

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

Jin Young Kim, Dong-Wan Kim¹, Hyun Suk Jung, Kug Sun Hong*

School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Republic of Korea

Available online 26 October 2005

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.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Dielectric properties; Strain; Capacitors

1. Introduction

(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O₇ (BZZN) thin films with cubic pyrochlore structure have attracted interest as alternatives for the ferroelectric thin films, such as (Ba,Sr)TiO₃, 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 Bi₂O₃–ZnO–Nb₂O₅–TiO₂ 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})O₇ 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 Bi₂O₃–ZnO–Nb₂O₅–TiO₂ thin films.

In the present study, thin films and bulk ceramics of (Bi_{2–x}Zn_x)(Ti_{2–x}Nb_x)O₇ (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})O₇ bulk ceramics and thin films with various compositions were prepared by the mixed oxide method

* Corresponding author.

E-mail addresses: dexter2@snu.ac.kr (J.Y. Kim), kshongss@plaza.snu.ac.kr (K.S. Hong).

¹ Present address: Department of Materials Science and Engineering, MIT, Cambridge, MA 02139, USA.

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 sub-

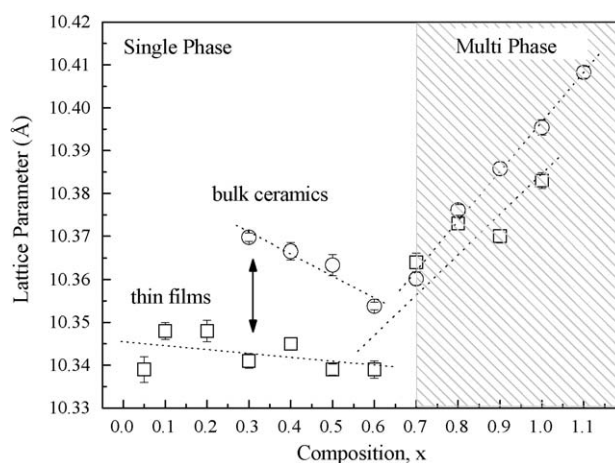


Fig. 1. Lattice parameter of $(\text{Bi}_{2-x}\text{Zn}_x)(\text{Ti}_{2-x}\text{Nb}_x)\text{O}_7$ bulk ceramics and thin films.

stitution 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.

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.

$$\varepsilon_{\text{thermal}} = \int_{T_1}^{T_2} (\alpha_{\text{film}} - \alpha_{\text{substrate}}) dT \quad (1)$$

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 $(\text{Bi}_{2-x}\text{Zn}_x)(\text{Ti}_{2-x}\text{Nb}_x)\text{O}_7$ (BZTN) bulk ceramics and thin films with various compositions

Download English Version:

<https://daneshyari.com/en/article/1478377>

Download Persian Version:

<https://daneshyari.com/article/1478377>

[Daneshyari.com](https://daneshyari.com)