

Effect of Repeated Application of Switching Electric Field on Al/Ba_{0.9}Sr_{0.1}TiO₃/Pt/Si and Al/Ba_{0.3}Sr_{0.7}TiO₃/Pt/Si Thin Films

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Abstract

Repeated application of switching the electric field on the electrical properties of the films, such as variation of capacitance with voltage and leakage current, were studied on thin films of Al/Ba_{0.9}Sr_{0.1}TiO₃/Pt/Si (BST-0.9) and Al/Ba_{0.3}Sr_{0.7}TiO₃/Pt/Si (BST-0.3) prepared by sol-gel method. The ferroelectric BST-0.9 films that exhibited degradation by applying a switching electric field showed hysteresis. Paraelectric BST-0.3 films did not show any degradation on repeated application of switching electric field. The resistivity, breakdown field, and Devonshire thermodynamic coefficient C_3 were calculated for all the films. These physical properties are essential in choosing a film for particular applications such as memory, dynamic random access memory, tunable phase shifter, photodiodes in light sensors, etc.

Keywords: Ba_{0.9}Sr_{0.1}TiO₃; Ba_{0.3}Sr_{0.7}TiO₃; Sol-gel thin film; Leakage current; Capacitance vs. voltage.

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1. Introduction

Ferroelectric materials find applications in numerous paraelectric devices and in the ferroelectric phase [1-5]. But, for applications like memory devices, it is essential to have films in the ferroelectric phase [1-3]. It is preferable to have the material in the paraelectric phase for other applications like DRAM (dynamic random-access memory), tunable phase shifters, light sensors, microwave devices, etc. [2-5]. It is generally observed that ferroelectric films undergo degradation with time, external electric field, temperature, and stress [6-9]. The three most important factors responsible for the degradation of ferroelectric films are ferroelectric fatigue, resistance degradation, and ferroelectric aging [8]. Repeated application of continuous switching electric field on ferroelectric materials and films usually results in loss of polarization, usually referred to as fatigue [6-8]. The polarization vs. electric field response change with time is called ferroelectric aging [8]. Insulating properties of dielectric materials show a degradation when subjected to dc bias and high temperature, called resistance degradation [8].

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The ferroelectric material, Barium-Strontium-Titanate, to be referred to hereafter as $Ba_xSr_{1-x}TiO_3$, BST, undergoes a phase transition from ferroelectric to paraelectric, where the transition temperature varies from $-238\text{ }^\circ\text{C}$ for $x=0.0$ to $120\text{ }^\circ\text{C}$ for $x=1.0$, depending on the ratio of Ba/Sr (x) [10]. We shall refer to a transition temperature as the temperature at which the thin film changes from ferroelectric to paraelectric phase. BST finds various applications in DRAM, various microwave devices, tunable phase shifters, photodiodes as light sensors in satellite technology, glucose sensors, etc. [11-15]. It is, therefore, imperative to study the effect of repeated application of switching the electric field on the films to find whether the ferroelectric films undergo degradation. Our study is focussed on this aspect so that the reliability of the prepared ferroelectric films can be ascertained. In the process, the choice of appropriate composition of BST thin film for certain applications can be made properly.

2. Methodology

Barium Strontium Titanate, thin films of compositions $Ba_{0.9}Sr_{0.1}TiO_3$ (BST-0.9) and $Ba_{0.3}Sr_{0.7}TiO_3$ (BST-0.3), were deposited by sol-gel method on Platinized silicon (Pt/Si) substrate as described in detail by Lahiry *et al.* [16]. BST-0.9 film exhibits a transition temperature of $110\text{ }^\circ\text{C}$ while BST-0.3 film exhibits a transition temperature of $-100\text{ }^\circ\text{C}$, as reported earlier [17]. Hence, at room temperature, $Ba_{0.9}Sr_{0.1}TiO_3$ is in the ferroelectric phase, while $Ba_{0.3}Sr_{0.7}TiO_3$ is in the paraelectric phase [17]. Aluminum dots, deposited by the vacuum evaporation method, having an area of $1.9625 \times 10^{-3}\text{ cm}^2$ were used as top electrodes. Fig. 1 gives a schematic diagram of the sample where Platinized Silicon (Pt/Si) was the substrate with Platinum (Pt) as the bottom electrode, BST film deposited by sol-gel method was the ferroelectric layer, and vacuum evaporated Aluminium (Al) dots were used as the top electrode so that the system behaves as a metal/ferroelectric/metal capacitor.

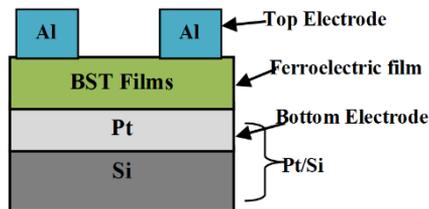


Fig. 1. Schematic diagram of Metal/Ferroelectric/Metal structure.

Characteristics of capacitance vs. voltage (C-V) and current vs. voltage (I-V) were measured on these films. Variation of capacitance with a bias voltage (C-V) of the samples was measured using a PAR 410 C-V plotter at 1MHz. The variation of capacitance with applied voltage was measured as the dc-field was varied between $-12.5 \rightarrow 0 \rightarrow 12.5 \rightarrow 0 \rightarrow -12.5$ volts, where the voltage was increased by 0.5 volts at a step rate of 1step/3s. The sweep in the dc field modulates the polarization states of the film. Keithley electrometer (Model 610C) and an Aplab DC power supply were used for

current vs. voltage (I-V) measurements. In order to study the repeated application of switching electric fields, both films were subjected to polarisation reversal by applying $\pm 11.0\text{V}$ at 1MHz. Films of comparable thickness were subjected to the same number of switching cycles. Hereafter, for the composition BST-0.9, the new film is marked A1, and the film subjected to a switching electric field of 10^9 cycles of $\pm 11.0\text{V}$ pulses of 1MHz is labeled B1. Similarly, corresponding films of fresh BST-0.3 and the film subjected to switching electric fields for the same composition are labeled A2 and B2, respectively. Now, the films of both compositions, BST-0.9 and BST-0.3, subjected to switching electric fields of 10^9 cycles, will hereafter be labeled as "treated films." C-V and I-V measurements were done on the fresh film and on the same film subjected to repeated application of switching field (treated films), i.e., on all four samples A1, B1, A2, and B2. The effect of repeated application of switching the electric field on the Devonshire thermodynamic parameter, C_3 , was also studied for both compositions.

3. Results and Discussion

3.1. Capacitance-voltage characteristics

The capacitance variation with voltage can be related to the dielectric constant with an electric field (E). The dielectric constant of the material is given by,

$$\epsilon' = \frac{Cd}{\epsilon_0 A} \quad (1)$$

where C is the capacitance of the film, A is the area of the top electrode, d is the thickness of the film, and ϵ_0 is the permittivity of free space. The measured thicknesses of our BST-0.9 and BST-0.3 films were 0.53 and 0.54 μm , respectively. The applied voltage (V) is related to the applied field (E) by the relation,

$$E = V/d \quad (2)$$

The dielectric constant of a ferroelectric material ϵ' is proportional to dP/dE , i.e., $\epsilon' \propto dP/dE$ where P is the material's polarization [16], the capacitance changes with dc-bias as the dielectric constant varies with the dc-field, resulting in ϵ' - V loop. By integrating the capacitance vs. voltage curve, the polarization (P) vs. applied field (E) curve is obtained [16]. Using Landau-Ginzburg-Devonshire theory, the electric field dependence of dielectric constant can be given in terms of zero field dielectric constant $\epsilon'(0)$, field dependent dielectric constant $\epsilon'(E)$, Devonshire thermodynamic parameter C_3 and applied field E in terms of eq. (3) as described by us in earlier papers [15,18,19]:

$$\epsilon'(E) = \frac{\epsilon'(0)}{[1+12C_3\epsilon_0^3\epsilon'(0)^3(E)^2]^{1/3}} \quad (3)$$

The parameter C_3 can be calculated from equation (3).

Effect of repeated application of switching the electric field on the parameter C_3 was investigated for both the compositions BST-0.9 and BST-0.3.

Results of Capacitance-Voltage (C-V) characteristics of the films for the compositions BST-0.9 and BST-0.3 are given in Figs. 2(a) and 2(b) respectively. Results are reported for all the samples A1, B1, A2, and B2. Polarization vs. Electric field curves obtained by integrating the C-V curves of Fig. 2 is shown in Fig. 3.

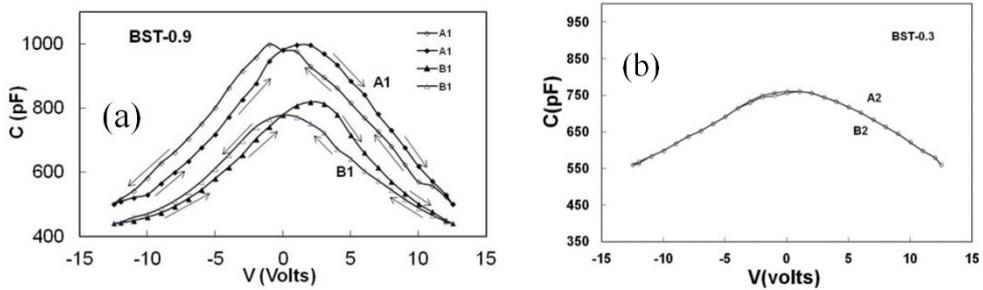


Fig. 2. Capacitance vs. applied voltage (C-V) characteristics of films of composition (a) BST-0.9 samples marked A1, B1 (b) BST-0.3 samples marked A2 and B2. Samples marked A1 and A2 are for the fresh films, and curves marked B1 and B2 refer to the films subjected to a switching electric field of 10^9 cycles (treated) for a particular composition.

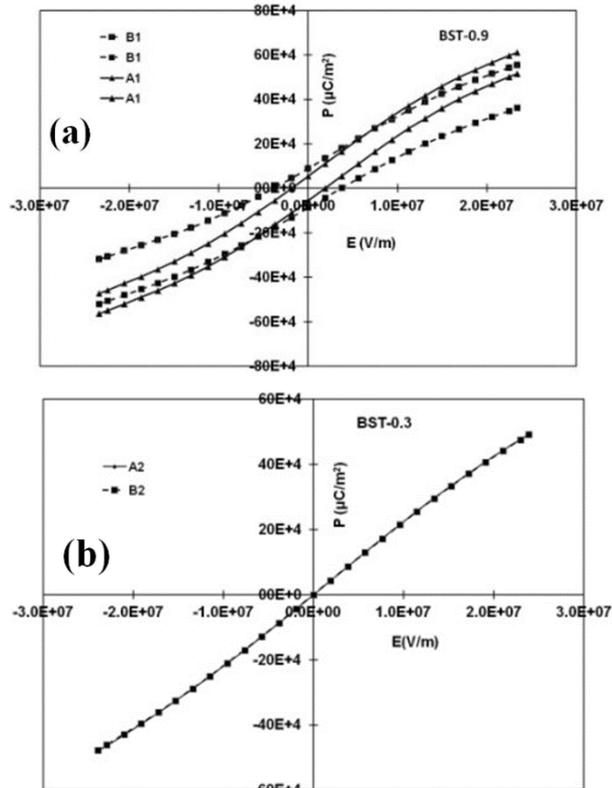


Fig. 3. Electric field curves for composition (a) BST-0.9 (b) BST-0.3 obtained by integrating the measured C-V curves of Figs. 2(a) and (b).

The C-V curves for both the compositions BST-0.9 and BST-0.3 were found to be bell-shaped (Figs. 2(a) and 2(b)). Capacitance values at both high +ve and -ve bias were appreciably smaller with respect to the peak capacitance values for both compositions. A well-defined butterfly loop was observed for the composition BST-0.9, while no butterfly loop was observed for BST-0.3, although the capacitance decreased with applied voltage. Hysteresis could also be seen from the P-E graphs for composition BST-0.9 (Fig. 3(a)). Samples A2 and B2 of composition BST-0.3 did not exhibit hysteresis (Fig. 3(b)). A comparison of curves A1 and B1 of Fig. 2(a) revealed that the treated ferroelectric films of composition BST-0.9 underwent degradation, while the treated paraelectric films of composition BST-0.3 did not exhibit any change at all (curves A2, B2 of Fig 2(b)). Next, the C-V loop of curve A1 (fresh film) was sharper than that of curve B1 (treated film) (Fig. 2(a)). We also found from curves A1 and B1 that zero bias capacitance decreased by about 18%. But, the capacitance for BST-0.3 films, fresh and treated, did not change at all, i.e., the curves A2 and B2 overlapped (Fig. 2(b)).

Sharma *et al.* [9] explained the butterfly loop observed in the C-V curve of their sol-gel deposited ferroelectric Barium Titanate (BT) films in terms of the domain reorientation process in ferroelectric material in an external field [7]. They reported that at a low field, an increase in polarization due to domain reversal was the primary contributor to the dielectric constant. The dielectric constant, or the capacitance values, at high fields were determined by the variation of the dipoles since, at these fields, most of the switchable domains were aligned parallel to the direction of the external field [9]. Further, the field within which domain reversal was active in Barium Titanate films was estimated from FWHM (Full Width at Half Maxima) of the C-V curve by Sharma *et al.* [9]. In the samples of BST-0.9 films, which exist in the ferroelectric phase at room temperature, the field values within which the domain reversal was active were found to be 31×10^6 V/m and 39×10^6 V/m for samples A1 (fresh) and B1 (treated) respectively. These values compare well with those reported by Sharma *et al.* for their BT films, 34×10^6 V/m, and 45×10^6 V/m, respectively, for their fresh and fatigued or degraded films [9]. A decrease in zero bias capacitance in sample B1 with respect to sample A1 may be attributed to a reduction in the mobility of the domain wall or to the active domain walls involved in the switching process [9,20].

Devonshire thermodynamic parameter C_3 was calculated for samples A1, B1, A2, and B2, i.e., for fresh films and for treated films, of both the compositions BST-0.9 and BST-0.3, using equation (3). Results are given in Table 1. $[\varepsilon'(0)/\varepsilon'(E)]^3$ vs E^2 curves for both the composition BST-0.9 and BST-0.3 are shown in Fig. 4(a) and 4(b).

Table 1. C_3 for compositions BST-0.9 and BST-0.3 for fresh and films subjected to repeated switching electric field.

| Composition | C_3 (for fresh film) ($\text{m}^5/\text{C}^2\text{F}$) | C_3 (for treated film) ($\text{m}^5/\text{C}^2\text{F}$) |
|-------------|---|---|
| BST-0.9 | 7.3×10^9 | 4.2×10^9 |
| BST-0.3 | 2.0×10^9 | 2.0×10^9 |

The parameter C_3 for A1 and B1 of composition BST-0.9 changes from $7.3 \times 10^9 \text{ m}^5/\text{C}^2\text{F}$ to $4.2 \times 10^9 \text{ m}^5/\text{C}^2\text{F}$; i.e., the magnitude of the thermodynamic parameter C_3 decreases with repeated application of switching electric field for the ferroelectric film (BST-0.9) although the order of magnitude remains the same. C_3 for B1 and B2 of BST-0.3 film remain the same (Table 1).

The material is assumed to be strain free in Devonshire theory. However, strains exist in materials, be it ceramics or thin films. Taking strains into account, the thermodynamic parameters can be expressed in terms of stress-polarization-related electrostrictive constants (G_{ij}) and elastic constants (c_{ij}) [21,22]. A decrease in zero-field dielectric constant with compressive strain and an increase in dielectric constant with tensile strain with respect to the dielectric constant of unstrained films were reported by us [21]. However, C_3 for samples A1 and B1 of ferroelectric BST-0.9 did not show a significant change. This indicated that additional strain induced by repeated application of switching electric field, if any, was not significant. Therefore, the strains already present in films decreased the dielectric constant from the bulk or single crystal value [22]. Since C_3 remained the same for samples A2 and B2 for the film of composition BST-0.3, one could infer that additional strains were not induced in the paraelectric phase samples subjected to repeated application of switching electric field.

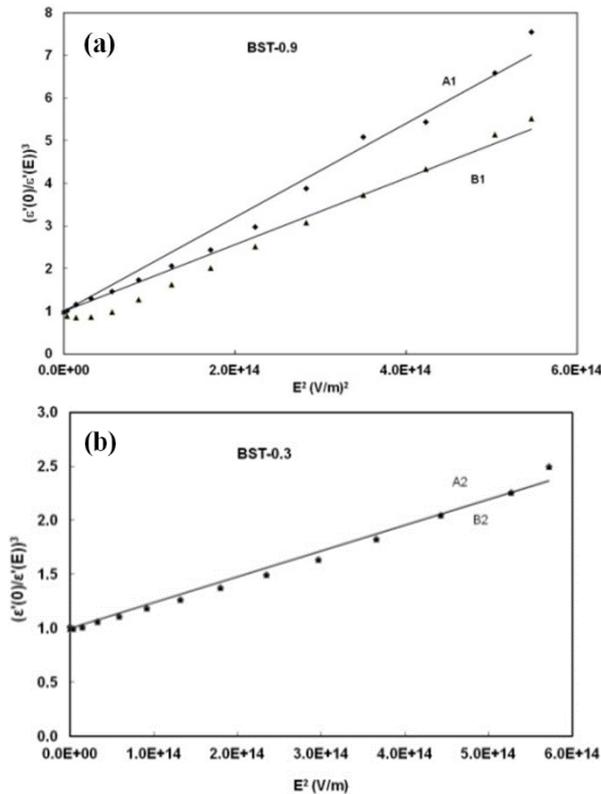


Fig. 4. $[\varepsilon'(0)/\varepsilon'(E)]^2$ vs. E^2 curves for (a) samples A1 and B1 for composition BST-0.9; (b) samples A2 and B2 for composition BST-0.3

3.2. Leakage current

The leakage current is important in determining whether ferroelectric films can be utilized for various applications. The effect of repeated application of switching the electric field on the current-voltage characteristics was also studied for these two compositions, BST-0.9 and BST-0.3. Current vs. Voltage (I-V) characteristics for the samples A1, B1 of BST-0.9 and A2, B2 of BST-0.3 are given in Figs. 5(a) and 5(b). Curves A1 and A2 refer to I-V characteristics for the fresh films, and B1 and B2 are for I-V characteristics for the treated films.

Fresh films of both the compositions, BST-0.9 and BST-0.3 (curves A1 and A2), exhibited an ohmic type behavior at low field ($<60 \text{ kV cm}^{-1}$), and the resistivities were $3.63 \times 10^9 \text{ } \Omega\text{cm}$ and $1.88 \times 10^{11} \text{ } \Omega\text{cm}$ respectively resistivity at low fields, for the composition BST-0.9, decreased to a value of $4.01 \times 10^8 \text{ } \Omega\text{cm}$ for the treated film (curve B1). The I-V characteristics for the films of composition BST-0.3, either fresh or treated, did not exhibit any difference in behavior (curves A2 and B2), i.e., they were superimposable. Breakdown fields of approximately $6.68 \times 10^5 \text{ V/cm}$ and $1.66 \times 10^5 \text{ V/cm}$ were observed for samples A1 and B1. For A2 and B2, the breakdown fields remained the same. They were approximately $5.10 \times 10^5 \text{ V/cm}$. Sharma *et al.* [9], suggested that charge point defects accumulated at the grain boundaries or on the surface of the grains could be considered to cause a lowering of resistivity and breakdown strength [9].

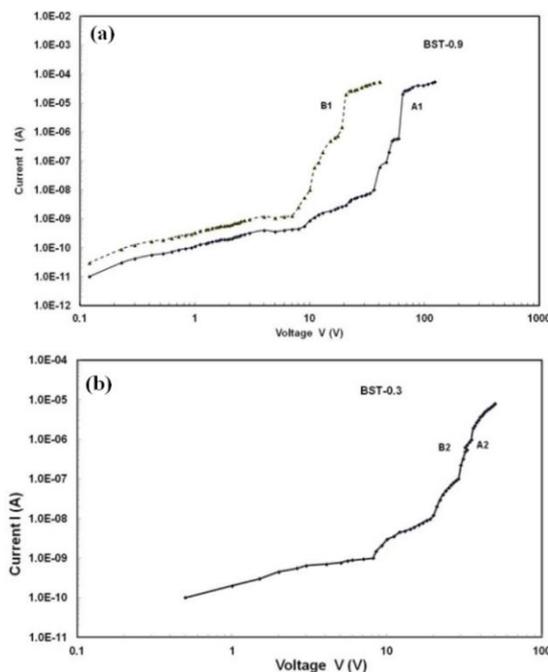


Fig. 5. Current Vs. Voltage (I-V) characteristics of the fresh and films after repeated application of switching electric field (treated films) of compositions (a) BST-0.9 (b) BST-0.3. Curves marked A1 and A2 refer to the fresh films, and curves marked B1 and B2 are for treated films for the particular composition.

Higher breakdown strengths were recently reported for modified heterostructure films with BST layers by Fan *et al.* They reported a breakdown strength of 5MV/cm for their BST-BMN ($0.88\text{Ba}_{0.55}\text{Sr}_{0.45}\text{TiO}_3\text{-}0.12\text{BiMg}_{2/3}\text{Nb}_{1/3}\text{O}_3$) films [23]. Zhang *et al.* [24] reported a breakdown strength of 1.26MV/cm for a heterostructure of $\text{SrTiO}_3/\text{LaNiO}_3/\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3/\text{SrTiO}_3$. Debnath *et al.* reported an average leakage current in the range of 100nA with a maximum memory window of 9V [25].

3.3. Comment on the degradation observed in ferroelectric BST-0.9 films subjected to switching the electric field

The degradation of the ferroelectric films has, in general, been attributed to various factors like ferroelectric fatigue, ferroelectric aging, and resistance degradation caused by the accumulation of charge point defects, pinning of domains by defect dipole moments, the role of oxygen vacancies, formation of microcracks, diffusion of electrodes, etc. [8,9,26]. All these factors appear to have some role in the degradation of the films. The exact reason for the degradation of a film of particular ferroelectric material like BST-0.9 cannot be pinpointed in this case. However, the most probable reason appears to be fatigue due to switching of polarisation rather than diffusion of the electrode, since for the same bias cycle, there is no effect in the paraelectric phase while degradation occurs in the ferroelectric phase. Fan *et al.* reported fatigue endurance of 10^7 cycles for BST-BMN($0.88\text{Ba}_{0.55}\text{Sr}_{0.45}\text{TiO}_3\text{-}0.12\text{BiMg}_{2/3}\text{Nb}_{1/3}\text{O}_3$) films [23]. Barium titanate films were reported to show fatigue at about 10^9 cycles by Sharma *et al.* [9].

4. Conclusion

The effect of repeated application of switching the electric field on the two compositions of BST, namely, BST-0.9 and BST-0.3, was studied. C-V and I-V characteristics of fresh and treated samples (subjected to a switching field of 10^9 cycles) were measured. The films of BST-0.9 and BST-0.3 subjected to a switching field of 10^9 cycles exhibited different C-V and I-V characteristics. BST-0.9 films showed degradation, while BST-0.3 did not degrade. Zero field capacitance decreased by 18 % for treated BST-0.9 films. BST-0.9 exhibited hysteresis clearly, while BST-0.3 did not show hysteresis. Using the I-V characteristics, resistivity and breakdown fields were calculated for fresh and treated films for both compositions, BST-0.9 and BST-0.3.

The properties and characteristics measured and calculated for the films of BST-0.9 and BST-0.3 would allow workers to choose a particular composition for a specific application. The hysteresis shown by BST-0.9 makes it suitable for memory applications, while BST-0.3 will be preferable for DRAM, tunable phase shifter applications. Since BST-0.3 films do not change the I-V characteristics of fresh and degraded samples, these BST-0.3 films can be a suitable candidate for photodiodes for their use as light sensors on satellite technology.

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