Electromechanical properties of BaTiO₃-xBaSnO₃ thin films prepared via combinatorial sputtering

Hongbo Cheng^{a,b}, Hirotaka Hida^b, Jun Ouyang^{a,c*} and Isaku Kanno^{b*}

^a Key Laboratory for Liquid–Solid Structural Evolution and Processing of Materials (Ministry of Education), School of Materials Science and Engineering, Shandong University, Jinan, 250061; Suzhou Institute of Shandong University, Suzhou, 215123, China

^b Department of Mechanical Engineering, Kobe University, Kobe, 657-8501, Japan

^c National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

* Corresponding author: *E-mail address:* ouyangjun@sdu.edu.cn (Jun Ouyang), kanno@mech.kobe-u.ac.jp (Isaku Kanno).

Abstract: (1-x)BaTiO₃-xBaSnO₃ (BT-xBS, 0 ≤ x ≤ 0.20) perovskite thin films were deposited on Pt/Ti/Si substrates with uniaxial graded composition by using a dual-target combinatorial sputtering technique. These films were highly (101)-oriented and showed strong composition dependence in their electromechanical properties. The maximum value of the relative dielectric constant was 925 at around x = 0.028, where the transverse piezoelectric coefficient $|e_{31,f}|$ also peaked at about 1.5–1.9 C/m². This $|e_{31,f}|$ value is higher than those of epitaxial BaTiO₃ thin films. Our results indicate that BT-xBS is a promising substitute of lead-based perovskites for applications in piezoelectric MEMS devices.

Keywords: BaTiO₃; doping; combinatorial method; magnetron sputtering; Si

1. Introduction

Piezoelectric thin films are of great importance to realize high-performance micro-electromechanical systems (MEMS), such as micro-sensors, actuators and energy harvesters [1–4] because of their excellent energy conversion efficiency between the electrical and mechanical energy forms. The most popular piezoelectric materials are lead-based perovskite compounds such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) or $\text{Pb}(\text{Mg,Nb})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) [1,5] due to their superior electromechanical performance. However, owing to the toxicity of lead, recent research efforts have been focused on improving the electromechanical properties of lead-free piezoelectrics for possible substitutions of lead-based perovskites. The materials under intensive investigations include $(\text{K,Na})\text{NbO}_3$ (KNN) [6–8], $\text{BiFeO}_3(\text{BF})$ [9] and BaTiO_3 (BT) [10–13] in pure and modified forms. Specifically, KNN- and BT-based high performance piezoelectrics have been discovered and systematically studied in the last decade [6,11,14,15]. These materials showed comparable piezoelectric coefficients to those of PZT ceramics.

Preparation of a piezoelectric material in a thin film form is necessary for various piezoelectric MEMS applications [6,8]. A Previous study revealed an excellent piezoelectric performance ($e_{31}^* = d_{31}/s_{11} = -14.4 \text{ C/m}^2$) in KNN-based films, which was comparable to those of the $\text{Pb}(\text{Zr,Ti})\text{O}_3$ -based films [16,17]. However, KNN-based thin films with competent ferroelectricity (and hence piezoelectricity) are still difficult to deposit due to volatile losses of K and Na during the film growth and annealing processes [18]. On the other side, the non-volatile BT-based piezoelectric thin films still don't have satisfactory piezoelectric performance for the applications in piezoelectric MEMS [12]. Some recent studies indicate that, a modest substitution of the Ti^{4+} ions with heavier quadravalence metal ions including Hf^{4+} , Sn^{4+} and Zr^{4+} can

significantly improve the piezoelectric performance of the BT ceramics [14,19,20]. The large piezoelectricity can be attributed to the B-site modifications which lead to increased stabilities of low-temperature phases. Consequently, temperatures of orthorhombic-tetragonal (O-T) and rhombohedral-orthorhombic (R-O) phase transitions are increased to around room temperature, resulting in a tunable mixed phase structure making large extrinsic contributions to electromechanical properties [21]. This phenomenon was denoted as polymorphic phase transition (PPT) [22]. Specifically, the PPT behavior in $(1-x)\text{BaTiO}_3\text{-}x\text{BaSnO}_3$ (BT-xBS) solid solutions have been intensively investigated, resulting in high piezoelectric d_{33} coefficients (near room temperature) in the range between ~ 350 pC/N and 425 pC/N [14,19,20]. There are multiple PPT regions existing in the BT-xBS system near the room temperature, O-T near $x = 0.02$, R-O near $x = 0.08$, and a quasi-quadruple point (C-T-O-R) near $x = 0.11$ at 40°C due to the convergence of the two PPT boundaries with the composition dependent Curie temperature ($T_C - x$ curve) [20]. It was revealed that the dielectric performance of the BT- xBS ceramics followed a similar trend as that of the piezoelectric response with respect to composition variations. Large room temperature dielectric constants up to the order of 10^4 were achieved at these phase-coexisting compositions and peaked at the quasi-quadruple point [20].

Despite the exciting electromechanical performance achieved in bulk materials, there have been very few reliable reports on the composition dependent dielectric and piezoelectric properties of BT-xBS thin films, especially on the latter. Major courses on the scarcity of reliable experiment data come from overlooking of the following effect:

(1) Substrate effect clamping, which not only degrades electromechanical performance of the piezoelectric materials, but also can change the phase transition temperatures and

1 hence shift the optimal performance point [13].

2 (2) Process variations, including (a) large property variations due to the different
3 qualities of thin films prepared by different research groups using the same or different
4 techniques; (b) non-negligible process variations in a given preparation process for
5 uniform thin films to study the composition dependence of electromechanical properties.

6 In this work, we aim at providing reliable electromechanical data of BT-xBS
7 polycrystalline films, wherein the process variations were minimized by using a
8 combinatorial rf-magnetron sputtering process (Fig. 1a). This deposition technique can
9 be used to fabricate thin films with a continuous composition gradient, enabling an
10 efficient and precise optimization of the films' composition. In our previous studies, we
11 deposited a variety of piezoelectric thin films by using this technique, and evaluated the
12 composition dependent electromechanical properties [12,23,24]. Here, polycrystalline
13 BT-xBS thin films with an uniaxial composition gradient were co-sputtered on Pt/Ti/Si
14 substrates. The piezoelectric and dielectric properties of BT-xBS thin films were
15 evaluated as functions of the Sn composition. The optimal composition with respect to
16 the electromechanical performance was determined and compared with that in bulk
17 ceramics, taking into account of the substrate effects. Lastly, the applicability of these
18 films in lead-free piezoelectric MEMS was discussed.

2. Materials and methods

BT-xBS thin films with an uniaxial composition gradient were prepared in a dual-target sputtering system, as shown in Fig. 1a. Prior to deposition of the BT-xBS films, Pt/Ti bottom electrode were sputtered on the (100) Si substrates. The thicknesses of the Pt and Ti layers were 5 nm and 145 nm, respectively. To achieve a combinatorial deposition, three square Pt/Ti/Si substrates ($20 \times 20 \text{ mm}^2$) were placed side by side above the BaTiO₃ (BT) and BaSnO₃ (BS) sputtering targets, which were simultaneously ignited to deposit BT-xBS thin films with an uniaxial composition gradient (along the *Y* axis) on these substrates. During the film deposition, the substrates were held at a constant temperature of 700 °C, and the chamber pressure was kept at 0.40 Pa in a mixed Ar/O₂ atmosphere. RF powers of 180 W and 40 W were simultaneously applied to the BT and BS targets (3 inches in diameter), respectively. Thicknesses of the sputtered BT-xBS thin films ranged between 1.2 and 2.2 μm depending on their *Y*-axis values. The detailed deposition parameters were summarized in Table I.

Figure. 1b shows the thicknesses of pure BT and BT-xBS thin films, together with the composition of the latter, as functions of the deposition positions (*Y*-axis values). Filled squares and triangles were measured thicknesses of BT-xBS and BT films with respect to their *Y*-axis locations, while the red and the black lines were fitted curves. The pure BT film was sputtered with the same deposition parameters as the BT-xBS film except that only the BT target was used. The thicknesses of pure BT and BT-xBS thin films were measured by using a stylus profilometer (Dektak-8, Veeco), while the compositions of the BT-xBS film were calculated by using the formula:

$$x = \frac{V_{BS} / v_{BS}}{\left(\frac{V_{BS}}{v_{BS}} + \frac{V_{BT}}{v_{BT}}\right)} = \frac{h_{BS} / v_{BS}}{\left(\frac{h_{BS}}{v_{BS}} + \frac{h_{BT}}{v_{BT}}\right)} = \frac{(h_{BT-xBS} - h_{BT}) / v_{BS}}{\left(\frac{h_{BS}}{v_{BS}} + \frac{h_{BT}}{v_{BT}}\right)} \quad (1)$$

where h , v and V are the film thickness, unit cell volume and volume of film, respectively. The subscript of BT , BS and $BT-xBS$ denote $BaTiO_3$, $BaSnO_3$ and $BT-xBS$ thin films, respectively. The unit cell volume are $3.992 \times 3.992 \times 4.036 \text{ \AA}^3$ for BT [25] and $4.116 \times 4.116 \times 4.116 \text{ \AA}^3$ for BS [26].

Following the deposition process, $BT-xBS$ thin films were annealed at 700°C for 1 hour to improve their crystallinity. The crystallographic structures of the annealed films were examined via X-ray $\theta/2\theta$ scan (Rigaku XRD diffractometer, multiflex, $\text{Cu-K}\alpha$ radiation with $\lambda = 1.54 \text{ \AA}$). Circular Pt top electrodes (0.3mm in diameter) were deposited using a shadow mask on these films for their electrical characterizations, and a LCR meter (NF ZM2371) was used to carry out the capacitance and dielectric loss measurements (at a testing frequency of 1 kHz and an AC amplitude under 100 mV). To measure piezoelectric properties, rectangular-shaped Pt top electrodes were deposited in the center region of the $BT-xBS$ thin films, and unimorph cantilevers about $20 \times 1.5 \text{ mm}^2$ in size were cut out along Z-axis (see Fig. 1b) from the film/substrate heterostructure using a dicing machine (DAD320, Disco). For evaluation of the piezoelectric properties, negative voltages in the form of a unipolar sinusoidal wave with their magnitudes ranging between 70 and 100 kV/cm were applied across the thickness of the unimorph cantilever, and the tip displacements were recorded by using a laser Doppler vibrometer (AT100, Graphtec). The transverse piezoelectric coefficients ($e_{31,f}$) of the $BT-xBS$ thin films were calculated using the following equation [27],

$$e_{31,f} = \frac{d_{31}}{(s_{11}^p + s_{12}^p)} \cong -\frac{h_s^2 E_s}{3(1-\nu_s)L^2V} \delta \quad (2)$$

where h , E , δ , ν , L , and V are the thickness, Young's modulus, tip displacement, Poisson's ratio, cantilever length and applied voltage, respectively. The subscripts p and

1 s denote the piezoelectric thin film and the substrate, respectively. It is noted that all the
2 above measurements were carried out at room temperature
3

3. Results and discussion

XRD patterns of the BT-xBS thin films in the composition range of $0 \leq x \leq 0.20$ were shown in Fig. 2a. All compositions of the films showed a single perovskite structure with a preferential (101) orientation. No noticeable differences can be observed among the XRD patterns when x was gradually increased from 0 to 0.20. Fig. 2 (b) and (c) were the surface and cross-sectional scanning electron microscopy (SEM) images of a BT-xBS thin film cantilever ($x = 0.028$). The film showed a dense and smooth morphology with an average grain size around 180 nm. It was noted that similar surface and cross-sectional morphologies were observed for all compositions with x between 0 and 0.20 in the BT-xBS thin films.

The relative dielectric constants (ϵ_r) and dielectric losses ($\tan\delta$) of these films were plotted in Fig. 3. Dielectric constants for the BT-xBS thin films did show strong composition dependence while dielectric losses stayed very low ($\tan\delta < 0.05$). Starting from ~ 363 in the pure BT film ($x = 0$), ϵ_r rapidly increased to a maximum value of ~ 925 at composition of $x = 0.028$, and then it slowly ramped down to a value of ~ 430 as x increased further to 0.20. The optimal composition point is close to the O-T phase boundary in BT-xBS bulk ceramics [20]. It should be noted that ϵ_r did not show a maximum near the bulk quasi-quadruple point ($x \sim 0.11$), possibly due to a shift of the Curie point away from room temperature in strained films [13].

The tip displacement of the BT-xBS/substrate ($x = 0.028$) unimorph cantilever was measured as a function of the applied voltage. The frequency of the input voltage signal was set at 500 Hz, much lower than the resonance frequency of the cantilever. The transverse piezoelectric coefficient $|e_{31,f}|$ was calculated from the tip displacement

and the results were shown in Fig. 4(a). The cantilever showed a non-linear displacement with the applied voltage, resulting in an increasing $|e_{31,f}|$ with voltage. As shown in Fig. 4(a), the measured $|e_{31,f}|$ is about 0.7 C/m² at 5 V and it increases to ~1.9 C/m² at 20 V. The large value of $|e_{31,f}|$ in the BT-xBS thin film (x= 0.028) is higher than those of epitaxial BT thin films [10]. Taking into account of the non-linear nature of the piezoelectric response, we can attribute this enhancement in $|e_{31,f}|$ to a substantial extrinsic effect from domain wall motions, which were promoted by the PPT behavior in the polycrystalline films under an external electric field [10,28].

The composition dependent piezoelectric coefficient $|e_{31,f}|$ of the BT-xBS films were given in Fig. 4(b). The open circles in the figure denote $|e_{31,f}|$ values calculated from the tip displacement at an electric field of 85 kV/cm. The bottom and top ends of the error bars denote the $|e_{31,f}|$ values under an applied electric field of 70 kV/cm and 100 kV/cm, respectively. The nominal piezoelectric coefficients $|e_{31,f}|$ (@ 85kV/cm) for the BT-xBS thin films varies between 0.3 and 1.7 C/m², depending on the Sn composition (x = 0 to 0.20). While a small doping amount of Sn (up to ~0.028) significantly increases the piezoelectric coefficient (up to ~3 times higher than pure BT), further addition of Sn ions leads to a drop in $|e_{31,f}|$, which eventually becomes lower than that of the pure BT ($|e_{31,f}| \sim 0.30$ C/m² at x = 0.2). The trend of room temperature piezoelectric property ($|e_{31,f}|$) as a function of Sn composition in our BT-xBS films was similar to those reported for BT-xBS ceramics [14,19]. The proximity of the optimal composition (x = 0.028) to a PPT boundary of orthorhombic-tetragonal phases explains the enhanced piezoelectric property [14,19,20].

The maximum value of $|e_{31,f}|$ (~ 1.7 C/m²) is higher than that for a BaTiO₃ (BT) epitaxial film of (001) orientation ($|e_{31,f}| = 0.6\text{--}0.8$ C/m²) [10], indicating that the doping

1 of Sn is effective to improve electromechanical properties of BaTiO₃-based
2 piezoelectric thin films. Optimizations in film growth, for example, realization of
3 epitaxial growth of BT-xBS thin films, would lead to further enhancement of the
4 piezoelectric property.
5

4. Conclusions

Compositional gradient polycrystalline BT-xBS thin films with Sn content varying between 0 and 0.20 were prepared by using a combinatorial sputtering technique. The composition dependent dielectric and piezoelectric properties of the films were evaluated. It was revealed that, a dilute substitution of Ti^{4+} by Sn^{4+} ($x = 0.028$) in BaTiO_3 films can lead to large enhancements in piezoelectric and dielectric properties ($|e_{31,f}|$ improved from $\sim 0.4 \text{ C/m}^2$ to 1.7 C/m^2 , ϵ_r increased from ~ 363 to 925). The large piezoelectric coefficient $|e_{31,f}|$ achieved in the polycrystalline BT-xBS thin films (higher than those of epitaxial BaTiO_3 thin films) indicates a good potential of this material for applications in lead-free piezoelectric MEMS. The combinatorial sputtering technique and the piezoelectric $e_{31,f}$ characterization of the resulting thin films with uniaxial composition gradients can be applied to experimental studies of ferroelectric thin films in other solid solution systems, especially for a fast and reliable location recognition of the optimal compositions with respect to electromechanical properties.

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Figure captions

Fig. 1(a) Schematic of the combinatorial sputtering process for the deposition of BT-xBS thin films with a composition gradient; (b) Thicknesses of pure BT (black line with filled triangle) and BT-xBS (red line with filled square) thin films as functions of their Y-axis values, as well as the computed compositions of the BT-xBS thin films.

Fig. 2(a) XRD patterns of BT-xBS thin films with compositions of $x = 0$, 0.028, 0.067, 0.124 and 0.20. (b) Surface and (c) cross-sectional SEM images of a BT-xBS thin film ($x = 0.028$).

Fig. 3 Relative dielectric constants and dielectric losses of the BT-xBS thin films as function of composition (@ a testing frequency of 1k Hz).

Fig. 4.(a) Tip displacement and piezoelectric coefficient $|e_{31,f}|$ of the unimorph cantilever made from the BT-xBS film with $x = 0.028$, as functions of the applied voltage; (b) piezoelectric coefficient $|e_{31,f}|$ of the BT-xBS thin films as a function of x . The open circles indicate the $|e_{31,f}|$ values measured at an electric field of 85 kV/cm. The error bars represent the variations in $|e_{31,f}|$ values under an applied electric field from 70 to 100 kV/cm.

Table I. Sputtering conditions of compositional gradient BT-xBS thin films.

Target	BaTiO ₃ , BaSnO ₃
Substrate	Pt/Ti/Si(100)
Set temperature [°C]	700
Sputtering gas [sccm]	Ar/O ₂ = 19.5/0.5
Film thickness [μm]	1.2-2.2
RF power [W]	BT: 180 W, BS: 40 W

1

2

1 **Fig .1**

(a) **Compositional gradient thin films**

1 Fig .2

1 Fig.3

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4

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1 Fig .4