11**, 33 (1998).
4. M.-C.Wnag, F.-Y. Hsiao, C.-S. His, and N.-C. Wu, *J. Crystal Growth*, **246**, 78 (2002).
5. G. Yang, W. Wang, L. Yan, H. Lu, G.. Yang, and Z. Chen, *Optics Commun.*, **209**, 445 (2002).
6. B.I. Lee and J. Zhang, *Mat. Res. Bull.*, **36**, 1065 (2001).
7. B.D. Stojanovic, C.R. Foschini, B.V. Pavlovic, V.M. Pavlovic, V. Pejovic, and J.A. Varela, *Ceram. Intern.*, **28**, 293 (2002).
8. B. Su and T.W. Button, *J. Euro. Ceram. Soc.*, **21**, 2641 (2001).
9. B. Su and T.W. Button, *J. Euro. Cearm. Soc.*, **21**, 2777 (2001).
10. A. Kawahara, H. Katsuki, and M. Egashira, *Sens. Actuators B*, **49**, 273 (1998).
11. A. Kawahara, K. Yoshihara, H. Katsuki, Y. Shimizu, and M. Egashira, *Sens. Actuators B*, **65**, 17 (2000).
12. T. Hyodo, T. Mori, A. Kawahara, H. Katsuki, Y. Shimizu, and M. Egashira, *Sens. Actuators B*, **77**, 41 (2001).
13. T. Hyodo, Y. Tominaga, T. Yamaguchi, A. Kawahara, H. Katsuki, Y. Shimizu, and M. Egashira, *Electrochemistry*, **71**, 481 (2003).