Dielectric properties of barium zirconate titanate nanocube 3D-ordered assemblies

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Single-crystalline barium zirconate titanate nanocubes (BZₜ NCs; x is Zr contents) with various composition of Zr/Ti ratio were synthesized by hydrothermal method using water-soluble titanium and zirconium complex and surfactants. The highly-ordered assemblies of the BZₜ NCs were directly fabricated on the substrate by dip-coating method with low withdrawal rate. High dielectric constant above 4200 and relative low loss tangent below 1 % with extremely small frequency dependence were achieved in the case of BZ₀.₂₅ NC assembly. The temperature dependence of capacitance of BZ₀.₁₅ NC assembly was quite small from ¹ 60 to 150°C. A specific peak in the Raman spectra of BZ₀.₂₅ NC assembly was slightly shifted to lower wavenumbers from 294 to 288 cm⁻¹ after heat-treatment which meant the change of local bonding condition was induced by local strains at the interfaces. Zr-substitution and local strain synergistically affected to the dielectric properties of BZₜ NC assemblies.

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1. Introduction

The next generation systems as typified by Internet of Things appeared in recent years. The miniaturized and high-performance electronic devices, for example, multilayered ceramic capacitors (MLCCs) have been developed. However, conventional materials and fabrication methods of these devices will meet the limitation on above demands in near future. The entirely innovative technologies using nano-sized materials are demanded for fabrication of the electronic devices. Nanocrystals are focused as new materials which have great potentials to obtain enhanced and/or unique properties compared with conventional materials.¹,² Barium titanate (BT) based ceramics are widely used for dielectric devices such as MLCCs. The dielectric constant of BT nanoparticles decreases when the size of the BT particles decreased because its ferroelectricity is disappeared. This is called as nanosize effect.³,⁴ However, the author and other groups reported that the BT single-crystalline nanocubes (BT NCs) maintained ferroelectricity in the size of sub-10 and 15 nm.⁵,⁶ The shape of nanocrystals plays a significant role to achieve high properties with overcoming the nanosize effect. Moreover, the highly-ordered 3D assemblies of the BT NCs are necessary for the application of the next generation devices. Solution self-assembly process of the nanocrystals is effective technique to gain large assemblies. The precise control of the size and shape distribution of the BT NCs is necessary for enlargement of assembly area with high ordering. The authors have already reported both synthesis of the BT NCs by hydrothermal reaction and fabrication of the highly-ordered BT NC assembly by using capillary force assisted self-assembly method.⁷⁻¹⁵ In the past, the solid solutions of BT-based ceramics have been reported, especially, Zr substitution of Ti (BZT) was useful method to tune the electrical properties.¹⁷,¹⁸ Recently, the authors reported that BZT NC was synthesized by water soluble compounds as starting materials.¹⁹,²⁰ In this paper, it is reported that the BZT NC assemblies with high ordering were directly fabricated on Pt-coated substrates. The microstructure and dielectric properties of BZT NC assemblies are discussed.

2. Experimental procedure

A typical process of BZₜ NCs (x is Zr content; 0 ≤ x ≤ 0.2) was the hydrothermal method similar to the previous our reports.²¹,²²,²³,²⁴ All reagents were used without any purifications. The barium hydroxide, titanium and zirconium ammonium lactates, oleic acid and tert-butylamine were chosen as starting materials, surfactant and additives, respectively.²⁵ Especially, oleic acid plays
an important role to control cubic shape due to capping on [100] facets of BT-based crystals. The reaction temperature and time was optimized at 493 K, 72 h for BZ$_{0.1}$T NCs and 503 K, 96 h for BZ$_{0.2}$T NCs. The molar ratio of tert-butylamine (t-BA) and oleic acid (OLA) to BZT was set as BZT:t-BA:OLA = 1:12:12 to obtain the cubic shaped BZT crystals. After the reaction, the viscous white slurry was centrifuged, and the precipitates were washed twice by ethanol. They were ultrasonically dispersed into toluene. The classification of BZT NCs was also done by centrifugation to fabricate 3D assemblies. BZ$_x$T NC dispersed solution was dip-coated on the Pt/Si substrate at low withdrawal rate about 10–20 nm/s using the NC dispersed mesitylene solution. The assembled films were irradiated by ultraviolet light for 2 h and dried at 200°C for 1.5 h in oven to remove the residual organic components. And then, BZT NC assembly films were calcined and sintered at 450°C for 1 h and 850°C for 1 h under O$_2$ gas flow. To characterize the dielectric properties, top electrodes were fabricated by electron beam deposition with a shadow mask ($\phi = 10\mu$m). The sample with top electrodes was post-annealed at 550°C for 10 min. The BZT NC assemblies were characterized by field emission scanning electron microscope (FE-SEM) (JEOL, JSM-6335FM) observations and Raman spectra (Horiba, XploRA). Dielectric properties depend on the frequency and temperature of BZT NC assemblies were also characterized by micro probe system with a cryostat and impedance analyzer (Agilent, 4294A). The accuracy of measurement of capacitance was about 3% at 1 MHz.

3. Results and discussions

Figure 1 shows FE-SEM images of BZ$_x$T ($x = 0.1, 0.2$) NC assemblies dip-coated on Pt/Si substrate after heat-treatment at 850°C. The 3D ordered assemblies were obtained independent of the composition of BZT NCs. The size of BZT NCs had been reported by the authors as about 15 nm with sharp edges. Cubic shape of BZT NC was kept after heat-treated at 850°C as shown in Figs. 1(a) and 1(b). These results were corresponding to the previous results on BT NC assembly. It is one of the reason why the grain growth did not occur is that the size and shape of the NCs was almost equal. The grain growth is caused by wide variation of grain size and shape. Especially, the conditions required to give minimum interfacial energy link the shape parameters with the size parameters and the structural parameters (the mean radius of curvatures, facets of a grain, and density in the structure). If the different surfaces of the particle with different particle size had attached each other in the heat-treatment process, the grain growth should be accelerated to fill the spaces and decrease the interfacial energy. On the other hand, the size and shape of BT-based NCs were quite homogeneously and the density of NC assembly is so high according to the 3D ordering structure. The grain growth of BT-based NC was less likely to evolve. Moreover, it is well known that oriented attachment between same facets easily occurred in the nanocrystal assembly systems. Local interface region only attached epitaxially each other without grain growth through the heat-treatment process. The cross-sectional image of BZ$_{0.2}$T NC assemblies were also shown in Figs. 1(c) and 1(d). Thickness of BZ$_{0.1}$T and BZ$_{0.2}$T assemblies were about 120 and 200 nm, respectively. Thickness of NC ordered structure fabricated by dip-coating assembly process could be controlled by tuning the dispersion density of colloidal solution.

Figure 2 shows frequency dependence on dielectric constant and loss of BZ$_{0.2}$T NC assembly after heat-treatment at 850°C measured at room temperature under vacuum below 5 × 10$^{-2}$ Pa to reduce the effect of leakage current. The dielectric constant of BZ$_{0.2}$T NC assembly reached 4200 at 1 MHz which was slightly higher than that.

![Fig. 1. Microstructures of BZ$_x$T NC assemblies after heat-treated at 850°C. (a) $x = 0.1$, (b) $x = 0.2$, (c) cross-sectional image of (a), and (d) cross-sectional image of (b).](image-url)
of BT NC assembly as previously reported by our group. However, the dielectric constant of BZ0.2T NC assembly had a small dependence on frequency. Moreover, the dielectric loss was less than 1% in the high frequency range.

The temperature dependence of capacitance and dielectric loss of BZT NC assemblies after heat-treatment at 850°C measured at 1 MHz was shown in Fig. 3. As the top electrodes on BT and BZT NC assemblies after measurement were broken by repetitive probing which was inevitable against the unexpected heat expansion of the sample stage, the correct dielectric constant could not be determined. This is serious problem to understand the properties of NC assemblies. We are now trying to solve this problem by enlargement NC assembly without cracks and must report the accurate temperature dependence of dielectric constant in near future. However, the dielectric properties of BT and BZT NC assemblies can be discussed by comparison of capacitance change. The capacitance was standardized at the value of 25°C as unity. In the case of BT NC assembly, the temperature of maximum capacitance ($T_{\text{max}}$) was appeared at 90–100°C. This temperature corresponds to the ferroelectric-paraelectric phase transition. On the other hand, capacitance of BZ0.1T NC assembly had only small change in the range from −60 to 150°C with low loss. This result indicates that BZT NC assemblies have an immense potential to be used for the dielectric application exposing to high temperature range such as the power electric semiconductor devices. Moreover, increasing Zr content at 20 at%, $T_{\text{max}}$ might be shifted to much lower temperature below −30°C. BZT ceramics showed similar behavior which $T_{\text{max}}$ became much lower with increasing Zr content.17) However, in the case of BZ0.2T ceramics, $T_{\text{max}}$ appeared at almost room temperature which did not correspond to the that of BZ0.2T NC assembly. In addition, it has been found that BT NC assembly had lower phase transition temperature compared with that of the bulk ceramics about 120°C. $T_{\text{max}}$ was shifted to lower temperature totally in BT-based NC assembly systems. The reason of no correspondence was considered due to the interface consisting of tilting angle between the nanocubes in assembly. In our previous study, it is revealed that the tilting angles induced local stress in the interface region and affected shifting phase transition temperature to lower temperature by numerical calculations using Gibbs function under 3D clamping condition in the case of BT NC.23) The phase transition temperature of BT NC assembly under 3D clamping was shifted to around 25°C with the tilting angle of 5.4°. Actual $T_{\text{max}}$ of BT NC assembly exhibited broad peak as shown Fig. 3(c). This means the tilting angles in the assembly had a variation. The actual tilting angles of BT NC monolayer joined interfaces were observed by TEM.24) The angles had a dispersion around 5–7°. Therefore, phase transition was relaxed in the assembly. The similar phenomenon may occur in the BZT NC assembly systems. Consequently, $T_{\text{max}}$ of all NC-based samples were totally shifted toward low temperature compared with bulk ceramics.

Temperature dependent of Raman spectra of BZ0.1T NC assembly after heat-treatment at 850°C showed almost no change in the spectra patterns from 25 to 150°C, as shown in Fig. 4. The shoulder peak at 300 cm$^{-1}$ is attributed to $E(\text{TO}_3)$ mode which indicates the tetragonal phase in this temperature region.25,26) These results suggested that the phase transition of BZ0.1T NC assembly did not occur from 25 to 150°C. Raman spectra from 250 to 350 cm$^{-1}$ of BZ0.2T NC assemblies before and after heat-treatment at 850°C were shown in Fig. 5. The positions of all peaks detected in the whole wavenumber range (200–1200 cm$^{-1}$) had almost no change in measurement temperature range from 40 to 150°C, which indicated no phase transition in the temperature.19) Otherwise, the peak top at 294 cm$^{-1}$ was slightly shifted to lower wavenumber at 288 cm$^{-1}$ after heat-treatment of 850°C. The Raman peak of BT crystal located at around 290 cm$^{-1}$ was attributed to $A_1(\text{TO}_2)$ mode.25) This mode contributes to the displacement of TiO$_6$ octahedron along with the c-axis. The displacement

![Fig. 2](image-url) Frequency dependence on dielectric properties of BZ0.2T NC assembly after heat-treated at 850°C. (a) dielectric constant and (b) dielectric loss measured at room temperature.

![Fig. 3](image-url) Temperature dependence of capacitance change and dielectric loss of BT and BZT NC assemblies after heat-treatment at 850°C measured at 1 MHz. Capacitance change of (a) BZ0.2T NC assembly, (b) BZ0.1T NC assembly, (c) BT NC assembly and dielectric loss of (d) BZ0.2T NC assembly, (e) BZ0.1T NC assembly, (f) BT NC assembly. The capacitance was standardized at the value of 25°C. [Plots of BT NC assembly was reproduced from Ref. 13. Copyright (2014) The Japan Society of Applied Physics.]
directions of TiO$_6$ octahedron and Ba-framework of the perovskite were opposite each other in this mode. The peak at 270 cm$^{-1}$ of the BT polycrystals was reported to be shifted to lower wavenumbers under high pressure by Venkateswaran et al.$^{26}$ According to their report, only A$_1$(TO$_2$) was shifted to lower wavenumbers in the first low pressure below 2 GPa. The amount of shift was estimated about 20.8 cm$^{-1}$/GPa in the range from −60 to 150°C which had a potential to be used for power electronic applications. Raman spectra of BZ$_{0.1}$T NC and BZ$_{0.2}$T NC assemblies showed almost no change at the measuring temperature up to 150°C. This means they have no phase transition in the temperature range. Otherwise, a broad peak of BZ$_{0.2}$T NC assembly located at 290 cm$^{-1}$ was shifted to lower wavenumbers after heat-treated at 850°C. This result indicated that the binding condition was changed by local strain at the interfaces of NCs. Small dependence of dielectric properties on frequency and temperature of BZT NC assemblies was caused by the synergistic effect of Zr-substitution to a part of Ti site in each NC and local strain at the interfaces between NCs.

4. Conclusions

BZ$_x$T (x = 0.1, 0.2) NC assemblies were fabricated by capillary force assisted self-assembly method through dip-coating process. The joined interfaces of BZT NC assemblies were formed by heat-treatment at 850°C. The frequency dependence of dielectric constant BZ$_{0.2}$T NC assembly had a small change with high value above 4200 and low loss value below 1%. Moreover, the temperature dependence of capacitance of BZ$_{0.1}$T NC assembly showed quite small in the range from −60 to 150°C which had a potential to be used for power electronic applications. Raman spectra of BZ$_{0.1}$T NC and BZ$_{0.2}$T NC assemblies showed almost no change at the measuring temperature up to 150°C. This means they have no phase transition in the temperature range. Otherwise, a broad peak of BZ$_{0.2}$T NC assembly located at 290 cm$^{-1}$ was shifted to lower wavenumbers after heat-treated at 850°C. This result indicated that the binding condition was changed by local strain at the interfaces of NCs. Small dependence of dielectric properties on frequency and temperature of BZT NC assemblies was caused by the synergistic effect of Zr-substitution to a part of Ti site in each NC and local strain at the interfaces between NCs.

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