Polarization and leakage current properties of self-supported bismuth sodium titanate ceramic films deposited by aerosol deposition method

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Self-supported (Bi0.5Na0.5)TiO3 (BNT) dense ceramic films with a thickness of approximately 20 μm have been fabricated by use of an aerosol deposition method with heat treatment and sapphire single crystal substrates. Investigations of their constitution phase and crystal structure, observation of their microstructure, and measurement of polarization properties and leakage current density (J) were performed. While the films heat-treated at 800 and 900°C in air indicated the low J ≈ 10−7 A/cm² at 150 kV/cm, the sintered bulks and the films annealed at 900°C in the BNT starting raw powder showed the relatively high J of approximately 10−6 A/cm² at 150 kV/cm. These films heat-treated at 800 and 1000°C in air and sintered bulks showed the almost the same coercive field (Ec) of approximately 57 kV/cm (in the 56 to 58 kV/cm range), and the films heat-treated at 1000°C in air exhibited good polarization properties and remanent polarization (Pr) of 25 μC/cm². The AD method is proposed to be effective for obtaining self-supported BNT thick films with good saturated hysteresis loops and low J.

1 Introduction

Since the use of Pb-based perovskite oxides in electronic materials will be restricted in the near future owing to the toxicity of lead, development of lead-free ferroelectric and piezoelectric materials with sufficient properties has been strongly demanded from the environmental point of view. Takenaka et al. have demonstrated that (Bi,Na)TiO3 (BNT) is an attractive piezoelectric material1-3 because it has a large spontaneous polarization. However, the piezoelectric properties of BNT are lost or drastically deteriorated above the depolarization temperature (Td) at 200°C for BNT4,5 due to the structural phase transition from rhombohedral (R3c symmetry: ferroelectric) to tetragonal (P4bm symmetry: ferriferroelectric).6 Recent investigations have focused on increasing the Td for solid solutions of BNT with other perovskite materials.4,5 The use of BNT-based ferroelectrics as piezoelectric materials is considered to help the development of lead-free piezoelectric devices with suitable properties in a cost-effective manner. Defects in ferroelectric materials markedly affect their leakage current, ferroelectric, and piezoelectric properties. The control of polarization states is the underlying principle of ferroelectric and piezoelectric devices. Polarization switching is achieved through the nucleation of domains and subsequent domain wall motions by the application of an electric field. The leakage current arising from defects, however, interferes with the polarization switching of Bi-based ferroelectrics.7-9 In addition, oxygen vacancies are known to obstruct polarization switching,10,11 resulting in a reduction in remanent polarization (Pr) by the clamping of the domain walls. The leakage current and clamping of the domain walls by oxygen vacancies make ferroelectric materials unsuitable for practical applications.12-15 Therefore, materials design based on defect chemistry is essential for fabricating high-quality Bi-based devices with superior piezoelectric properties. It is advantageous to investigate single crystals in order to study the influences of defects on the properties of ferroelectric materials since these properties are unaffected by the microstructure and grain size of the materials. Based on this standpoint, high-Po2 (partial oxygen pressure) crystal growth in order to be suppressed Bi vaporization is demonstrated to be effective for enhancing the polarization and piezoelectric properties of BNT single crystals.16

In a ceramic processing based on solid-state reaction, BNT has been sintered at a high temperature at around 1200°C to obtain dense ceramics. Such a high-temperature treatment induced a vaporization of Bi with a high vapor pressure, which lead to a formation of vacancies of Bi and oxygen. The polarization and piezoelectric properties of BNT ceramics sintered at high temperatures are influenced to some extent by leakage current and clamping of domain walls.17 Nagata et al. reported the influence of oxygen vacancies on ferroelectric and piezoelectric properties for sintered body of BNT ceramics with the excess Bi2O3 fabricated by conventional solid phase reaction and hot-press method.18

The Aerosol Deposition (AD) method, which is based on room temperature impact consolidation (RTIC) phenomena, is attracting attention because it can form thick ceramic layers of simple or complex compositions at a room temperature.19-26 The use of AD method has been already reported for the fabrication of the piezoelectric Pb(Zr,Ti)O3 (PZT),19,21 and its application as a component in a piezoelectric actuator.18 Dense BTO ceramics on resin substrates were also successfully fabricated by AD and they were investigated taking into consideration their possible application to low temperature co-fired ceramics (LTCC).22

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Previously, we investigated the polarization and the leakage current properties for the BNT thick films deposited on Pt coated Al2O3 ceramic substrates by the AD method.27) However, it was difficult to differentiate the influence of the stress from the substrates. In this paper, self-supported BNT thick films were prepared by use of the AD method with heat treatment in order to investigate the influence of the heat treatment on the microstructure, ferroelectric and leakage current properties for the BNT ceramics. It is well-known that there are two means for self-supported thick films obtained by using the AD method. One is use of the polycarbonate substrates.28) The thick ceramic films can be deposited on the polycarbonate substrates by the AD method, and then the substrates are burned in air. The other is applied for the difference of the thermal expansion coefficient between the films and substrates materials.29) If the magnitude of interfacial stress is higher than the adhesion strength between the film and the substrate during heat treatment, the difference of the thermal expansion detaches the films from the substrate. We chose the latter in this study. Microstructure observations, crystal structure analysis and measurements of polarization and leakage current density properties for the obtained self-supported BNT ceramic thick films with thickness of around 20 μm were performed. It has been confirmed that a heat treatment at 800–1000°C in air are expected to be important condition in order to obtain the BNT ceramic films with good saturated ferroelectric properties and low J.

2. Experimental procedure

The starting BNT powder was synthesized by a solid-state reaction using Bi₂O₃, TiO₂ (purity >99.99%) and Na₂CO₃ (purity >99%). These materials were weighted with a composition of Bi₀.₅Na₀.₅TiO₃. They were thoroughly mixed by planetary ball milling for 1 h in ethanol initially, and then calcined in an alumina crucible at 800°C for 4 h in air prior to deposition. Scanning electron microscopy (SEM) observation revealed that obtained starting powder had spherically-shaped particles with the size of 0.1–1.0 μm, and included a small amount of aggregate with the size of 1–5 μm (Fig. 1). BNT films with thickness of around 20 μm were deposited on the sapphire single crystal substrates deposited by AD method. The pressure of the deposition chamber was around 200 Pa for all deposition experiments. The nozzle had an orifice size of 10 mm × 400 μm, total N₂ gas flow rate was about 4–6 l/min, and the distance between the nozzle and substrate was from 2.5 to 10 mm. A heat treatment temperature of 500–1000°C in air detaches BNT thick films from the sapphire single crystal substrates [Fig. 2(a)]. Additionally, obtained self-supported BNT films heat-treated at 500°C in air annealed at 900 and 1000°C in the BNT starting raw powder [Fig. 2(b)]. For comparison, sintered bulks of BNT were prepared by a conventional solid-state reaction using the same starting raw powder used for the AD method. The starting raw powders were pressed into disks followed by cold isostatic pressing and then sintered at 1200°C for 4 h in the BNT starting raw powder. This process provides dense BNT ceramics with a relative density of 97% and 15 mm high. The BNT sintered bulks were cut into 100-μm-thick plates. Constitution phase, crystal structure and crystallite size measurement were analyzed by X-ray diffraction (XRD). Microstructure observation and measurement for the thickness of the self-supported films and the plates fabricated from the BNT sintered bulk were performed by the SEM. For the measurements of polarization hysteresis and leakage current properties, Au dots of 0.5 × 0.5 mm² were sputtered onto both surfaces of the self-

![Fig. 1. SEM images of BNT starting raw powder prepared by a solid state reaction.](image1)

![Fig. 2. Schematics of (a) fabrication process for self-supported BNT thick films and (b) annealing process in the BNT starting raw powder for obtained self-supported BNT films peeled at 500°C in air.](image2)
supported films and the plates prepared from central part of the BNT sintered bulks.

3. Result and discussion

Figure 3 indicates changes in the XRD patterns of the BNT starting raw powder and the resultant self-supported BNT films [procedure; Fig. 2(a)] together with the different heat treatment at 500–1000°C in air. A single phase of perovskite structure was confirmed for these specimens. While the crystalline system of starting raw powder and the self-supported films heat-treated at 800°C or above in air were specifically-identified as rhombohedral (R3c symmetry: ferroelectric), that of the films heat-treated at less than or equal to 700°C in air were not able to be identified because of their weak broad peaks [Fig. 3(a)]. The full width at half maximum (FWHM) of the 2θ peak decreased with increasing heat treatment temperature [Fig. 3(b)] for the obtained films. For the BNT thick films deposited on Pt coated Al2O3, the 2θ of the peaks were shifted toward high angle with increase the annealing temperature,27) while there was disrelation between annealing temperatures and 2θ of the peaks for the self-supported BNT films [Fig. 3(b)]. Therefore, it is considered that the self-supported BNT films heat treated at more than 500°C had stress-free.

Figure 4 illustrates the SEM images for the films delaminated by the various heat treatment at 500–1000°C in air. The films heat-treated at 500°C in air had a fine microstructure without pores, which agrees well with that reported for various films prepared by the AD method. The heat treatment at 800°C or above in air allows the AD films to promote obvious grain growth. Although the grain size increased up to 130–900 nm (average grain size of 300 nm) at 800°C [Fig. 4(c)], those of the films heat-treated at 900–1000°C in air were totally smaller than that of the films heat-treated at 800°C in air [Figs. 4(d) and 4(e)]. Note that the films heat-treated at 900–1000°C in air represented the marked abnormal grain growth. Contrastingly, the abnormal grain growth was not confirmed for the films annealed at 900–1000°C in the BNT starting raw powder [procedure; Fig. 2(b)] (Fig. 5).

In the case of annealing in the BNT starting raw powder, the films annealed at 900°C showed the average grain size of 230 nm, and that of the films annealed at 1000°C increased up to 830 nm.

From FHWM of the peaks, crystallite size (D) can be estimated using the following formula (Scherrer’s equation): $D = \frac{K \lambda}{(B - b) \cos \theta}$, where “λ” is wavelength of X-ray, “B” is FHWM of the diffraction peaks, “b” is FHWM of ideal crystal, “θ” is half of diffraction angle of 2θ and K is Scherrer constant. On the assumption that it is appropriate to use the $K = 0.9394$, $b$ of

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0.132° estimated by the measurement of Si single crystal, diffraction peaks of 202 [Fig. 3(b)] refined by smoothing, **sonnerveld method** (background removal) and **Rachinger method** (CuKα2 peaks removal), and J of 0.15406 nm (CuKα1), Fig. 6 indicates the detailed relationship among heat treatment temperature, D, grain size estimated from SEM images (Figs. 4 and 5). It seems that the films heat-treated at 500°C in air had a D of approximately 27 nm since the D of the films heat-treated at 800 and 900°C in air were roughly in accordance with the grain size estimated from SEM images. This result clearly demonstrates that the heat treatment at around 800°C or above induces to drastically promote grain growth, and the relationship between grain growth and heat treatment is distinctly-different from that of annealed SrBi2Ta2O9 (SBTa) films deposited by the AD method.33) For the SBTa thick films annealed at less than or equal to 1000°C, abnormal grain growth was not confirmed, and the D and grain size continuously increased with increasing annealing temperature. It is well-known that abnormal grain growth is induced by (I) liquid phase in the grain boundary, (II) interposition of second phase fine particles, (III) promoting activation of atomic element in grain boundary and (or) (IV) appropriate thermal gradient. It is hard to consider the abnormal grain growth due to (II) and (IV) because the one of the feature of the AD process is easy to obtain super fine and uniform thick films [Figs. 4(a) and 4(b)] without mismatched composition from the starting raw powder, and soaking furnace was used for the heat treatment in this study. We can make a good guess that abnormal grain growth was induced by (I) since Bi is able to be vaporized from the BNT at more than approximately 800°C, and melting point of Bi2O3 is 817°C. However, it is of great difficulty to be explained by the only (I) that the abnormal grain growth was not confirmed for the films annealed at 900–1000°C in the BNT starting raw powder, and that average grain size of BNT films heat-treated at 800°C in air was larger than that of BNT films annealed at 900°C in BNT starting raw powder. Thus, it seems that the grain growth mechanism is predominated by not only liquid phase in the grain boundary, but also alternatives, such as promoting activation of atomic element in grain boundary.

It was quite certain that all of obtained BNT self-supported films had fully dense microstructures that seemed to be required by measurements for the polarization and leakage current properties. **Figure 7** shows leakage current density (J) properties measured at 25°C for the sintered bulk, the films heat-treated at 800 and 900°C in air, and the films annealed at 900°C in BNT starting raw powder. Although both of the films heat-treated in air indicated the superior insulating properties (J ≈ 10−10 A/cm² at 150 kV/cm), the sintered bulks and the films annealed in the BNT starting raw powder showed the relatively high J of approximately 10−9 A/cm² at 150 kV/cm. The vacancy formation of BNT at high temperatures is expressed by

\[ 2\text{Bi}^{+} + 3\text{O}^{*} \rightarrow 2\text{V}_{\text{Bi}}^{*} + 3\text{V}_{\text{O}}^{*} + \text{Bi}_{2}\text{O}_{3}(\text{gas}), \]

where \( \text{V}_{\text{Bi}}^{*} \) and \( \text{V}_{\text{O}}^{*} \) represent vacancies at Bi site and O site, and \( \text{Bi}_{2}\text{O}_{3}(\text{gas}) \). If the partial pressure of BiO becomes inappreciable high due to the Bi vaporization from BNT starting raw powder at 900°C, negligible decrease of partial pressure of oxygen is induced along the O site, and primes and dots represent negative and positive charges. Yoshimoto et al. reported that the conductive carriers are originated from the electron hole (h⁺) which is produced by oxidation reaction for the BNT single crystals, as expressed by

\[ \text{V}_{\text{O}}^{*} + 1/2\text{O}_{2} \rightarrow \text{O}_{2}^{2*} + 2h^{+}. \]

It is thought that heat treatment at 900°C or above certainly formed vacancies of Bi and oxygen for these films. The films heat-treated at 900°C in air exhibited an extremely low J since the charge neutrality seemed to be satisfied only by \( \text{V}_{\text{Bi}}^{*} \) and \( \text{V}_{\text{O}}^{*} \). In contrast, the films heat-treated at 900°C in BNT starting raw powder represented a relative high J at room temperature. One possible reason for this relative high J is inappreciable increased partial pressure of vaporized BiO [\( \text{Bi}_{2}\text{O}_{3}(\text{gas}) \)]. If the partial pressure of BiO(gas) becomes inappreciable high due to the Bi vaporization from BNT starting raw powder at 900°C, negligible decrease of partial pressure of oxygen is induced along Dalton’s law. Thus, compared with the film heat-treated 900°C in air, the films annealed at 900°C in the BNT starting raw powder is expected to be included the negligible lower amount of \( \text{V}_{\text{Bi}}^{*} \) and negligible higher amount of \( \text{V}_{\text{O}}^{*} \).

**Figure 8** represents polarization properties measured in 1 Hz at room temperature for the films heat-treated at 500, 800 and 1000°C in air, and sintered bulks. Although no ferroelectricity was confirmed for the films heat-treated at 500°C in air [Fig. 8(a)] because of the size effect [Figs. 4(a) and 4(b)], polarization hysteresis loops were observed for the films heat-treated at 800 and 1000°C in air and sintered bulks [Fig. 8(c)]. In particular, the films heat-treated at 1000°C in air exhibited good polarization properties and remanent polarization (\( P_{r} \)) of 25 μC/cm², which was however smaller than that of sintered bulks (\( P_{r} = 39 \mu\text{C/cm²} \)) and films heat-treated at 800°C (\( P_{r} = 34 \mu\text{C/cm²} \)). These films...
and sintered bulks showed the almost the same coercive field ($E_c$) of approximately 57 kV/cm (in the 56 to 58 kV/cm range). Figure 9 illustrates the saturation properties of the $P_r$ for the sintered bulk [Fig. 8(d)] and the films heat-treated at 800 and 1000°C in air [Figs. 8(b) and 8(c)]. Although the shape of hysteresis loops of the films heat-treated at 800°C in air seemed not to be well-saturated [Fig. 8(b)], this saturation properties indicated “well-saturated” along with the films heat-treated at 1000°C in air. Note that it confirmed that polarization properties of sintered bulk [Fig. 8(d)] were not saturated enough; hysteresis loops of sintered bulks affected by the large leakage current density of more than $10^{-6}$ A/cm² at 150 kV/cm (Fig. 7). Here, we discuss the polarization properties between the polycrystalline and single crystal of BNT. The values of $P_r$ of obtained these specimens are considerably-low compared with the “ideal $P_r$ in polycrystalline ($P_r_{\text{poly}}$)” estimated from spontaneous polarization ($P_s$) of high quality single crystal of BNT grown in high partial oxygen pressure of 1 MPa. The $P_r_{\text{poly}}$ can be estimated using the following formula: 

$$P_r_{\text{poly}} = (1 - \sqrt{3}/9)P_s.$$ 

In fact, polycrystalline BNT ceramics is expected to be represented the $P_r_{\text{poly}}$ of 45 $\mu$C/cm² or larger. It is though that the oxygen vacancies clamp not only reversible rotation of non-180° domains for the films heat-treated at 800 and 1000°C in air.

By using the AD method, we achieved to show the low $J$ of $10^{-7}$ A/cm² at 150 kV/cm for BNT films heat-treated at 800–1000°C in air, and these BNT films indicated well-saturated ferroelectric properties compared with sintered bulks.

4. Conclusions

BNT ceramic thick films with the thickness of around 20 $\mu$m on sapphire single crystal substrates were deposited by the AD method, and then the heat treatment temperature of 500°C or above in air allow obtaining the self-supported BNT films. Their constitution phase, crystal structure, microstructure, polarization and leakage current properties were investigated. The heat treatment of around 800°C or above induces to drastically promote grain growth. Although the abnormal grain growth were confirmed for the films heat-treated at 900 and 1000°C in air, the films annealed at 900°C in the BNT starting raw powder had roughly uniformly-sized grains. While the films heat-treated at 800 and 900°C in air indicated the superior insulating properties ($J \approx 10^{-6}$ A/cm² at 150 kV/cm), the sintered bulks and the films annealed at 900°C in the BNT starting raw powder showed the relatively high $J$ of approximately $10^{-6}$ A/cm² at 150 kV/cm. These films heat-treated at 800 and 1000°C in air and sintered bulks showed the almost the same coercive field ($E_c$) of approximately 57 kV/cm (in the 56 to 58 kV/cm range), and the films heat-treated at 1000°C in air exhibited good polarization properties and remanent polarization ($P_r$) of 25 $\mu$C/cm². The AD method is proposed to be effective for obtaining self-supported BNT thick films with good saturated polarization and insulation properties.
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