Energy storage properties of surface-modified BaTiO₃ ceramic films for multilayer capacitors applications

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Surface-modified BaTiO₃ of 230 nm average grain size were synthesized by coating BaTiO₃ particles with 3 wt.% Al₂O₃ and 1 wt.% SiO₂. Ceramic films of different thicknesses were prepared via tape casting and laminating processes followed by two-steps sintering method. After sintering, the average grain size of Surface-modified BaTiO₃ ceramic slightly increased to 275 nm, and great enhancement of AC breakdown strength (BDS) from 184 kV/cm to 665 kV/cm was obtained as the thickness of ceramic films decreased from 63 μm to 12 μm, resulting in improvement of discharge energy density from 1.14 J/cm³ to 4.06 J/cm³. Because of their low-cost, easily fabrication, lead-free, improved AC BDS and discharge energy density, surface-modified BaTiO₃ ceramic films appeared promising for applications in multilayer energy storage capacitors.

Keywords: Ceramic films; multilayer ceramic capacitors; ferroelectrics; energy storage.

1. Introduction

Recently, multilayer ceramic capacitors (MLCC) have been widely investigated owing to their potential use as energy storage devices. Compared with the other energy storage devices such as batteries, fuel cells, and super-capacitors, ferroelectric ceramic capacitors possess high working voltage, great temperature stability, and fast charge–discharge cycles, despite their low energy storage density.¹ By integrating multiple layers of ceramic capacitors, relatively higher energy storage density has been achieved in MLCC. The energy density (U) can be calculated by integrating the electric field (E) with the polarization (P) from the P – E hysteresis loop as

$$U = \int_0^P E dP.$$

BaTiO₃ (BT)-based ceramics, one kind of lead-free ferroelectric, has high permittivity and good temperature stability, making them promising as environmental friendly energy storage materials. However, they have relatively low electric breakdown strength (BDS) and nonlinear polarization response which drops rapidly with increasing external electric field, resulting in relatively low energy storage density and limiting their industrial applications.² Improving the BDS and adjusting the nonlinear permittivity to linear are promising approaches to achieve high energy storage density in BT-based ceramics. Considering the fabrication, optimization

of the morphology and micro-structures such as porosity, grain size, defects, and the addition of secondary phases will be extremely important.

Introducing secondary phase with high BDS into BT-based ceramics has been reported as an efficient approach for enhancing energy storage properties. The existence of secondary phase prevents the BT-based ceramic from breaking down at the boundaries, which improves BDS without obviously decreasing permittivity.³ Liquid-phase sintering has been also reported to improve the sintering properties by forming glass phase, decreasing ceramic defects.² Introducing Al₂O₃ into BT ceramics appears to improve BDS and refine the grain size.⁴ Moreover, SiO₂ has been found to reduce the number of defects and suppress grain growth. Therefore, adding Al₂O₃, SiO₂, or both to BT-based ceramics could produce uniform micro-structures and fine grains.⁵

In previous work, fine-grained bulk ceramic was prepared with maximum discharge energy density ($U_{\max}$) of 0.725 J/cm³ and BDS of 190 kV/cm via aqueous chemical coating of nanocrystalline BT particles with 3 wt.% Al₂O₃ and 1 wt.% SiO₂ (BTAS).⁶ Thus, BTAS ceramics with fine grains would be promising in the MLCC industry, especially which require ultra thin dielectric layers (<2 μm). In this work, massive (~8 kg) BTAS powders were synthesized as described in previous work⁶ under industrial conditions. BTAS ceramic films with different thicknesses were prepared via tape casting, laminating, and hot isostatic pressing processes.

The micro-structures of the BTAS particles and ceramic films were characterized, and the energy storage properties of ceramic films were tested. The effects of film thickness (D) on BDS and $U_{\max}$ were discussed.

2. Material and Methods

BTAS powders were synthesized via aqueous chemical coating, and then calcined at 600°C for 3 h forming stable structures. The compositions of BTAS tape casting slurry were listed Table 1. After sequentially adding solvent, dispersant, binder, and then plasticizer to the BTAS powders, the slurry was ball-milled for 48 h. Continuous BTAS tapes were prepared via roll-to-roll tape casting using a test coater (CMD-S1.7/D/4.OH/3-778, Yasui Seiki Corp, Japan). BTAS films with various thicknesses were fabricated via laminating different layers using an automatic lamination machine (NSM-1Y01, Yodogawa NCC Co., Ltd, Japan), and then hot-isostatic pressed under 90 MPa at 60°C for 20 min.

BTAS films were cut into 10×10 mm pieces and sintered by two-steps sintering method: at 1190–1210°C for 10 min, and then at 1040–1060°C for 6 h in air. To avoid the uncertain evaporation of the inner electrode during MLCC sintering process,⁷ samples were coated with Pt via high-vacuum evaporation, and the samples were covered with a mask to precisely control the size ($\phi = 3$ mm) of the conductive coating. The micro-structures of the BTAS particles and ceramic were characterized by field-emission scanning electron microscopy (FE-SEM, Supra 40/40 vp, Carl Zeiss Jena Corp, Germany) with the operating voltage of 15 kV and

field-emission transmission electron microscope (FE-TEM-2010F, JEOL Co., Ltd., Tokyo, Japan), with the operating voltage of 200 kV. The phases of the BTAS powders and ceramic films were identified by X-ray diffraction (XRD; D8 advance-A25, Bruker Co., Ltd., Karlsruhe, Germany). The hysteresis loops were measured by a ferroelectric measuring system (TF ANALYZER 2000E, aix ACCT Systems GmbH, Aachen, Germany) at 10 Hz at room temperature.

3. Results and Discussion

Figure 1 showed the micro-structures of BTAS particles after calcination, suggesting that fine-grained BT particles (230 nm average grain size) were uniformly coated with Al_2O_3 and SiO_2 . The parameters of roll-to-roll tape casting were: moving speed of 1 m/min and pump supply pressure of 0.08 MPa. After drying at 80°C, 18 μm thickness BTAS tapes were fabricated. As shown in Fig. 2, BTAS particles were uniformly distributed in both surface and cross-section of tapes, meanwhile the relatively low porosity of tapes ensured high density after sintering.

Figure 3 showed micro-structures of 12 μm thickness BTAS ceramic films. Narrowly-size-distributed grain with average size of 275 nm were obtained after two-steps sintering, which was only 19.6% larger than before. The samples exhibited low porosity and slightly abnormal grain growth of secondary phases. In addition, a liquid phase formed between ceramic grains. The existence of both fine grains and liquid phase would be the fundamental to improve the BDS.⁸ The relationship between the BDS and grain size (G) of ceramic could be described as

$$\text{BDS} \propto \frac{1}{\sqrt{G}}.$$

Figure 4 showed XRD patterns of BTAS powders and ceramic films. Main phase of perovskite BaTiO_3 was observed in all samples and small amounts of secondary phase of $\text{Ba}_4\text{Ti}_{10}\text{Al}_2\text{O}_{27}$ were observed in BTAS ceramic films after sintering. The XRD patterns results were consistent with the SEM images of BTAS ceramic films and in both the secondary phases of $\text{Ba}_4\text{Ti}_{10}\text{Al}_2\text{O}_{27}$, they were detected. So it

Table 1. Tape casting formulation.

Component	Function	Proportion (wt.%)
Barium Titanate	Ceramic powder	40
Ethanol	Solvent	27
Ethyl acetate	Solvent	27
Triglycerides	Dispersant	0.4
Polyvinyl Butyral	Binder	4.4
Butyl Benzyl Phthalate	Plasticizer	0.6
polyethylene glycol-400	Plasticizer	0.6

Fig. 1. TEM (a) and SEM (b) images for calcined BTAS particles.

Fig. 2. SEM images for (a) surface and (b) cross-section of BTAS tapes.

Fig. 3. (a) Surface, (b) cross-section SEM images and (c) grain size distributions of 12 μm thickness BTAS ceramic films.

could be concluded that during sintering process, Al_2O_3 diffused into the BaTiO_3 lattices forming a homogenous perovskite solid solution $\text{Ba}_4\text{Ti}_{10}\text{Al}_2\text{O}_{27}$, which was confirmed suppressing seriously abnormal grain growth for BaTiO_3 .^{4,9} No detection of SiO_2 peaks suggested that the superfluous SiO_2 possibly formed amorphous composites.

BTAS ceramic films with thicknesses of 12, 24, 35, and 63 μm were fabricated by laminating 1, 2, 3, and 6 layers BTAS tapes, respectively. The hysteresis loops of BTAS ceramic films were shown in Figs. 5(a)–5(d). Slim ferroelectric

hysteresis was observed for all samples. BTAS ceramic films possessed relative higher discharge/charge efficiency (E_{eff}) from 64.1% to 72.5% owing to their smaller remnant polarization and coercive electric field compared to pure BT, thus resulting in much higher U_{max} causing by the obvious increasing BDS, of which pure BT ceramic films were around 200 kV/cm.¹ Figure 5(e) showed the BDS and U_{max} of BTAS ceramic films varied as a function of film thickness. As the thickness decreased from 63 μm to 12 μm , the BDS increased from 184 kV/cm to 665 kV/cm, while maximum polarization increased from 19.1 $\mu\text{C}/\text{cm}^2$ to 33.8 $\mu\text{C}/\text{cm}^2$. Despite the polarization nonlinear and hysteresis, great enhancement in BDS still made U_{max} of BTAS ceramic films improve from 1.14 J/cm³ to 4.06 J/cm³, which was about 5.6 times the value of bulk BTAS ceramics.⁶ Figure 5(f) shows the U and E_{eff} of BTAS ceramic films varied as a function of E . U of different thicknesses BTAS ceramic films were consistent with each other as a function of E , and it showed closing-linear relationship between U and E at high electric field. Higher E_{eff} at the same E were obtained for thinner BTAS ceramic film owing to less porosity as D decreased, confirming that D is beneficial for both enhancements of BDS and E_{eff} . Overall, the U_{max} of BTAS ceramic films with a thickness of 12 μm were improved to 4.06 J/cm³ at E_{max} of 665 kV/cm, and the average grain size was only 275 nm. According to the relationship between BDS/ U_{max} and D , 2 μm thickness BTAS ceramic films may show impressive U_{max} and BDS, so they can be used in MLCC applications such as energy storage

Fig. 4. XRD patterns of BTAS powders and ceramic films.

Fig. 5. Hysteresis loops of BTAS ceramic films with thicknesses of (a) 12 μm , (b) 24 μm , (c) 35 μm , and (d) 63 μm . (e) BDS and U_{max} varied as a function of film thickness. (f) U and E_{eff} varied as a function of electric field.

devices, especially satisfying the requirement of ultra thin dielectric layers.

4. Conclusion

Surface-modified BaTiO₃ particles with an average grain size of 230 nm were synthesized by coating BaTiO₃ particles with 3 wt.% Al₂O₃ and 1 wt.% SiO₂. Uniformly distributed

as-synthesized particles were obtained in BTAS tapes via roll-to-roll tape casting. After lamination process, BTAS ceramic films with thickness from 12 μm to 63 μm were prepared by two-steps sintering method. Ceramic films possessed relatively low porosity and average grain size of 275 nm. Enhancement of electric BDS to 665 kV/cm were obtained when the thickness of BTAS ceramic film decreased to 12 μm , improving the maximum discharge energy density

to 4.06 J/cm^3 . With low cost, easy fabrication, environmental friendliness, and improved electric BDS and energy storage density, BTAS ceramic will be promising materials for use in multilayer energy-storage capacitors.

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