Lead-free ferroelectric barium titanate -based thin film for tunable microwave device application

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Abstract. Lead-free ferroelectric barium titanate-based (Ba0.85Sr0.15Zr0.1Ti0.9O3, BSZT) thin films have been successfully deposited on Pt-coated silicon substrates by a spin-coating sol-gel method. Microstructure and dielectric responses of the Pt/BSZT/Pt thin film capacitors were investigated in detail. X-ray diffraction analysis results indicated that BSZT thin films were well crystallized in tetragonal perovskite structure with a random crystal orientation at rather low temperature of 650 °C. Dielectric constant and dielectric loss of the thin film capacitors were performed at various bias voltage ranges and frequency from 1kHz up to 5MHz. Hysteresis C-V curves with two maxima confirmed the ferroelectric nature in the film. The BSZT capacitors provide excellent dielectric tunability ~ 42–69% and high figure-of-merit (FOM) ~ 4–17 at different bias voltages.

1. Introduction

Ferroelectric materials possess many outstanding properties including large dielectric constant, high piezoelectric & pyroelectric coefficients with a wide Curie temperature range. Thus, they have been the subject of intense research for various applications including dynamic random access memories (DRAMs), non-volatile random access memories (NVRAMs), high-frequency (GHz) bypass capacitors and microwave tunable devices [1–3]. For many years, lead-based ferroelectric family (commonly abbreviated as PbZr1−xTiO3 or PZT) of both ceramic and thin film has always been the leading commercial material for above-mentioned applications owing to their superior ferroelectric properties. Nevertheless, the rather high Pb content (~ 60 wt%) raises environment and human health concerns during their utilization. The US and European countries have restricted and even banned electronic devices containing lead element since 2002 [4]. As a consequence, research and development of friendly environmental ferroelectric materials which completely do not contain lead (Pb) with properties that closely match those of PZT has been becoming an urgent issue until nowadays [5,6].

Among the various lead-free ferroelectric materials, such as BaTiO3 (BT), BiFeO3 (BFO), (Na0.5K0.5)Bi4Ti3O12 (BNKT), Na0.8K0.2NbO3 (KNN), recently, the complex system barium titanate-based [Ba1−xSr2−xZrxTi1−yO3] has received much attention as promising candidates for application in electrically tunable microwave devices at room temperature because of the compatibility between dielectric constant as well as the dissipation factor of these composition systems [7]. Additionally, the advance in recent development of thin and thick ferroelectric film technology also aids to integrate with microelectronic circuits, then leads to substantial miniaturization of microwave device and reduction in producing cost. Therefore, intensive research efforts have been concentrated on this direction during the past decade to obtain desired material properties with high tunability and large figure of merit [8]. However, it is well documented that a small change in composition, porosity, grain size, grain boundaries etc., will lead to remarkable modification the physical properties of ferroelectrics. These effects are of the most important issues for practical applications of ferroelectric
materials. In general, the Curie temperature ($T_C$) of barium titanate-based thin films, which intimately involves to the working temperature of the microelectronic devices, are still low, while the dielectric loss is rather high (up to few ten percent) [9]. Many experimental efforts are still underway in order to clarify the underlying physics for interplays between the microstructure and ferroelectric properties [10–12]. For instance, Chong et al. reported that 40% aluminum oxide doped $Ba_{0.5}Sr_{0.5}TiO_3$ thin film on (100)-LaAlO3 substrates by the pulsed laser deposition technique reduced the loss tangent from 3% to 1.1% and enhanced the FOM ~ 7.33 up to 15.45 in comparison to the pure one [13]. For $Ba_1_xSr_3TiO_7$ (BST) ferroelectric materials, $Ba/Sr$ ratio was attributed to strongly effect on their dielectric properties. Recently, Kuppusami and co-workers noted that decreasing Sr content from $x = 0.5$ to 0.3 resulted to shift of Curie point near to room temperature and reduced the oxygen vacancy concentration approximately one magnitude order, however, the better dielectric properties (larger dielectric constant and lowest loss tangent) were observed for $x=0.4$ [14]. There still exists considerable debate about the “doping effect”. Hence, it is necessary to put more effort into understanding such role of dopant on both microstructure and the overall properties of ferroelectric materials based on barium titanate.

In this study, we focused on tailoring composition via simultaneously substituting $Ba$ and $Ti$ elements in barium titanate (BT) with 15% mol of Sr and 10% mol of Zr to investigate its influence on the microstructure and dielectric properties of the resulting BSZT thin films. The thin film samples were fabricated on platinum electrode (Pt-coated Si substrates) via the simple sol-gel techniques. The dielectric response as well as the tenability of the BSZT films were studied as a function of frequency and different external applied electric field ranges.

2. Experimental

2.1. BSZT thin film fabrication

$Ba_{0.85}Sr_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BSZT) thin films were fabricated on Pt/Ti/SiO$_2$/Si(100) substrate via sol-gel techniques. Starting materials for preparing BSZT sol are salts $Ba(CH_3COO)_2$,$3H_2O$, $Sr(CH_3COO)_2$, and alkoxides $Zr(OC_3H_7)_4$ (Merck, 70% in propanol) and $Ti(OC_3H_7)_4$ (Merck, 98%). Aetic acid ($CH_3COOH$, glacial) was used as solvent to dissolve barium and strontinium acetate salts. While 2-methoxyethanol ($CH_3OCH_2CH_2OH$, 2-MOE) was used for diluting the two alkoxides. After dissolving $Ba(CH_3COO)_2$ and $Sr(CH_3COO)_2$ in glacial acetic acid, then the so-called mixture 1 was heated up at 120 oC for five hours with a constant stirring. The mixture 2 included $Zr(OC_3H_7)_4$ and $Ti(OC_3H_7)_4$ with the desired molar ratio was diluted using 2-MOE solvent at 120 oC during stirring for at least three hours. Mixture 1 and 2 were then added together under continuous stirring at 80 oC to get a homogeneous and transparent solution. To adjust viscosity and stabilize the sol, formamide ($NH_2CHO$) and acetylacetone ($CH_3COCH_2COCH_3$) were added to the resulting solution. The whole solution was then refluxed for at least 1 hour to obtain homogeneous mixing among the components. In final, BSZT sol was filtered through the 2 μm diameter filter paper to get stock solution.

The above-mentioned stock sol was coated onto Pt/Ti/SiO$_2$/Si substrates at 4000 rpm for 30 s by a Spinner 150i. The as-deposited BSZT thin films were followed by a heating procedure: first dried at a low temperature of 150 °C for 12 min to get rid of the water vapour and residual solvent; then pyrolyzed at 450 °C in air for 10 min. In order to achieve a desired film thickness (~ 400 nm), the coating and deposition process were usually done from 6 to ten times. The films finally were crystalized at about 650 °C in the air by rapid annealing (flowing rate was ~25 °C/min) for 30 min to obtain polycrystalline perovskite phase.

2.2. Microstructure and electrical characterizations
The crystal structure of the BSZT powder samples was examined by Synchrotron X–ray diffraction (SXRD) experiments with a Beamline SAXS of the Synchrotron Light Research Institute (Thailand). The corresponding crystal structure for BSZT thin films were examined by X-ray diffractometer using CuKα radiation (XRD; Philips X’pert). The surface morphology of the films was performed by scanning electron microscopy (SEM) using a Nova NanoLab 600 microscope at 15 kV. For electrical measurements, series of capacitors with structure metal–insulator–metal (MIM) were patterned. Pt top electrodes (100 nm thick) were sputtered through a shadow mask ~100×100; 150×150 and 200×200 μm² in area. The capacitance–voltage (C–V) and capacitance–frequency (C–f) characterizations were measured via a four probes-station equipped with Keithley SCS-4200 Semiconductor characterization system. The voltage limitation of this equipment is ± 30V.

3. Results and discussion

Figure 1 shows the X-ray diffraction (XRD) results of BSZT thin films deposited on Pt electrode, and SXRD pattern of the BSZT powders prepared with the same precursor solution. The film and the powder exhibited single phase perovskite structure with no detectable impurity or secondary phase such as pyroclore phase. The XRD patterns of BSZT thin films are indexed in tetragonal perovskite structure with space group $P_{mm}4$ according to the analysis of SXRD data of BSZT powder [15]. Four well-defined peaks, identified as the (100), (110), (200), and (210) diffraction planes of BSZT tetragonal perovskite structure, are clearly observed in the XRD patterns.

In order to obtain the information concerning the crystallite size, $D$, and preferential film orientation from XRD data, the Scherrer’s formula and texture coefficient $TC(hkl)$ according to the Harris’s expression as given by equation 1 and 2 [16]:

$$D = \frac{K \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

$$TC(hkl) = \frac{I(hkl)}{n \sum I(hkl)} \frac{I_o(hkl)}{I_o(hkl)}$$  \hspace{1cm} (2)

where $K = 0.9$, $\beta$ is the full width at half-maximum (FWHM) of highest (110) diffraction peaks in radian, $\theta$ is the Bragg angle, and $\lambda$ is the CuKα wavelength (1.54439 Å). For the equation 2, $I(hkl)$ is the integrated intensity of (hkl) plane of the BSZT thin films, $I_o(hkl)$ is the relative intensity taken from JCPDS card no.: 34-0129 and $n$ is the number of diffraction peaks. The calculated data for the crystallite size and the preferred orientation of the BSZT thin films is listed in table 1.

It is well known that X-ray intensities are function of atomic structure. Any certain deviation in the texture coefficient from unity for a particular Miller plane corresponds to change in atomic structures in respect to the plane. The result of texture analysis
shows that the BSZT thin films on Pt substrate exhibit randomly oriented crystallites. And the crystallite sizes in the BSZT thin films as estimated from XRD data is around 25.18 nm.

Table 1. Parameters on crystallite size, $D$, and texture coefficients TC(hkl) of the BSZT thin films and nano powder.

| Plaens (hkl) | 2θ   | TC(hkl) |
|--------------|------|---------|
|              | BSZT powder | BSZT/Pt | BSZT/Pt |
| (100)        | 22.00 | 22.13   | 1.15    |
| (110)        | 31.28 | 31.56   | 1.03    |
| (111)        | 38.62 | -       | -       |
| (200)        | 44.91 | 45.23   | 1.02    |
| (210)        | 50.64 | 50.95   | 1.27    |
| (211)        | 55.88 | 56.20   | 1.28    |
| Crystallite size, $D$ (nm) | | | 25.18 |

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The surface morphology of the BSZT thin films were examined by SEM over a $1 \times 1 \ \mu m^2$ scan area. Figure 2 presents the typical SEM images of BSZT films on Si substrate.

The BSZT thin film possesses a smooth and dense surface with grain sizes ranging from 27 to 49 nm. The lower parts of figure 2 show the cross-section profiles of the BSZT film. As seen in the image, the thickness of the BSZT is approximately 355 nm for 10 layers, which turns out approximately 35.5 nm for each coating layer. The BSZT film on Pt-coated Si substrate exhibits coherently interfaces between the films and the substrates.

Figure 2: Surface morphology and cross-sectional SEM images of BSZT films on Pt electrode.
The dependence of capacitance measurements on the external applied dc voltages for Pt/BSZT/Pt thin film capacitor structures were performed with a small ac signal of 30 mV amplitude and dc bias voltage up to ± 30V. The corresponding dielectric constant–electric field (ε–E) and dielectric loss–electric field (tanδ–E) curves as shown in figure 3 and figure 4 were calculated from the capacitance data using the paralleled plate capacitor formula and assuming the homogeneous film thickness.

As observed, the dielectric constant curves exhibited apparent hysteresis, the so-called butterfly shape at lower sweeping bias voltage ranges. The occurrence of butterfly hysteresis in the C–V curves is usually described to the process of ferroelectric polarization switching, the films are ferroelectric in nature at low applied voltages. Increasing the dc bias voltage, the butterfly shape trails off gradually decrease and disappears completely in higher electric field. These observations were also noted by Bao and co-worker for BZT-xBCT thin film [17], and Chan et al. for (Ba,Sr)(Zr,Ti)O₃ samples [18]. This phenomenon is often attributed to the presence of local polar nanoregions (PNRs) or micropolar clusters, which are associated with the typical ferroelectric relaxor behaviour due to the heterogeneity of polarization domain structure [19,20]. In addition to the reduced ferroelectricity of the sample, the dielectric constants of the capacitors are found to increase with increasing sweeping voltage range. The maximum capacitance densities at zero bias voltage of Pt/BSZT/Pt measured at the maximum applied voltage (30 V) is ~ 0.50 µF/cm². It corresponds to the dielectric constant, ε of ~ 214.58 and dielectric loss, tanδ ~ 0.186 (figure 4 and table 2). In contrast to the capacitance density trend, tanδ varies considerably with applied electric field. Specifically, the tanδ increases and decreases suddenly when the capacitor was switched to the higher electric field range (E ≥ 600 kV/cm). It was stated that dielectric loss of parallel-plate ferroelectric thin-film capacitor contributes from many sources. In sol-gel BSZT thin films, it cannot rule out the presence of defects such as oxygen vacancies. Beside, residual stress due to lattice mismatch or different thermal coefficient between thin film and substrate, free carriers, and interfacial effects between film material and top/bottom electrodes are all possible sources of higher loss. Experimental studies aimed to elucidate the mechanisms of dielectric loss as well as minimize them are currently underway on the BSZT thin films deposited on different types of electrode (noble metal Pt, Au and conductive oxide LaNiO₃ and SrRuO₃) and different multi-valent dopants such as Mn and La.
In order to estimate the possibility of these materials for tunable capacitor applications, the overall voltage dependence of capacitance as well as the dielectric loss for Pt/BSZT/Pt capacitor are evaluated. Interestingly, figure 5 indicates that the Pt/BSZT/Pt capacitor provides rather excellent tenability with applied dc electric field, \(E\). The tunability of capacitance is defined as \(\delta C = \left| \frac{C(E)}{C(0)} \right| - 1\), where \(C(E)\) and \(C(0)\) are the capacitance at nonzero and zero electric field, respectively. For \(E = 800\) kV/cm (i.e. at a bias voltage of \(\pm 30\) V), the \(\delta C\) reaches to maximum value \(\sim 69\) \%. The figure of merit \([FOM = \frac{\delta C}{\tan\delta}]\) is \(\sim 4 - 17\) for BSZT capacitor in the higher electric field region (table 2). These obtained values are comparable to those values (\(\delta C \sim 40 - 50\%\) and \(FOM \sim 6 - 16\)) observed for SRO/(Ba,Sr)TiO\(_3\)/SRO capacitor [21].

Table 2. Dielectric parameters of BSZT thin films obtained at different bias voltages.

| Bias Voltage (V) | Dielectric constant, \(\varepsilon (E=0V)\) | Dielectric loss, \(\tan\delta (E=0V)\) | Tunability, \(\delta C\) (%) | FOM |
|-----------------|---------------------------------|-------------------------------|-----------------|-----|
| \(\pm 15\)     | 172.87                          | 0.024                         | 42.08           | 17.03|
| \(\pm 20\)     | 175.72                          | 0.054                         | 53.13           | 9.84 |
| \(\pm 25\)     | 204.51                          | 0.071                         | 63.12           | 8.89 |
| \(\pm 30\)     | 214.58                          | 0.186                         | 69.09           | 3.83 |

Figure 6 displays the dielectric constant and dielectric loss of BSZT thin films as a function of frequency in the range from 1 kHz – 5 MHz. The thin-film capacitor exhibited a noticeable dielectric dispersion and dielectric relaxations in the measured frequency range with a peak in \(\tan\delta-f\) curve.
around 10 kHz.

In dielectric materials, several mechanisms are responsible for polarization such as electronic, ionic, dipole reorientation-related, and space charge or interfacial polarization [22,23]. The degree to which each mechanism contributing to the overall polarization of the material depends on the applied frequency range. Generally, electronic and ionic relaxation are often related to very fast switching of weak dipoles. These oscillations can be measured at very high frequencies from gigahertz (GHz) to petahertz (PHz) (10⁹–10¹⁵ cycle/s). Permanent dipole reorientation can be tuned only frequencies from megahertz (MHz) to GHz (10⁶–10⁹ cycle/s) [2]. However, the dielectric properties, in fact, are strongly influenced by the complexity of porosity, the grain boundary densities, domain wall motion, crystallographic structure, and ionic space charge carriers. Therefore, it is speculated that the relaxation observed at several ten kHz spectrum in figure 6 might relate to ionic space charge carriers, such as the oxygen vacancies and defects generated during film growth, interface polarization located at grain boundary or the interface between the film and electrode. Waser and co-authors reported that oxygen vacancy and related defects were the main reasons for higher dc conductivity and increasing loss tangent in oxide ferroelectric materials in the low frequency region [24]. Because of their positively charged with respect to the regular lattice, thus oxygen vacancies experience an electromigration toward the cathode under a dc electric field. The oxygen vacancies pile up at the cathode and are supposed to be compensated by electrons injected from external applied bias voltage. This could be the reason why the tanδ observed in figure 4 in the negative electric field region is often greater than that of the dielectric loss in the positive electric field band. In addition, during the degradation, coloration effects near the electrodes is also observed quite clearly. Specifically, the BSZT thin film area under measured capacitor structure was blistered, which resulted in the top electrode peeling off the thin film surface.

4. Conclusions

Lead-free ferroelectric barium titanate-based (BSZT) thin films were fabricated on metal Pt/Ti/SiO₂/Si(100) substrates by the effective sol-gel method. The films are of polycrystalline perovskite phase with the grain sizes ranging from 27 to 49 nm and coherent grain boundary. Butterfly-shaped (C–V)/or (ε–E) characteristics revealed the ferroelectricity of thin films. Capacitance of Pt/BSZT/Pt can be easily tuned in the wide voltage range without broken structure. The best parameters to compare the quality of the films are obtained with a tenability of 42% and figure of merit, FOM ~ 17 at 15 V. This result demonstrates that the as-deposited BSZT thin film on Pt/Ti/SiO₂/Si(100) substrate are highly potential candidate to apply for electrically tunable devices.

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References

[1] J.F. Scott, Applications of Modern Ferroelectrics, Science 315 (2007) 954–959.
[2] K. Uchino, Ferroelectrics Devices, 2nd Ed., CRC Press, Inc., FL, United States, 2019.
[3] L.W. Martin, A.M. Rappe, Thin-film ferroelectric materials and their applications, Nat. Rev. Mater. 2 (2017) 16087.
[4] EU-Directive 2002/95/EC: Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS), Off. J. Eur. Union. 46 (2003) [L37] 19–23.
[5] W.W. Wolny, European approach to development of new environmentally sustainable electroceramics, Ceram. Int. 30 (2004) 1079–1083.
[6] T.R. Shrout, S.J. Zhang, Lead-free piezoelectric ceramics: Alternatives for PZT?, J. Electroceram. 19 (2007) 111–124.
[7] C.L. Sengupta, S. Sengupta, Breakthrough advances in low loss, tunable dielectric materials, Mat Res Innov. 2 (1999) 278–282.
[8] A.K. Tagantsev, V.O. Sherman, K.F. Astafiev, J. Venkatesh, N. Setter, Ferroelectric Materials for Microwave Tunable Applications, J. Electroceramics. 11 (2005) 5–66.
[9] S. Ezhilvalavan, T. Tseng, Progress in the developments of (Ba,Sr)TiO$_3$ (BST) thin films for Gigabit era DRAMs, Mater. Chem. Phys. 65 (2000) 227–248.
[10] X.G. Tang, K. Chew, H.L.W. Chan, Diffuse phase transition and dielectric tunability of Ba(Zr$_{1-y}$Ti$_y$)$_3$O$_9$ relaxor ferroelectric ceramics, Acta Mater. 52 (2004) 5177–5183.
[11] J. Chen, Y. Zhang, C. Deng, X. Dai, L. Li, Effect of the Ba/Ti Ratio on the Microstructure and Dielectric Properties of Barium Titanate-Based Glass–Ceramics, J. Am. Ceram. Soc. 90 (2009) 1350–1353.
[12] S. Tio, V. Ramana, L. Feng, W. Lin, B.S. Murty, Effect of grain size on dielectric and ferroelectric properties of, J. Adv. Ceram. 4 (2015) 46–53.
[13] K. Chong, L.B. Kong, L. Chen, L. Yan, C.Y. Tan, T. Yang, et al., Improvement of dielectric loss of doped Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ thin films for tunable microwave devices, J. Appl. Phys. 95 (2004) 1416.
[14] B. Vigneshwaran, P. Kuppusami, S. Ajithkumar, H. Sreemoolanadhan, Study of low-temperature dependent structural, dielectric, and ferroelectric properties of Ba$_x$Sr$_{1-x}$TiO$_3$ (x = 0.5, 0.6, 0.7) ceramics, J. Mater. Sci. Mater. Electron. 31 (2020) 10446–10459.
[15] P.T. Nguyet, N. Thi, M. Phuong, V.T. Hien, Preparation and Microstructure of Acetate-based Lead-free BSZT Ferroelectric Thin Films Using Sol-gel Technique, VNU J. Sci. Math. - Phys. 35 (2019) 55–61.
[16] G.B. Harris, X. Quantitative measurement of preferred orientation in rolled uranium bars, Philos. Mag. Ser. 7. 43 (1952) 113–123.
[17] Y. Lin, G. Wu, N. Qin, D. Bao, Structure, dielectric, ferroelectric, and optical properties of (1–x)Ba(Zr$_{0.3}$Ti$_{0.7}$)O$_3$–x(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ thin films prepared by sol–gel method, Thin Solid Films. 520 (2012) 2800–2804.
[18] N.Y. Chan, D.Y. Wang, Y. Wang, J.Y. Dai, H.L.W. Chan, The structural and in-plane dielectric/ferroelectric properties of the epitaxial (Ba, Sr)(Zr, Ti)O$_3$ thin films, J. Appl. Phys. 115 (2014) 234102.
[19] P. Taylor, G.H. Haertling, Ferroelectrics PLZT electrooptic materials and applications — a review, Ferroelectrics. 75 (1987) 25–55.
[20] I. Stolichnov, A. Tagantsev, N. Setter, S. Okhonin, P. Fazan, J.S. Cross, et al., Dielectric breakdown in (Pb,La)(Zr,Ti)O$_3$ ferroelectric thin films with Pt and oxide electrodes, J. Appl. Phys. 87 (2000) 1925.
[21] Y.A. Boikov, T. Claeson, Dielectric Response of Ba$_{0.05}$ Sr$_{0.95}$TiO$_3$ (110) Films to Variations in Temperature and Electric Field, Phys. Solid State. 57 (2015) 957–961.
[22] A.A. Bokov, Z.-G. Ye, Dielectric Relaxation in Relaxor Ferroelectrics, J. Adv. Dielectr. 2 (2012) 1241010.
[23] L. Dissado, Chap. 10: Dielectric Response, in: S. Kasap, P. Capper (Eds.), Handb. Electron. Photonic Mater., 2nd Ed., Springer, Cham, 2017: pp. 219–245.
[24] R. Waser, T. Waiatu, K.-H. Hardt, de Electrical Degradation of Perovskite-Type Titanates: I, Ceramics, J Am Ceram Soc. 73 (1990) 1645–1653.