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Dielectric properties of nano-crystalline $BaTiO_3$ synthesized by micro-emulsion method

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Abstract

Ferroelectricity of the thin films consisting of nano-crystalline $BaTiO_3$ by micro-emulsion (ME) method was investigated. Ultra-fine $BaTiO_3$ particle of 8 nm in diameter was obtained. A clear solution of the well-dispersed powder was spin-coated on $Si/SiO_2/Al_2O_3/Pt$ substrate. The crystallinity and particle size were changed with post-annealing from 600 to 1000 °C. Dielectric properties of the films were measured as a function of biasing field, frequency and temperature. It was revealed from the evaluation of dielectric properties and microstructure that annealing at higher than 700 °C provided $BaTiO_3$ thin film with ferroelectricity. Typical ferroelectric D–E hysteresis was observed with thin films of 360 nm thick fired at 700 °C. The ceramic consists of the fine-grains of 18 nm in diameter. Dielectric constant and dissipation factor were 770 and 2.4%, respectively. The grain growth was taken place with elevating the heating temperature. But the grain growth was not as serious as expected. The sample fired at 1000 °C had still fine grain size of 67 nm. The insulation resistance was higher than 109 Ω cm, which is an acceptable vale for capacitor applications.

Keywords: Films; Ferroelectric properties; Grain size; $BaTiO_3$; Capacitors

1. Introduction

Progressively thinner dielectric layers of multilayer capacitors (MLC) are in high demand these days. However, ferroelectric ceramics lose their ferroelectricity when their particle size is decreased and lose ferroelectricity at a critical size. This is known as a size effect and makes a difficulty on progress of MLC. However, ferroelectricity in nanometer size ceramics is still not fully understood despite many recent investigations. In fact, there has been substantial disagreement in the critical sizes of $BaTiO_3$ that have been reported.[1–7] Nano-sized ceramics are generally synthesized by wet processes, such as hydrolysis and hydrothermal methods, because of the cost advantages and the ability to control compositions, as compared to vapor processes. In this case, the synthesized powder takes many hydroxyls inside resulting in poor crystallinity and low dielectric performance. Therefore, in a production line of dielectric powder, hydrolysis $BaTiO_3$ of about 30 nm in diameter, for example, grow to over 100 nm during calcination. If we can synthesize the finer $BaTiO_3$ particles, hopefully under 10 nm, and calcine them to have average particle size of 20 nm in diameter, we can obtain ultra-fine $BaTiO_3$ particles with high crystallinity, which can provide MLCs with ultra-thin dielectric layers.

Micro-emulsion (ME) method is one of the promising method to prepare the ultra-fine ceramic powder of narrow grain size distribution. This involves hydrolysis proceeding in water droplets of inverse micelles as microreactors dispersed in oil.[8–12] Particle sizes are controlled by the diameter of the water droplets in nanometer range. $BaTiO_3$ particles with a mean size of 8 nm and narrow grain size distribution were obtained by this method. Optimizing the composition of ME made it possible to keep synthesized particles well dispersed in the solution as they are synthesized. Thus, the solution was applied to prepare thin films consisting of nano-crystalline $BaTiO_3$ via spin coating.

Thin film samples with different average particle size were processed by varying the post-annealing temperatures to characterize their electrical properties associated with particle size. In this report, we focus on the electrical properties of $BaTiO_3$ thin films with nano-crystalline particles using ME

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process, which showed ferroelectricity and high permittivity in spite of having nano-dimension in particle size.

2. Experimental

Fig. 1 shows the flow chart of thin film fabrication using the clear solution containing well-dispersed $BaTiO_3$ nano-crystalline particles prepared by ME method. Cycrohexane/NP-10/1-octanol/water system for ME was used. The (Ba, Ti) double alkoxide solution was prepared by mixing equimolar amount of barium and titanium isopropoxides with isopropanol containing benzene, to avoid polymerization of barium alkoxide in the Ar atmosphere. The double alkoxide solution was added to the ME and stirred for 12 h. This resulted in a clear solution of well-dispersed synthesized nano-crystalline $BaTiO_3$ particles.

The solution was spin-coated on $Si/SiO_2/Al_2O_3/Pt$ substrates, and the films were treated on hotplates to dry and to remove the surfactant NP-10, at 150 °C for 2 min and at 460 °C for 3 min, respectively. This process was repeated five times. Then the films were annealed at 600 °C in O_2 atmosphere. The sequence of this spin-coating through 600 °C annealing process was repeated five times, finally the $BaTiO_3$ thin film samples annealed at 600 °C were prepared.

Surface and cross-sectional SEM micrographs of the 600 °C annealed sample were shown in Fig. 2. The film was dense and consisted of ultra-fine nano-crystals whose average diameter was 17 nm, and thickness was about 360 nm.

Then these films were post-annealed at different temperatures ranging from 600 to 1000 °C to prepare $BaTiO_3$ thin films with different crystallinity and particle size. Particle sizes were estimated from one hundred of particles in SEM micrographs by using a digitizer. The dielectric properties of the films were measured as a function of applied bias, frequency and temperature by using a LCR meter (HP-4284A). The P–E hysteresis loops were observed by using a Radiant RT-6000HVS.

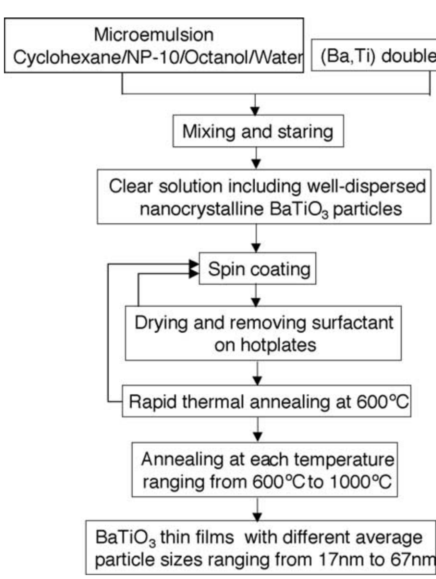

Fig. 1. Flow chart of thin film fabrication.

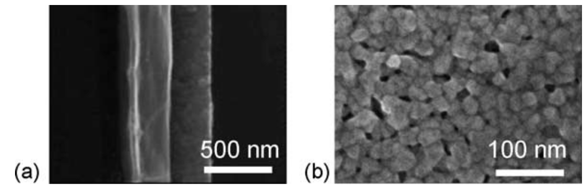

Fig. 2. SEM micrographs of the sample annealed at 600 °C: (a) cross-section and (b) surface.

3. Results and discussion

Average particle sizes of the $BaTiO_3$ thin film samples annealed at each temperatures are given in Table 1.The samples annealed at lower than 800 °C did not show much grain growth and kept the sizes under 20 nm. Grain growth took place at higher temperatures than 800 °C, e.g., annealing at 900 °C and 1000 °C. They grew up to 30 and 67 nm in diameter, respectively.

The electrical properties of these samples were measured. Table 2 gives the dielectric properties of the sample annealed at 700 °C measured at 1 kHz. The dielectric constant of 770, dielectric loss of 2.4% and high resistivity of $>10^9$ were obtained with the sample of 370 nm thick.

Dependence of dielectric constant on annealing temperature is shown in Fig. 3. The dielectric constant was about 320 when the sample annealed at 600 °C, but it remarkably increased to 770 with heating at 700 °C. Then dielectric constant increased monotonically with the grain size. Annealing at 1000 °C provided the sample with dielectric constant of more than 1100.

We found that the $BaTiO_3$ thin films prepared by the solution of well-dispersed nano-crystalline particles has excellent dielectric properties.

Table 1
The summary of the average particle sizes

Annealing temperature (°C)	Average particle size (nm)
600	17
700	18
800	20
900	30
1000	67

Table 2
Dielectric properties of the $BaTiO_3$ thin film annealed at 700 °C

Annealing temperature (°C)	700
Dielectric thickness (nm)	360
Average particle size (nm)	18
Dielectric constant	770
Dissipation factor (%)	2.4
Resistivity (Ω cm)	$>10^9$

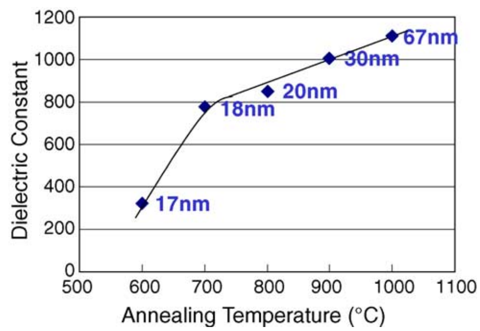

Fig. 3. Dependence of dielectric constant on annealing temperature.

Fig. 4 shows the hysteresis loops of the samples annealed at 600, 700 and 800 °C. All of the samples have smaller average particle sizes than 20 nm. Even though consisting of nano-crystalline $BaTiO_3$ particles smaller than 20 nm, ferroelectric D–E hysteresis loops were observed. The loop of the 600 °C annealed sample looks like as one of the paraelectrics, but those of the 700 and 800 °C gave an typical ferroelectric D–E curves. The behavior of hysteresis curves on annealing temperature corresponds with the dependence of dielectric constant on annealing temperature as shown in Fig. 3. Dependence of capacitance on DC biasing voltage for the samples annealed at each temperature (shown in Fig. 5) also corresponded with the behavior of the hysteresis curves. DC bias voltage dependence of capacitance was small in the 600 °C annealed sample, but the samples annealed at higher than 700 °C showed large DC voltage dependences, and butterfly like C–V curve, which is characterized in ferroelectricity, was observed.

These results are one of the evidence that the $BaTiO_3$ thin film consisting of nano-crystalline particles of 18 nm in average particle size has ferroelectricity. Dielectric constant changes with frequency and temperature are shown in Figs. 6 and 7, respectively. The sample annealed at 600 °C has relatively small frequency and temperature dependence. The dielectric constant increased with annealing temperature, and it changed with applied frequency. The dielectric constant showed moderate temperature dependence, i.e., gradually changed with negative slope at higher than room temperature. However, the dielectric constants at a vicinity of 60 °C increased with increasing annealing temperature, resulting in rather flat curve. At around 60 °C, small chance in

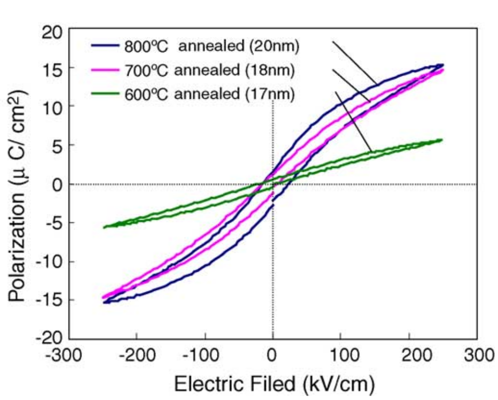

Fig. 4. D–E hysteresis loops of $BaTiO_3$ thin films with average particle sizes of under 20 nm annealed at 600, 700 and 800 °C.

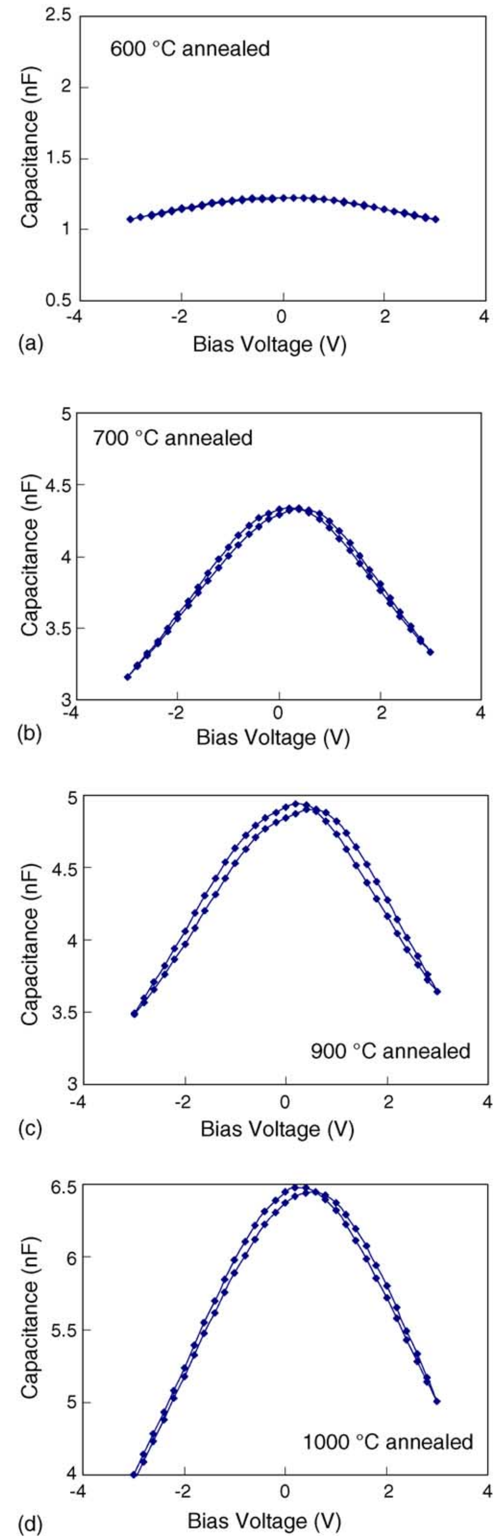

Fig. 5. Dependence of capacitance on DC bias voltage for the samples annealed at each temperatures: (a) 600 °C; (b) 700 °C; (c) 900 °C; and (d) 1000 °C.

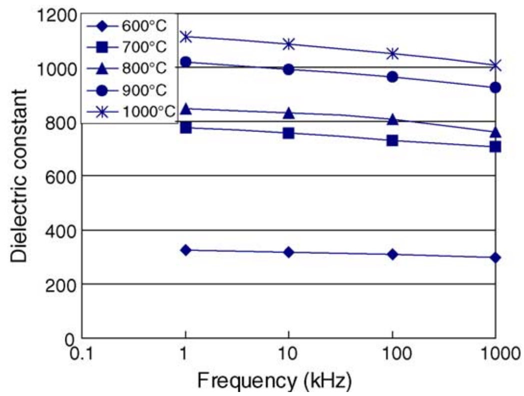

Fig. 6. Frequency dependence of dielectric constant.

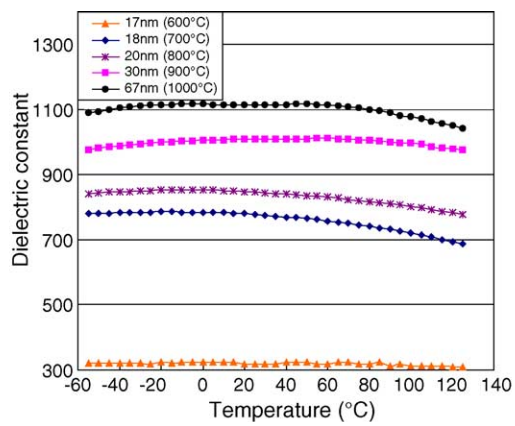

Fig. 7. Temperature dependence of dielectric constant.

capacitance was observed, which may be due to the ferroelectric phase transition. The change appears more clearly in the curve of the 1000 °C annealed sample. The obtained dielectric constant was not as high as that of the dielectrics prepared by the conventional powder method, however, the dielectrics employed theses newly developed $BaTiO_3$ is promising material for ultra-thin dielectric layer, e.g., half micron meter thick. We can design the ceramic capacitor of much higher volumetric efficiency and stable characteristics.

4. Conclusion

Employing the micro-emulsion method and optimizing the emulsion composition, the clear solution of well-dispersed nano-crystalline $BaTiO_3$ particles was obtained. Using the solution of $BaTiO_3$, thin films consisting of the nano-sized particles ranging from 17 to 67 nm were successfully prepared by spin coating on $Si/SiO_2/Al_2O_3/Pt$ substrates and annealing them at temperatures in the range from 600 to 1000 °C. It was revealed from the measurement of the electrical properties that the sample annealed at 600 °C, which had an average particle size of 17 nm, showed paraelectric properties, but the samples annealed at temperatures higher than 700 °C showed a ferroelectricity. D–E hysteresis loop was observed with the sample even an average particle size was 18 nm. Dielectric constant was 770 and dielectric loss was 2.4%, which was acceptable, values for designing the ceramic capacitors.

We conclude that the $BaTiO_3$ thin films prepared by using the solution from micro-emersion process provide stable dielectric properties even consisting of nano-crystalline particles of about 20 nm in diameter, and are highly expected in applications for ultra-thin film and/or multi-layer capacitors of high volume metric efficiency and high frequency performances.

References

1. Akdogan, E. K. and Safari, A., Phenomenological theory of size effects on cubic-tetragonal phase transition in $BaTiO_3$ nanocrystals. *Jpn. J. Appl. Phys.*, 2002, **41**, 7170–7175.
2. Hsiang, H. I. and Yen, F. S., Effect of crystallite size on the ferroelectric domain growth of ultrafine $BaTiO_3$ powders. *J. Am. Ceram. Soc.*, 1996, **79**(4), 1053–1060.
3. Li, X. and Shih, W. H., Size effects in barium titanate particles and clusters. *J. Am. Ceram. Soc.*, 1997, **80**(11), 2844–2852.
4. McCauley, D., Newnham, R. E. and Randall, C. A., Intrinsic size effects in a barium titanate glass-ceramic. *J. Am. Ceram. Soc*, 1998, **81**(4), 979–987.
5. Sakabe, Y., Wada, N. and Hamaji, Y., Grain size effects on dielectric properties and crystal structure of fine-grain $BaTiO_3$ ceramics. *J. Korean Phys. Soc.*, 1998, **32**, 260–264.
6. Miyoshi, T., Deguchi, Y., Yamamoto, H. and Sakabe, Y., In *Proceeding of the Annual Meeting of The Ceramics Sosicety of Japan*, 2000, p. 87.
7. Tsunekawa, S., Ito, S., Ishikawa, K., Li, Z. Q. and Kawazoe, Y., Critical size and anomalous lattice expansion in nanocrystalline $BaTiO_3$ particles. *Phys. Rev. B*, 2000, **62**(5), 3065–3070.
8. Herring, H. and Hempelmann, R., A colloidal approach to nanometre-sized mixed oxide ceramic powders. *Mater. Lett.*, 1996, **27**, 287–292.
9. Beck, Ch., Hartl, W. and Hempelmann, R., Size-controlled synthesis of nanocrystalline BaTiO3 by a sol–gel type hydrolysis in microemulsion-provided nanoreactors. *J. Mater. Res.*, 1998, **13**(11), 3174–3180.
10. Wang, J., Fang, J., Ng, S., Mag, L., Chew, C., Wang, X. *et al.*, Ultrafine barium titanate powders via microemulsion processing routes. *J. Am. Ceram. Soc.*, 1999, **82**, 873–881.
11. Zarur, A. J. and Ying, J. Y., Reverse microemulsion synthesis of nanostructured complex oxides for catalytic combustion. *Nature*, 2000, **403**, 65–67.
12. Gan, L. M., Zhang, L. H., Chan, H. S. O., Chew, C. H. and Loo, B. H., A novel method for the synthesis of perovskite-type mixed metal oxides by the inverse microemulsion technique. *J. Mater. Sci.*, 1996, **31**, 1071–1079.