Research Article

Nanoscale Ferroelectric Switchable Polarization and Leakage Current Behavior in $(\text{Ba}_{0.50}\text{Sr}_{0.50})(\text{Ti}_{0.80}\text{Sn}_{0.20})\text{O}_3$ Thin Films Prepared Using Chemical Solution Deposition

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Received 19 March 2015; Accepted 20 April 2015

Academic Editor: Hassan Karimi-Maleh

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Nanoscale switchable ferroelectric $(\text{Ba}_{0.50}\text{Sr}_{0.50})(\text{Ti}_{0.80}\text{Sn}_{0.20})\text{O}_3$ -BSTS polycrystalline thin films with a perovskite structure were prepared on $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrate by chemical solution deposition. X-ray diffraction (XRD) spectra indicate that a cubic perovskite crystalline structure and Raman spectra revealed that a tetragonal perovskite crystalline structure is present in the thin films. Sr^{2+} and Sn^{4+} cosubstituted film exhibited the lowest leakage current density. Piezoresponse Force Microscopy (PFM) technique has been employed to acquire out-of-plane (OPP) piezoresponse images and local piezoelectric hysteresis loop in polycrystalline BSTS films. PFM phase and amplitude images reveal nanoscale ferroelectric switching behavior at room temperature. Square patterns with dark and bright contrasts were written by local poling and reversible nature of the piezoresponse behavior was established. Local piezoelectric butterfly amplitude and phase hysteresis loops display ferroelectric nature at nanoscale level. The significance of this paper is to present ferroelectric/piezoelectric nature in present BSTS films at nanoscale level and corroborating ferroelectric behavior by utilizing Raman spectroscopy. Thus, further optimizing physical and electrical properties, BSTS films might be useful for practical applications which include nonvolatile ferroelectric memories, data-storage media, piezoelectric actuators, and electric energy storage capacitors.

1. Introduction

Perovskite oxide materials are the most studied functional materials for ferroelectric, ferromagnetic, magnetoresistive, and memristive applications. BaTiO_3 and its solid solutions are attractive candidate materials for multifunctional applications. These ferroelectric ceramics and thin films are key materials for nonvolatile ferroelectric random access memories (FE-RAMs) and volatile dynamic random access memories (DRAMs), capacitors, and various other applications [1, 2]. By suitable site engineering (chemical doping/substitution) with either isovalent or aliovalent elements at Ba^{2+} or/and Ti^{4+} site in BaTiO_3 (BTO) leads to changes in

the structure with improved electrical properties, the magnitude of dielectric constant, ferroelectric to paraelectric phase transition temperature, and dielectric tunable properties in the wide range of temperature to meet the variety of device applications.

Various BTO based solid solutions have attracted considerable attention due to their remarkable dielectric, ferroelectric, piezoelectric, pyroelectric, and optical properties which are suitable for high energy storage capacitors and multilayer ceramic capacitor (MLCC) applications and they have been extensively studied for improved electrical properties, which include $\text{Ba}(\text{Ti}, \text{Sn})\text{O}_3$ [3], $(\text{Ba}, \text{Sr})(\text{Ti}, \text{Sn})\text{O}_3$ [4], $\text{Ba}(\text{Zr}, \text{Ti})\text{O}_3$ [5], $(\text{Ba}, \text{Ca})\text{TiO}_3$ [5–7],

$\text{Ba}(\text{Ti}, \text{Sn})\text{O}_3-x(\text{Ba}, \text{Ca})\text{TiO}_3$ [8], $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ [9–13], $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.92}\text{Sn}_{0.08})\text{O}_3$ [14], and $(1-x)(\text{Ba}, \text{Ca})(\text{Ti}, \text{Sn})\text{O}_3-x(\text{Ba}, \text{Ca})(\text{Ti}, \text{Zr})\text{O}_3$ [15]. Shift in the Curie temperature to lower temperature to that of pure BTO ($T_c \sim 120\text{--}130^\circ\text{C}$) is often observed when isovalent ions are doped (e.g., Sr^{2+} doping for Ba^{2+} site or Zr^{4+} doping for Ti^{4+} site) in BTO lattice [16]. Improved electrical properties were also observed for Ca substituted BTO, with a modest increase in T_c [5]. By varying wt.% of Sn^{4+} in $(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3(\text{BCTS}_x)$ ceramics, a series of phase transitions were evolved which include inceptive orthorhombic phase (O) at $0 \leq x \leq 0.04$ to a two-phase coexistence of pseudocubic-orthorhombic phase (PC-O) at $0.06 \leq x \leq 0.10$ and further to a multiphase coexistence of rhombohedral-pseudocubic-orthorhombic phase (R-PC-O) at $x = 0.11$ with an ultrahigh piezoelectric response ($d_{33} \sim 670$ pC/N, $dS/dE \sim 1214$ pm/V) at room temperature [8]. Similar phase transition behavior was observed for Er-doped BiFeO_3 films, with enhanced electrical properties such as ferroelectric and leakage properties derived from the phase transition of rhombohedral to tetragonal and orthorhombic symmetry structure as Er-doped concentration (x) increased gradually to 0.15 then to the orthorhombic structure when $x = 0.20$ [17]. By varying Sr^{2+} content at Ba^{2+} site in $(\text{Ba}_{0.91}\text{Ca}_{0.09-x}\text{Sr}_x)(\text{Ti}_{0.92}\text{Sn}_{0.08})\text{O}_3$ ceramics, the phase transition of rhombohedral-orthorhombic and orthorhombic-tetragonal merged to near room temperature and outstanding electrical properties were obtained at room temperature due to phase coexistence (orthorhombic and tetragonal) [18].

Particularly, ferroelectric barium strontium titanate $[\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3\text{-(BST)}]$ ($0 \leq x \leq 1$) ceramics and thin films are promising for capacitor applications due to their low leakage current at operable voltages, large breakdown voltage, and high dielectric constant with low dielectric loss [19]. Various compositions of BST thin films were well studied for tunable microwave device applications such as phase shifters, delay lines, tunable filters, and voltage controlled oscillators due to high dielectric constant and tunability (change in the dielectric constant under an applied electric field) and good temperature stability [20, 21].

Barium tin titanate $[\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3\text{-(BTS)}]$ also received much research attention because of its high dielectric constant and relaxor ferroelectric characteristics and these are good candidate materials for applications in microelectronic devices [22–24]. Ferroelectric-paraelectric phase transition temperature decreased with increasing Sn^{4+} concentration in $\text{Ba}(\text{Ti}_{0.85}\text{Sn}_{0.15})\text{O}_3$, with more diffused phase transition behavior [25]. BTS solid solutions have a ferroelectric phase transition between 0° and 130°C , when the Sn^{4+} ratio is between $x = 0$ and 0.20 and these solid solutions exhibit stable ferroelectric properties with a Curie temperature around room temperature at $x = 0.1$ to 0.15 [26, 27]. However to further improve the reproducibility and stability with improved physical and electrical properties of these materials, codoping/substitution at both Ba^{2+} and Ti^{4+} site in BTO lattice is essential and various research groups around the globe are working in this direction. Wang et al. [28]

reported $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Ti}_{0.9}\text{Sn}_{0.1})\text{O}_3$ ($0 \leq x \leq 0.3$ -BS_xTS) thin films prepared by radio frequency magnetron sputtering with a large ferroelectric hysteresis behavior and low leakage current behavior at 25°C . Souza et al. [4] reported BSTS nanopowder synthesis using soft chemical method and pseudocubic crystallographic structure was obtained for these powders. They also reported dielectric and ferroelectric properties for BSTS polycrystalline pseudocubic thin films prepared using soft chemical method [29]. Further, it was noticed that only few reports exist in literature about the local piezoelectric properties measurement on BST [30, 31] and BSTS ceramics [32] at nanoscale level. In general, nanoscale science (nanoscience) and nanotechnology best describe the materials' properties at nanometer length scale, which is one billionth (10^{-9}) of a meter. Materials' properties at nanoscale level behave differently from that of micron sized materials. Improved properties at nanoscale architecture are due to altered atomic configurations and increased surface area to volume ratio. Both nanoscience and nanotechnology are interdisciplinary and have vast variety of applications in scientific, industrial, and biological fields. However, to the best of our knowledge, nanoscale ferroelectric switchable polarization studies have not been performed in complete so far on the BSTS system by utilizing piezoresponse force microscopy (PFM) technique. Therefore, the present study focuses on the ferroelectric switching behavior at nanoscale level by utilizing PFM studies along with other bulk properties including X-ray diffraction ~XRD, Raman spectroscopy, and leakage current (current density-voltage) behavior of the BSTS films deposited on $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrates by chemical solution deposition (spin coating). Temperature and electric field dependent dielectric properties, micro Raman, and ferroelectric polarization measurements on this film are in progress and will be reported elsewhere.

2. Experimental Details

Stoichiometric $(\text{Ba}_{0.50}\text{Sr}_{0.50})(\text{Ti}_{0.80}\text{Sn}_{0.20})\text{O}_3\text{-(BSTS)}$ used in this study was prepared using chemical solution deposition as outlined in Figure 1. Barium acetate ($\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, Aldrich), strontium acetate ($\text{Sr}(\text{CH}_3\text{CO}_2)_2$, Aldrich), tin acetate ($\text{Sn}(\text{CH}_3\text{CO}_2)_2$, Aldrich), and titanium (IV) butoxide ($\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$, Aldrich) were used as precursors. 2-Methoxy ethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, 99.8%, Aldrich) was used as a solvent to facilitate the dehydration by boiling as it boils at 125°C and Acetic acid (CH_3COOH , 99.99% Aldrich) was used as the chelating agent for the alkoxides. Stock solution was directly deposited onto $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrates by spin coating (precoating 1000 rpm 10 s followed by 3000 rpm for 30 s). Resultant films underwent two different preannealing (pyrolysis) heat treatments. In the first step, films were heat-treated at 250°C for 2 min. These steps were repeated for obtaining desired thickness, and finally in the second step the films were annealed at 750°C temperature for obtaining crystalline dense BSTS films. Flow chart of the preparation of BSTS thin film by chemical solution deposition process is shown in Figure 1.

FIGURE 1: Flow chart of the preparation of $(\text{Ba}_{0.50}\text{Sr}_{0.50})(\text{Sn}_{0.20}\text{Ti}_{0.80})\text{O}_3$ -BSTS thin film by chemical solution deposition process.

The crystal structure of BSTS films was characterized using an X-ray diffractometer (Rigaku) employing the Bragg-Brentano (θ - 2θ) method with $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) as the radiation source. Room temperature Raman spectroscopy measurements were performed using SA T64000 spectrograph consisting of a double monochromator coupled to the third stage with 1800 grooves mm^{-1} grating. Radiation $\sim 514.532 \text{ nm}$ from a Coherent Innova 99 argon ion laser was focused over a less than 2 mm diameter circle area by using a Raman microprobe with an 80x objective. Thickness of the BSTS films was determined independently using an Ambios XP-200 profilometer and a spectral reflectance based Filmetrics instrument which was around 360 nm.

Platinum (Pt) dots were sputtered to form the top electrode ($250 \mu\text{m}$) by utilizing a shadow mask by means of direct current (DC) magnetron sputtering. Electrical properties were measured on thin films grown on Pt (top electrode) and Pt/ TiO_x / SiO_2 /Si (bottom electrode) substrate in metal-insulator-metal (M-I-M) configuration. Leakage current measurements were done under vacuum (10^{-4} torr) with Keithley electrometer (model 6517A). And nanoscale ferroelectric switching behavior of the films was measured by a Veeco piezoresponse force microscope (PFM) operated in contact mode and local piezoelectric hysteresis loops were

FIGURE 2: XRD patterns with 2θ - θ scans of $(\text{Ba}_{0.50}\text{Sr}_{0.50})(\text{Sn}_{0.20}\text{Ti}_{0.80})\text{O}_3$ -BSTS thin film.

obtained without top electrode (whereas tip itself acts as top electrode in these measurements).

3. Results and Discussion

XRD profiles of BSTS film samples are measured at room temperature. The XRD patterns indicate that BSTS has a perovskite crystalline structure as shown in Figure 2, which is also demonstrated by the Raman spectroscopic measurements. However from the XRD patterns it is not clear what the exact phase at room temperature is and we cannot obtain detailed information about the structure of the films. Hence we made room temperature Raman spectroscopic measurements to obtain the information on the crystal structure of the BSTS films from vibrational spectroscopy.

A close relationship between lattice dynamics and ferroelectricity is obtained using Raman spectroscopy. Crystalline phase is confirmed using Raman spectra. There are fifteen degrees of freedom in ABO_3 perovskite materials above the cubic-tetragonal phase transition, which are divisible into $4F_{1u} + 1F_{2u}$ [33]. However, one of the F_{1u} symmetry modes corresponds to the acoustic branch and the remaining $3F_{1u}$ and $1F_{2u}$ belong to the optical branches in the cubic phase with O_h^1 or $Pm3m$ point group symmetry [33]. In paraelectric cubic phase in ABO_3 perovskites there are 12 optical modes, which transform into the triply degenerate irreducible representations of the O_h^1 point group ($\Gamma_{\text{cub}} = 3F_{1u} + 1F_{2u}$) [33]. In cubic perovskite phase, the F_{1u} modes are IR active and the F_{2u} mode is neither IR nor Raman active, the so-called “silent mode”, whereas in the ferroelectric tetragonal phase each triply degenerate F_{1u} mode splits into $A_1 + E$ modes, while the F_{2u} silent mode splits into $B_1 + E$ modes. These Raman modes include $3 A_1(\text{TO}) + 3 A_1(\text{LO}) + 3 E(\text{TO}) + 3 E(\text{LO}) + 1 E(\text{LO} + \text{TO}) + 1 B_1$ [34]. However, all the A_1 and E modes are both Raman and IR active, whereas B_1 mode is only Raman active. The high temperature cubic-phase Raman optical modes (A_1 and E) are further split into longitudinal optical (LO) and transverse optical (TO) branches due to

FIGURE 3: Raman spectroscopic images of $(\text{Ba}_{0.50}\text{Sr}_{0.50})(\text{Sn}_{0.20}\text{Ti}_{0.80})\text{O}_3$ -BSTS thin film and BaTiO_3 (BTO) thin films (inset).

presence of long-range ordering electrostatic forces [34]. It is well known that the Raman peaks should not be present in the ideal cubic phase. Figure 3 illustrates the room temperature Raman spectra for BSTS thin films. The room-temperature Raman spectra of the polycrystalline BSTS films are very similar and contain all main features typical of BaTiO_3 (BTO) (Figure 3 inset).

Six characteristic major Raman modes centered were indexed as $E_1(\text{TO}_1) \sim 115 \text{ cm}^{-1}$, $A_1(\text{TO}_1) \sim 177 \text{ cm}^{-1}$, $A_1(\text{TO}_2) \sim 222 \text{ cm}^{-1}$, $B_1/E(\text{TO}_2) \sim 301 \text{ cm}^{-1}$, $A_1(\text{TO}_3) \sim 511 \text{ cm}^{-1}$, and $A_1(\text{LO})/E(\text{LO}) \sim 742 \text{ cm}^{-1}$. Similar to pure BaTiO_3 film sample, BSTS thin film. The $E(\text{TO}_1)$ soft mode is underdamped and shifted to $\sim 115 \text{ cm}^{-1}$ [34, 35]. As shown in Figure 3, the A_1 soft mode only exists in ferroelectric phase and this $A_1(\text{TO}_2)$ mode is observed at 221 cm^{-1} ; on the contrary to that of pure BTO at 262 cm^{-1} , a considerable downshift in Raman frequency is noticed; similar results were reported for BST-0.3 ceramics and thin films [35].

However the weak $B_1/E(\text{TO}_2)$ mode which has been associated with the tetragonal-cubic phase transition was observed at around 301 cm^{-1} . This mode has a mixed character of the B_1 and $E(\text{TO}_2)$ derived from the F_{2u} cubic silent mode [36, 37]. The interference of the asymmetric sharp $A_1(\text{TO}_1)$ mode at 177 cm^{-1} with the broad $A_1(\text{TO}_2)$ mode at about 222 cm^{-1} results in an antiresonance effect at 177 cm^{-1} . The asymmetric $A_1(\text{TO}_3)$ mode couples weakly with the $A_1(\text{TO}_2)$ mode [38]. The presence of well-built peak related to the $A_1(\text{LO})$ mode confirms tetragonal structure in the BSTS films at room temperature [39, 40].

Shift in $A_1(\text{TO}_1)$ and $A_1(\text{TO}_2)$ modes either to lower or higher wave number region is attributed to the asymmetric Ti-O phonon vibrations in BaTiO_3 lattice, while the $A_1(\text{TO}_3)/E(\text{TO}_3)$ mode at around 511 cm^{-1} is due to O-Ti-O symmetric stretching vibrations. On the other hand, the peak position of Raman mode $B_1/E(\text{TO}_2)$ shifted to lower wave number region and $A_1(\text{LO})/E(\text{LO})$ mode is shifted to higher wave number region when compared to pure BaTiO_3

FIGURE 4: Leakage current behavior (current density versus voltage) of BSTS thin film.

films. It is well known from the literature that the phonon frequencies may shift to either lower or higher peak positions and are compositional dependent. Due to either tensile or compressive stress, the phonon wave numbers are expected to shift towards either higher or lower region [35]. Increasing Sr^{2+} concentration at BST thin film, the lattice of the films is compressed; thus the tensile stress which is deduced from the lattice compression might be accountable for the $A_1(\text{LO})/E(\text{LO})$ mode shift towards a higher wave number region in Raman spectra and as well residual stress is not released in the films [39].

Moreover we also observed an additional disordered activated Raman mode at about 567 cm^{-1} in the BSTS films marked by asterisk which does not appear for pure BaTiO_3 . Similar Raman mode was reported for $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films [35, 39]. Wang et al. [41] also reported similar Raman modes around 535 cm^{-1} and 750 cm^{-1} and they shifted to higher wavenumber region for compositionally graded multilayered $(\text{Ba}_{0.8}\text{Sr}_{0.2})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ (BSTZ) thin films, which might be attributed to increasing internal strain in the films. Presence of this disordered activated Raman mode is also expected from the eight-site model due to disorder of Ti ions, which can occupy four off-center sites in the tetragonal phase in perovskite oxides [35]. Apparently Sr^{2+} substitution at Ba^{2+} site in BTO lattice caused local distortions and partially breaks the translational symmetry in the lattice and there it is more complicated in disorder-activated background in BST films [35]. All the main Raman modes in BSTS films become broadened which is attributed to structural disorder in the crystalline BSTS lattice [39].

To investigate the leakage current behavior of the films, current density ($\log J$) versus the dc bias voltage (V) characteristics on the metal-insulator-metal (MIM) configuration for the BSTS film annealed at 750°C for 30 min and Figure 4

FIGURE 5: (a) Surface topography (PFM) image, (b) PFM amplitude image, (c) PFM phase image, and square patterns of different areas written on the surface confirm the switchability of ferroelectric polarization under ± 12 V bias voltage of BSTS films.

presents the obtained results. The voltage-step and the delay-time after applying each voltage-step were fixed at 0.5 V and 1 s, respectively. The films exhibit low to moderate leakage current density ($\sim 10^{-5}$ – 10^{-2} A/cm²). For low voltages the leakage current is low and at high voltages the leakage currents are increased from the beginning 0 to 20 V. The observed log J - V -loops are noticeably asymmetrical (Figure 4). The possible asymmetry of the two branches in the leakage currents might be due to the fact that the positive and negative bias were measured on single pad (top electrode Pt dot on shadow mask), rather than using different Pt top electrode pad. Low to moderate leakage current density might be due to the possible degradation effect of the film. Thin film degradation and asymmetry can be avoidable by measuring the leakage current for positive and negative bias are measured on different top Pt electrode pads [42]. Controlling this asymmetric behavior in thin films improved device reliability and stability can be achieved.

Ferroelectric (piezoelectric) nature at the nanoscale level is determined by piezoresponse force microscopy (PFM). PFM is a powerful tool for imaging and characterizing ferroelectric domain structures at nanoscale level [43, 44]. The piezoresponse for the BSTS films is obtained utilizing commercially available Si-tip of the PFM in contact mode by applying a DC voltage between the tip (top electrode) and the Pt/TiO_x/SiO₂/Si substrate as bottom electrode of

the film. As shown in Figure 5(a), the BSTS films exhibit atomically flat surface with overall mesh-like pattern with a root-mean-square roughness of approximately 1.5 nm over an area of $8 \times 8 \mu\text{m}^2$. The topographical height image also reveals a polycrystalline structure with 0.2 Å sized grains. Square patterns were written on the film with $8 \times 8 \mu\text{m}^2$ areas (outer square) at -12 V; the domain changes its orientation and the central $4 \times 4 \mu\text{m}^2$ area (inner square) with $+12$ V DC bias is applied; it reverses its polarity. Figures 5(b) and 5(c) show the representative out-of-plane PFM phase and amplitude of ferroelectric domains written on the BSTS film surface at room temperature. From Figures 5(b) and 5(c) it is observed that the ferroelectric switching contrast in the BSTS film. It is also clear from the phase and amplitude images that there exists a strong domain switching response for both negative (outer square) and positive bias (inner square). The square patterns clearly show the oppositely written regions establishing that the BSTS films show nanoscale switching behavior which confirms ferroelectric piezoelectric nature. The out-of-plane piezoresponse local hysteresis loops were determined as a function of applied voltage and the PFM hysteresis loop both in amplitude and phase is shown in Figure 6. The phase change is about 180° and is observed for a complete polarization reversal of the grain. Butterfly shaped amplitude hysteresis and phase images confirm the ferroelectric piezoelectric properties at the nanoscale level.

FIGURE 6: Local hysteresis loops measured by PFM amplitude and phase loops from microscopic measurements of BSTS films.

The observed local coercive voltage minima from the amplitude loops are found to be +0.75 V and −0.10 V.

4. Conclusion

In summary, we have investigated the structural, leakage current, and nanoscale ferroelectric switching behavior of $(\text{Ba}_{0.50}\text{Sr}_{0.50})(\text{Sn}_{0.20}\text{Ti}_{0.80})\text{O}_3$ -BSTS thin films by chemical solution deposition on $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrates. XRD and Raman spectra confirm perovskite crystalline structure in the BSTS films. All the main peaks corresponding to tetragonal symmetric group were present in the room temperature Raman spectra. Tetragonal $A_1(\text{LO})/\text{E}(\text{LO})$ mode shift towards a higher wave number region in Raman spectra might be attributed to tensile stress in the films. Local piezoelectric activity of the BSTS films was investigated by Piezoresponse Force Microscopy (PFM) technique. PFM studies revealed nanoscale ferroelectric switching in the chemical solution deposited annealed samples.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

This work was supported by the National Science Foundation under Grant NSF-EFRI RESTOR no. 1038272.

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