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Influence of strain on the dielectric properties of Bi–Zn–Ti–Nb–O solid solution thin films

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Abstract

Bi–Zn–Ti–Nb–O (BZTN) solid solution thin films with various compositions were prepared by metalorganic decomposition (MOD) process on the platinized Si substrates. BZTN thin films showed a wide solid solubility since the thin films maintained the single phase of cubic pyrochlore structure in a broad range of composition. Crystal structure and dielectric properties of BZTN thin films were compared to those of BZTN bulk ceramics and the difference in dielectric properties such as dielectric constant, dielectric loss and tunability between thin films and bulk ceramics were understood to originate from the strain in the thin films since there was no apparent difference in the other factors such as microstructure and preferred orientation. The existence of strain in the thin films was confirmed by two ways. One is the rate of lattice shrinking. Shrinkage in the lattice parameter of thin films was depressed compared to that of bulk ceramics, which might introduce the internal strain in the thin films. Another is the thermal expansion coefficient (α, TEC) of BZTN solid solutions. TEC measured from the bulk ceramics varied with composition and the difference in the TEC between the polycrystalline thin film and underlying substrate would result in the thermal strain of thin films. Thin films with various compositions were under different degree of tensile stress state and the BZTN thin films with optimal composition demonstrated the high tunability of 30% under 1100 kV/cm with dielectric constant of 242 and dielectric loss of 0.004.

Keywords: Dielectric properties; Strain; Capacitors

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1. Introduction

$(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O_7$ (BZZN) thin films with cubic pyrochlore structure have attracted interest as alternatives for the ferroelectric thin films, such as $(Ba,Sr)TiO_3$, due to their electric field tunability as well as the low loss ($<5 \times 10^{-3}$) and relatively high dielectric constants (~150). Because of the increased interest, dielectric properties of BZZN thin films prepared by various methods, such as RF-magnetron sputtering,[1–3] and metalorganic decomposition process [4,5] have been intensively studied.

It has been known that several synthetic compounds have the cubic pyrochlore structure and that the substitution of cations imparts an enormous range of physical properties. For instance, Valant and Davis performed a detailed investigation on the synthesis and dielectric properties of Bi_2O_3–ZnO–Nb_2O_5–TiO_2 systems.[6] Introduction of titanium was found to enhance the dielectric properties of bismuth-based pyrochlore; $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$ cubic pyrochlore has a high dielectric constant of 200 and low dielectric loss of 1×10^{-4} at 1 MHz. Nevertheless, only BZZN thin films have been applied as electronic devices, especially as voltage tunable devices [1–5] and not much attention has been paid to the dielectric properties and tunability of Bi_2O_3–ZnO–Nb_2O_5–TiO_2 thin films.

In the present study, thin films and bulk ceramics of $(Bi_{2-x}Zn_x)(Ti_{2-x}Nb_x)O_7$ (BZTN) solid solution were prepared by metalorganic decomposition (MOD) process and mixed oxide method, respectively. Strain in the thin films was confirmed by the lattice shrinkage and the thermal mismatch between thin films and substrates. Dielectric properties of the BZTN thin films, such as dielectric constant, dielectric loss, and tunability were investigated in comparison to those of bulk ceramics and the difference between thin films and bulk ceramics were discussed from the viewpoint of strain in the thin films.

2. Experimental procedure

$(Bi_{2-x}Zn_x)(Nb_xTi_{2-x})O_7$ bulk ceramics and thin films with various compositions were prepared by the mixed oxide method

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and the MOD process, respectively. Starting materials for the MOD process were bismuth acetate (Aldrich, 99.99%), zinc acetate dihydrate (Aldrich, 98%), titanium isopropoxide (Aldrich, 97%), and niobium ethoxide (CERAC, 99.999%). 2-Methoxyethanol (Aldrich, 99%), pyridine (Aldrich, 99%), and acetic acid (Aldrich, glacial) were selected as solvents and diethanolamine (Aldrich, 98%) was used as a stabilizing agent. All of the organic reagents were utilized without any purification. Zinc acetate dihydrate was dissolved in 2-methoxyethanol and stabilized with diethanolamine and then Zn-solution was distilled at 120 °C to remove the hydrated water. After titanium isopropoxide was added to the Zn-solution, niobium ethoxide was added to the (Zn,Ti)-solution. In another beaker, bismuth acetate was suspended in pyridine and acetic acid was added to the suspension. The solution became clear within 30 min at room temperature. The Bi-solution was added to the (Zn,Ti,Nb)-solution, followed by refluxing at 120 °C for 1 h to yield final concentration of around 0.13 M. All reactions were carried out in the Ar-filled glove box. The precursor solutions were spin-coated on the platinized Si substrates at 3000 rpm for 30 s and the films were pyrolyzed at 400 °C in air for 5 min to remove the organic residues. Coating and pyrolysis procedures were repeated until the thickness was about 400 nm. As-deposited films were annealed at 750 °C for 1 h since thin films fired at 750 °C showed good crystallinity and higher temperatures might degrade the interface of thin films and substrates. Bulk ceramics were calcined at 850 °C for 2 h and pellets with various compositions were sintered at 1050 °C for 2 h. Relative density of bulk ceramics were over 95% regardless of composition. All annealing processes were conducted in air atmosphere.

The crystal structure, lattice parameter, thickness and morphology of thin films and/or bulk ceramics were investigated using X-ray diffractometer (XRD; M18XHF, MacScience Instruments, Japan) and field emission scanning electron microscopy (FE-SEM; JSM-6330F, JEOL, Japan). Compositions of the prepared thin films were confirmed by electron probe X-ray micro analyzer (EPMA; JXA-8900R, JEOL, Japan). Thermal expansion coefficients of BZTN bulk ceramics were measured using dilatometer (DIL402C, Netzsch Instruments, Germany). Dielectric properties of bulk ceramics and thin films were measured by high precision LCR-meter (Agilent 4284A, Agilent Technologies Inc., USA) and impedance analyzer (HP 4194A, Agilent Technologies Inc., USA). To measure dielectric properties of thin films, platinum top electrodes (200 μm in diameter) were sputtered onto films.

3. Results and discussion

Fig. 1 shows the lattice parameters of BZTN thin films in comparison with those of bulk ceramics. With increasing x, lattice parameter decreases linearly in single-phase regions (below about $x = 0.6$) for both thin films and bulk ceramics, which confirms the successful formation of solid solutions. Solid solubility of BZTN bulk ceramics and thin films was determined in our ancillary experiments to be $x = 0.30$–0.65 and $x = 0.10$–0.65, respectively. Increasing lattice parameter in higher x region ($x \geq 0.6$) can be understood by the change in substitution mechanism originating from the formation of Zn-rich secondary phases. It is interesting to note that the lattice parameter of thin films slightly decreased from 10.348 to 10.339 Å ($\Delta a = 0.009$ Å), in contrast that the lattice parameter of bulk ceramics decreased from 10.370 to 10.354 Å ($\Delta a = 0.026$ Å) with increasing x. Difference of lattice parameter between bulk ceramics and thin films increases with decreasing x values. In other words, strain in the thin films goes to lower tensile state with decreasing x values. This can be explained by the interaction between substrates and thin films. Assuming that internal stress in bulk ceramics are released during relatively slow cooling procedure after sintering, the differences in the lattice shrinkage rate between bulk ceramics and thin films will introduce internal stress in the thin films.

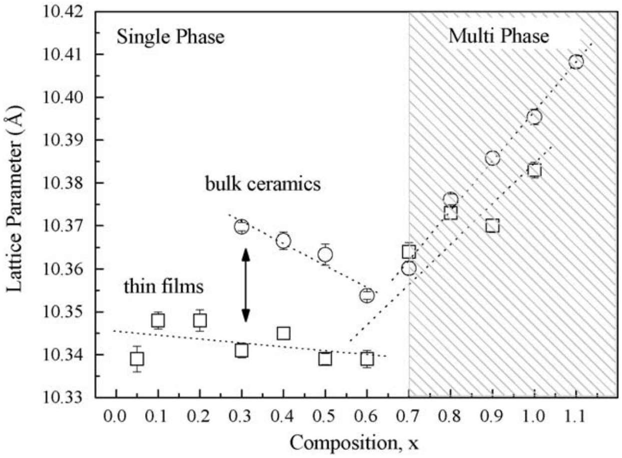

Fig. 1. Lattice parameter of $(Bi_{2-x}Zn_x)(Ti_{2-x}Nb_x)O_7$ bulk ceramics and thin films.

Strain in the thin films can be confirmed at the viewpoint of thermal expansion coefficient since the other factors such as volume shrinkage during pyrolysis and annealing process have exhibited no differences with the composition of thin films. In general, ceramic films on Si substrate receives in-plane tensile stress during cooling from the processing temperature (750 °C in this work) since the thermal expansion coefficient of ceramics (~10 ppm/°C) is larger than Si (~3 ppm/°C). The thermal strain, $\varepsilon_{\text{thermal}}$, in the thin films can be estimated from the thermal expansion coefficients of thin films and substrates by the following equation.

$$\varepsilon_{\text{thermal}} = \int_{T_1}^{T_2} (\alpha_{\text{film}} - \alpha_{\text{substrate}})\,\mathrm{d}T \tag{1}$$

where α is the thermal expansion coefficient. The thermal expansion coefficient and the estimated thermal strain are listed in Table 1, where the thermal expansion coefficients of BZTN bulk ceramics with various compositions were measured by the dilatometer. The estimated thermal strain of BZTN thin films decreases with decreasing x values when $x \leq 0.5$, which is in accordance with the results of lattice shrinkage data.

In order to investigate the effects of strain, which has been confirmed in prior paragraphs, on dielectric properties of thin films, dielectric properties of $(Bi_{2-x}Zn_x)(Ti_{2-x}Nb_x)O_7$ (BZTN) bulk ceramics and thin films with various compositions

Table 1
Thermal expansion coefficient and estimated thermal strain of $(Bi_{2-x}Zn_x)(Ti_{2-x}Nb_x)O_7$ thin films with various compositions

x[a]	α(25/750 °C) x ppm/°C	$\varepsilon_{thermal}$ (%)
0.3	5.14/8.55	0.24
0.4	6.35/8.43	0.28
0.5	8.09/8.30	0.34
0.6	7.38/8.09	0.31
0.7	6.54/6.22	0.21
Si[b]	2.618/4.4	

[a] $(Bi_{2-x}Zn_x)(Ti_{2-x}Nb_x)O_7$ bulk ceramics.

[b] Between 27 and 723 °C, see ref.[7]

are presented in Fig. 2. As shown in Fig. 2(a), dielectric constants of bulk ceramics decrease monotonically with increasing x in the single-phase region because of the decrease in the concentration of Bi^{3+} and Ti^{4+} having high polarizability.[6] On the other hands, dielectric constants of BZTN thin films are maximal at around $x = 0.5$–0.6, while dielectric losses show the opposite trend as shown in Fig. 2(b). The maximum dielectric constant of BZTN thin films is 242 with minimum dielectric losses of 0.004. Dielectric constants of thin films show different behavior from those of bulk ceramics in the single-phase region. Since thin films with various compositions showed no apparent differences in the crystallinity, preferred orientation, morphology, and grain size,[8] the different behaviors between bulk ceramics and thin films can be explained from the viewpoint of strain in the thin films. Tensile strain in the thin films increases with x values as discussed on the lattice shrinkage and thermal strain data and the dielectric constants of BZTN thin films also increase with x values. Tensile strain can be expected to liberate the response of the polarization to the AC field. With respect to the results above, larger tensile strain appears to increase the dielectric constants of thin films. For the perovskite ferroelectric thin films, such as $(Ba,Sr)TiO_3$, the tensile stresses were reported to reduce the dielectric constants in their paraelectric state due to their negative electrostrictive coefficient.[9,10] However no electrostrictive coefficients of pyrochlores have been reported in literature and the similar result of increased dielectric constant due to the tensile strain has been reported for other Bi–pyrochlore system.[3]

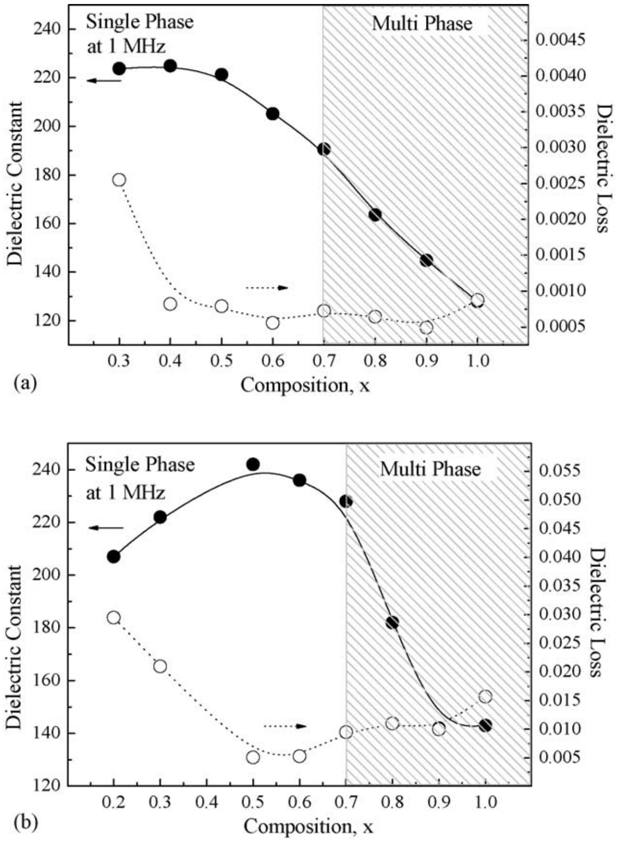

Fig. 2. Dielectric constant and dielectric loss of $(Bi_{2-x}Zn_x)(Ti_{2-x}Nb_x)O_7$: (a) bulk ceramics; and (b) thin films.

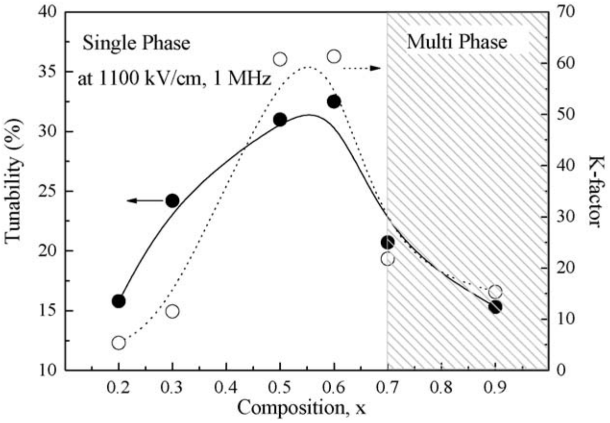

Fig. 3. Tunability and K-factor of $(Bi_{2-x}Zn_x)(Ti_{2-x}Nb_x)O_7$ thin films.

Electric field dependencies of dielectric properties of BZTN thin films were investigated by capacitance–voltage measurement at 1 MHz as shown in Fig. 3. Tunability is also maximal at about $x = 0.5$–0.6 with value of 32% under 1100 kV/cm, which is comparable to the reported tunability of low-loss thin films, such as BZZN systems, deposited with RF-magnetron sputtering.[2] Considering that the reported tunability of BZZN thin films from MOD process was below 15% under similar electric field,[4] BZTN thin films in this work exhibit much improved voltage tunable properties. K-factor (defined by tunability/loss) of BZTN thin films are also presented in Fig. 3. When $x = 0.5$–0.6, BZTN thin films exhibit the largest values of 61 under applied field of 1100 kV/cm due to the higher tunability and lower dielectric loss. Tunability is also reported to be affected by stress and/or strain in thin films. According to the study of Park et al., tunability of $(Ba,Sr)TiO_3$ thin films decreased with increasing both tensile and compressive stress except for the case of small tensile stress.[11] In a recent research on cubic pyrochlore BZZN thin films by Lu and Stemmer,[2] tensile stress caused by the thermal mismatch between thin films and substrates was proposed to be a possible reason for the high tunability.

4. Conclusions

Solid solution thin films of Bi–Ti–Zn–Nb–O system were successfully prepared by MOD process followed by the investigation of their dielectric properties. Strain in the $(Bi_{2-x}Zn_x)(Nb_xTi_{2-x})O_7$ (BZTN) thin films was confirmed in two ways. One is the qualitative way from the difference in the lattice shrinking rate between bulk ceramics and thin films and another is the quantitative way from the mismatch of thermal expansion coefficients. In-plane tensile strain increased with x values in single-phase region, which had effects on the dielectric properties of BZTN thin films.

Although dielectric constant of BZTN bulk ceramics monotonically decreased with increasing x in single-phase region, dielectric constant, tunability, and K-factor were maximized in thin films at $x = 0.5$–0.6. Superior properties at $x = 0.5$–0.6 were speculated to be yielded due to the in-plane tensile strain in thin films. BZTN thin films demonstrated much improved tunable properties with low dielectric losses, as compared to the existing low-loss tunable materials such as MOD-derived BZZN system. Especially, the large values of K-factor make this BZTN thin films promising for the tunable capacitor applications.

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