Pyroelectric properties of barium strontium titanate films: Effect of thermal stresses

J. Zhang,1 M. W. Cole,2 and S. P. Alpay1,a

1Department of Chemical, Materials, and Biomolecular Engineering, Materials Science and Engineering Program, University of Connecticut, Storrs, Connecticut 06269, USA
2U.S. Army Research Laboratory, Weapons and Materials Research Directorate, Aberdeen Proving Ground, Maryland 21005, USA

(Received 13 June 2010; accepted 3 July 2010; published online 7 September 2010)

A nonlinear thermodynamic model is used to investigate the influence of thermal stresses on the room temperature (RT) pyroelectric properties of (001)-textured polycrystalline barium strontium titanate (Ba$_x$Sr$_{1-x}$TiO$_3$, BST) films with four different compositions on three integrated circuit-friendly substrates: Si, (0001) and (1120) sapphire. It is found that the in-plane tensile thermal strain in BST increases with increasing deposition/processing temperature $T_D$ due to the difference of thermal expansion coefficients between the BST film and the selected substrate materials. Considering the variations in the ferroelectric phase transformation due to thermal strains, our findings show that relatively lower processing temperatures would result in better pyroelectric response. For BST 60/40 and 70/30 on all the substrates, the film is in the paraelectric state for $T_G$=25–800 °C and the pyroelectric response is due to the interplay of the electric field and thermal strain dependence of the dielectric constant and the $T_G$-dependence of the thermal strains. While the RT pyroelectric response of these films is expected to be relatively low (0.02–0.05 $\mu$C/cm$^2$ K at $\sim$200 kV/cm), at high applied fields the pyroelectric properties do not display a significant dependence on the temperature at which the material was treated. On the other hand, BST 80/20 and BST 90/10 films may be in the ferroelectric state at RT depending on $T_G$. If $T_G$ can be adjusted such that the ferroelectric phase transformation is near RT, a relatively high bulklike pyroelectric response ($>$0.5–1.0 $\mu$C/cm$^2$ K) can be realized. However, the pyroelectric coefficient decreases sharply above and below these “critical” $T_G$, and thus a precise temperature control during processing would be required. © 2010 American Institute of Physics. [doi:10.1063/1.3475482]

I. INTRODUCTION

The large pyroelectric response of ferroelectric (FE) materials can be employed in uncooled infrared (IR) devices due to their relatively low cost, low power consumption, and wide operating range of temperature compared to photoconductive detectors. Pyroelectric IR devices may be used in intruder alarms, fire detection, environmental monitoring, gas analysis, radiometers, laser detectors, and two-dimensional arrays for uncooled thermal imaging. There are essentially two modes of operation for pyroelectric IR sensors. One mode operates at a temperature below (but typically near) the Curie temperature $T_C$ of the FE where the variation in the spontaneous polarization as a function of temperature is large. In the dielectric bolometer mode, one works slightly above $T_C$ in the paraelectric (PE) state of the FE and with an applied bias field to induce polarization. In either case, it is required that the FE is deposited in a thin film form on an integrated circuit (IC) compatible substrate. However, our previous theoretical results based on a modified Landau–Ginzburg–Devonshire thermodynamics indicate that internal stresses in FE thin films could significantly deteriorate all functional properties of FE films, including its pyroelectric response. Internal stresses arise from the lattice mismatch between the film and the substrate, the difference in thermal expansion coefficients (TECs) of the film and the substrate, and the self-strain of the PE–FE phase transformation. It was found that the pyroresponse of Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ (BST 60/40) epitaxial films on Si substrate was suppressed compared to bulk BST 60/40 due to internal stresses. By taking into account internal stresses as well as the formation of misfit dislocations at the growth temperature, the effects of the film thickness and operating temperature on the pyroelectric coefficients of epitaxial (001) BST 60/40 and Pb$_{0.7}$Zr$_{0.3}$TiO$_3$ (PZT 50/50) thin films on different substrates were investigated. It was shown that the pyroelectric coefficients increased with increasing film thickness for these films on (001) LaAlO$_3$ and 0.29-LaAlO$_3$:0.35-Sr$_2$TaAlO$_6$ substrates by stress relaxation by misfit dislocations. These studies show that an optimum pyroelectric response can be realized by tuning the operating temperature and the film thickness to adjust the internal stresses. Using a similar approach, Cao et al. investigated pyroelectric and dielectric properties of epitaxial BST 70/30 thin films on anisotropic substrates. Considering the direct relation between the pyroelectric and electrocaloric coefficients, we have recently adopted our theoretical formalism to describe the giant electrocaloric properties of FE films as well.

BaTiO$_3$ is a prototypical perovskite FE material with $T_C$=120 °C. The PE–FE transition temperature can be re-

---

1Electronic mail: p.alpay@ims.uconn.edu.
duced by adding Sr$^{2+}$ which substitutes for the Ba$^{2+}$ cations in the ABO$_3$ lattice. As such, barium strontium titanate (Ba$_{1-x}$Sr$_x$TiO$_3$, BST) is an attractive material system that has received a great deal of interest in several device applications, in particular for dielectrically tunable phase shifters in telecommunications. It has also been demonstrated experimentally that high-quality BST films with good dielectric properties can be grown on Pt–Si and other IC friendly substrates. For example, Cole et al. measured a real (relative) permittivity of 348 and a dissipation factor of 0.024 in BST 90/10 thin films doped with 1 mol % Mg at 10 GHz. Pervez et al. obtained by varying the O$_2$-partial pressure. The effect of strain on dielectric properties of either epitaxial or nonepitaxial BST films on different substrates (including Pt–Si and Al$_2$O$_3$) were studied as well. Hu et al. found that Sn-doped BST thin films on LaNiO$_3$-coated Si substrate displayed a relatively low dielectric constant (less than 200 at frequency higher than 100 Hz) but had low dielectric loss (less than 1% at 100 Hz) and improved leakage current characteristics. In addition, thin films of Ba(Ti$_{1-x}$Sn$_x$)O$_3$, BST/STI bilayers, and BST films with extremely small grain size (~25 nm) on IC-friendly substrates were also investigated recently.

Based on previous experimental work and theoretical studies discussed above, it is clear that BST films are ideally suited for applications in IR detection. When industry-standard deposition techniques such as sputtering or metal-organic chemical vapor deposition, the synthesis technique. For physical vapor deposition methods such as pulsed laser deposition, $T_G$ is substrate temperature during growth. For chemical deposition techniques such as spin coating or metal-organic chemical vapor deposition, $T_G$ corresponds to the temperature at which the final annealing is carried out. Thermal stresses will develop in the film due to the differences in the TECs between the film and the substrate upon cooling from $T_G$. The in-plane strain due to the thermal stresses can be expressed as:

$$ u_T(T_G) = \frac{\alpha_F dT}{\alpha_T dT} - \frac{\alpha_T dT}{\alpha_F dT}, $$

where $\alpha_F$ and $\alpha_T$ are the in-plane TECs of the film and the substrate, respectively. The TECs of the film materials (BST 60/40, BST 70/30, BST 80/20, and BST 90/10) and the substrates [(001) Si, c-sapphire, and a-sapphire] used in our calculations are given in Tables I and II.

Assuming that the thickness of the substrate is much larger than the film thickness so that all internal stresses are concentrated in the film, for BST films on Si and c-sapphire substrates which have isotropic in-plane TECs, the free energy density of the film taking into account the in-plane thermal stresses can be expressed as:

$$ G_{iso}(P,T,u_T,E) = \bar{\alpha}_I P^2 + \bar{\alpha}_{11} P^1 + \alpha_{11} P^6 + \frac{u_T^2}{S_{11} + S_{12}}, $$

where $P$ is the polarization and $E$ is the applied (external) electric field. Both $P$ and $E$ are along the [001] direction. The modified dielectric stiffness coefficients $\bar{\alpha}_I$ and $\bar{\alpha}_{11}$ are given by:

$$ \bar{\alpha}_I = \alpha_I - u_T \frac{2Q_{12}}{S_{11} + S_{12}}, $$

$$ \bar{\alpha}_{11} = \alpha_{11}. $$

### II. THEORY

Consider a (001)-textured polycrystalline BST film deposited on a thick substrate at a growth/processing temperature $T_G$, and then cooled down to room temperature (RT = 25 °C). The way $T_G$ is defined in this analysis depends on

<table>
<thead>
<tr>
<th>Substrate</th>
<th>TEC of the substrate × 10^6 (°C⁻¹, T in °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>3.725×(1−exp[−5.88×10⁻³(T+149)])+5.548×10⁻⁴</td>
</tr>
<tr>
<td>Sapphire c-axis</td>
<td>8.026+8.17×10⁻⁴×T−3.279×exp(−2.91×10⁻³×T)</td>
</tr>
<tr>
<td>Sapphire a-axis</td>
<td>7.419+6.43×10⁻⁴×T−3.211×exp(−2.59×10⁻³×T)</td>
</tr>
</tbody>
</table>

### Table I. TECs of Si and sapphire.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>29</td>
</tr>
<tr>
<td>Sapphire c-axis</td>
<td>30</td>
</tr>
<tr>
<td>Sapphire a-axis</td>
<td>30</td>
</tr>
</tbody>
</table>
Weiss law, where the pyroelectric coefficient along the polarization.

\[ a_{11} = a_{11} + \frac{Q_{12}^2}{S_{11} + S_{12}}, \]

where \( a_{11}, a_{111}, \) and \( a_{1111} \) are the dielectric stiffness coefficients. The quadratic coefficient \( a_{1} \) is given by the Curie–Weiss law, \( a_{1} = (T - T_C)/2\varepsilon_0C \), where \( \varepsilon_0 \) is the permittivity of free space and \( C \) is the Curie–Weiss constant. \( Q_{12} \) is the electrostrictive coefficient, and \( S_{11} \) and \( S_{12} \) are the elastic compliances of the film at constant polarization. It is assumed that the thermodynamic, elastic, and electromechanical coefficients of the BST films are a linear function of composition determined by averaging corresponding values of BaTiO\(_3\) and SrTiO\(_3\) (Table III).

The condition for thermodynamic equilibrium is given by the equation of state \( \partial G_{iso}/\partial P = E \) such that:

\[ \frac{\partial G_{iso}}{\partial P} = 2a_1P + 4a_{11}P^3 + 6a_{111}P^5 = E. \]

Thus, the dielectric response along [001] is:

\[ \varepsilon_{iso} = \left( \frac{\partial^2 G_{iso}}{\partial P^2} \right)^{-1} = \frac{1}{2(a_1 + 6a_{11}P^2 + 15a_{111}P^4)}, \]

and the pyroelectric coefficient along [001] can be expressed as:

\[ P_{iso} = \frac{dP_S}{dT} + \int_0^T \left( \frac{\partial \varepsilon_{iso}}{\partial T} \right)_E dE, \]

where \( P_S \) is the spontaneous polarization along [001] corresponding to the solution of \( \partial G_{iso}/\partial P = 0 \), and \( T \) is the operating temperature of the pyroelectric. The first term in Eq. (7) is purely from the spontaneous polarization in the FE phase below \( T_C \) and the second term provides the pyroelectric contribution from the temperature variation in the induced polarization.

For a-sapphire substrate which has anisotropic in-plane TECs along its \( a \)-axis and \( c \)-axis, the in-plane stresses due to the thermal stresses along \( a \)-axis and \( c \)-axis are different. The free energy density taking into account the in-plane thermal stresses can be expressed as:

\[ G_{aniso}(P, T, u_{T1}, u_{T2}, E) = a_{33}P^2 + a_{33}P^4 + a_{111}P^6 + \frac{S_{11}(u_{T1}^2 + u_{T2}^2)}{2(S_{11}^2 - S_{12}^2)} - EP, \]

where \( u_{T1}(T_C) \) and \( u_{T2}(T_C) \) are the in-plane strains along \( a \)-axis and \( c \)-axis, respectively, and the modified dielectric stiffness coefficients \( \bar{a}_{33} \) and \( \bar{a}_{33} \) are given by:

\[ \bar{a}_{33} = a_1 - \frac{Q_{12}}{S_{11} + S_{12}}(u_{T1} + u_{T2}), \]

and

\[ \bar{a}_{33} = a_{11} + \frac{Q_{12}^2}{S_{11} + S_{12}}. \]

The equation of state is \( \partial G_{aniso}/\partial P = E \) from which the polarization and its dependence on \( u_{T1}, u_{T2}, \) and \( E \) can be determined. The dielectric and pyroelectric coefficients follow from Eqs. (6) and (7) with appropriate changes in the renormalized Landau coefficients [Eqs. (9) and (10)].

### III. RESULTS AND DISCUSSION

Figure 1 plots the in-plane tensile thermal strain as a function of \( T_C \) for BST 70/30 as an example. For this case, since (on average) the TECs of the substrates are lower than the TEC of the BST 70/30 film in the temperature range of our analysis (25 °C ≤ \( T_C ≤ 800 \) °C), the in-plane thermal strains are positive and increase with \( T_C \). For BST 70/30 on (001) Si and c-sapphire which have isotropic in-plane TECs, the thermal strains are equibiaxial. The magnitudes of the in-plane strain on Si and on c-sapphire as a function of \( T_C \) are given by the open squares and triangles in Fig. 1, respectively. For films on a-sapphire, however, the in-plane thermal strains are anisotropic; the two orthogonal components of the thermal strain are given by the open circles and open tri-

![FIG. 1. (Color online) In-plane thermal strain of BST 70/30 films at RT as a function of the growth temperature on Si and sapphire along \( a \)-axis and \( c \)-axis.](image-url)
angles in Fig. 1 as a function of $T_G$. The other three compositions (BST 60/40, BST 80/20, and BST 90/10) show similar behavior: increase in tensile in-plane thermal strains with increasing $T_G$ (not included). As large tensile strains suppress ferroelectricity and reduce all functional properties of FEs, a lower processing temperature would be needed for BST films on these particular substrates. This will be discussed in detail with respect to the pyroelectric response.

The calculated pyroelectric coefficients at RT of the four BST compositions as a function of $T_G$ and the applied electric field $E$ on the three substrates are shown in Fig. 2 (on (001) Si), Fig. 3 (on c-sapphire), and Fig. 4 (on a-sapphire) for $25 \, ^\circ C \leq T_G \leq 800 \, ^\circ C$ and $0 \leq E \leq 200 \, kV/cm$. In Figs. 2–4, plots (a), (b), (c), and (d) correspond to the RT pyroelectric response of BST 60/40, BST 70/30, BST 80/20, and BST 90/10, respectively. As the temperature decreases from $T_G$ to RT, thermal strains develop in the film due to the difference of TECs between the film and the substrate.

Table II shows that for bulk, unstressed BST 60/40 and BST 70/30 $T_C$ is below RT ($\sim -29 \, ^\circ C$ and $8 \, ^\circ C$, respectively) while for BST 80/20 and BST 90/10 $T_C$ is above RT ($45 \, ^\circ C$ and $82 \, ^\circ C$, respectively). In thin film form, $T_C$ will shift from its bulk value due to the modification of the quadratic dielectric stiffness coefficient depending on the magnitude of the thermal strain, see Eqs. (3) and (9). In the range of $T_G$ that was employed in this analysis, BST 60/40 [Figs. 2(a), 3(a), and 4(a)] and BST 70/30 [Figs. 2(b), 3(b), and 4(b)] compositions on all three substrates will be in the PE state. As such, the pyroelectric response is entirely due to the polarization induced by an applied electric field (hence $p \neq 0$ when $E=0$) giving rise to a magnitude of the order of $10^{-2} \, \mu C/cm^2 K$. As the $T_G$ increases, i.e., an increase in the in-plane tensile thermal strain, the magnitude of $p$ decreases. In certain $T_G$ ranges, $|p|$ does not vary substantially as $E$ is further increased. For instance, for BST 70/30 films on c-sapphire [Fig. 3(b)], the pyroelectric coefficient remains relatively unchanged for $300 \, ^\circ C < T_G < 500 \, ^\circ C$ when $100 \, kV/cm < E < 200 \, kV/cm$. For pyroelectric IR detectors

FIG. 2. (Color online) The RT pyroelectric coefficient of BST films with composition (a) BST 60/40, (b) BST 70/30, (c) BST 80/20, (d) BST 90/10 as a function of the growth temperature and the applied electric field on Si substrates.

FIG. 3. (Color online) The RT pyroelectric coefficient of BST films with composition (a) BST 60/40, (b) BST 70/30, (c) BST 80/20, (d) BST 90/10 as a function of the growth temperature and the applied electric field on c-sapphire substrates.
in the dielectric bolometer mode, this might be a useful attribute that can produce a pyroelectric response that is relatively insensitive to the processing temperature. It essentially provides a rather large “processing window” and would not require an extremely sensitive temperature control. However, there are two other regions, most prominently seen in Fig. 3, where there are considerable variations in $\varepsilon$. This is because of the temperature and electric field dependence of the dielectric response [see Eq. (7)]. We will discuss this in detail in connection with the data presented in Fig. 5.

For BST 80/20 thin film, $T_C$=RT if $T_G$=95 °C on Si [Fig. 2(c)], $T_G$=123 °C on c-sapphire [Fig. 3(c)], and $T_G$=130 °C on a-sapphire [Fig. 4(c)]. These processing temperatures change for the BST 90/10 films; $T_G$=208 °C on Si [Fig. 2(d)], $T_G$=278 °C on c-sapphire [Fig. 3(d)], and $T_G$=294 °C on a-sapphire [Fig. 4(d)]. When $T_G$ is lower than these critical values, $T_C$>RT, and the BST films are in the FE state at RT. Analogous to the cases discussed above for BST 60/40 and 70/30, in the PE state above $T_C$, $p$=0 when $E$=0. In the FE state, the pyroelectric response now contains contribution from the temperature dependence of $P_S$. This can be considerably larger than the temperature dependence.
of the induced polarization and increases dramatically as $T_C$ is approached. If the thermal strains are engineered in such a way that $T_C$ corresponds to RT, one can realize pyroelectric coefficients of the order of 1.0 $\mu C/cm^2 K$ or larger. For example, if a BST 90/10 film on (001) Si is processed at $T_G = 208^\circ C$, the $\lambda$-type anomaly associated with the PE–FE transition occurs at RT and such films would thus have exceptionally high pyroelectric properties. However, the downside of this is that the processing temperature (whether this is the substrate temperature at deposition or annealing temperature) has to be controlled extremely precisely (within 1 $^\circ C$).

To discuss the pyroelectric response in the PE in more detail, we present in Fig. 5(a) the induced polarization in BST 70/30 on c-sapphire as a function of $T_G$. Since the film is in PE state, there is no polarization when $E=0$. At a given $T_G$, the induced polarization increases with $E$, and at a given $E$, higher induced polarizations are possible for smaller in-plane thermal strains resulting from a lower $T_G$. This is also shown in Fig. 5(b) where polarization is plotted as a function of $E$ for $T_G=100$ $^\circ C$ and 700 $^\circ C$. Figure 5(c) displays the variation in the relative dielectric constant of BST 70/30 on c-sapphire as a function of $E$ for $T_G=100$ and 700 $^\circ C$. For $T_G=100$ $^\circ C$, the relative dielectric constant is extremely high at $E=0$ (4530) and decreases nonlinearly with $E$ to 330 at 200 kV/cm; a common property of FE s. The relatively large value of $e_r$ at $E=0$ indicates that while the material is in PE state, $T_C$ is not far off (-14 $^\circ C$) compared to the condition of $T_G=700$ $^\circ C$ for which $e_r=800$ at $E=0$ and $T_C$ is well below RT (-196 $^\circ C$). The RT pyroelectric response in the PE state [Fig. 5(d)] hence results from the complicated interplay of the electric field and thermal strain dependence of the dielectric constant and the $T_G$-dependence of the thermal strains. As such, the pyroelectric coefficient in the PE state can be rewritten as

$$p(E, u_T) = \int_0^E \left( \frac{\partial p(E, u_T)}{\partial T} \right)_E dE,$$

for the case of isotropic equibiaxial strain [$p(E, u_{T1}, u_{T2})$ for anisotropic substrates]. This leads to the behavior given in Fig. 5(d) where |$p$| decreases for $T_G=100$ $^\circ C$ when $E$ is increased but rises with $E$ for the case of $T_G=700$ $^\circ C$.

### IV. CONCLUSIONS

We used a nonlinear thermodynamic model to investigate the role of thermal stresses on the RT pyroelectric properties of (001)-textured polycrystalline BST films with four different compositions (BST 60/40, 70/30, 80/20, and 90/10) on three IC-friendly substrates: Si, (0001) sapphire, and (1120) sapphire. The main findings of this study are summarized below:

- Due to the TEC difference between the BST film compositions and the substrate materials analyzed in this study, the in-plane tensile thermal strain in BST increases with increasing deposition/processing temperature $T_G$. This leads to a depression of the FE–PE phase transformation. As such, relatively lower deposition/processing temperature would result in better pyroelectric response.
- For BST 60/40 and 70/30 on all the substrates, the film is in the PE state for $T_G=25$–800 $^\circ C$ and the pyroelectric response is due to interplay of the electric field and thermal strain dependence of the dielectric constant and the $T_G$-dependence of the thermal strains. While the RT pyroelectric response of these films is expected to be relatively low (0.02–0.05 $\mu C/cm^2 K$ at ~200 kV/cm), at high applied fields the pyroelectric response does not display a significant dependence on the temperature at which the material was treated.
- BST 80/20 and BST 90/10 films may be in the PE state at RT depending on $T_G$. If $T_G$ can be adjusted such that it coincides with the FE–PE transition temperature, a relatively high bulklike pyroelectric response (0.5–1.0 $\mu C/cm^2 K$) can be realized. Depending on the BST composition and the substrate material analyzed in this study, $T_G$ varies between 95 $^\circ C$ (BST 80/20 on Si) and 294 $^\circ C$ (BST 90/10 on a-sapphire).

### ACKNOWLEDGMENTS

The work at UConn was supported by the U.S. Army Research Office through Grant Nos. W911NF-05-1-0528 and W911NF-08-C-0124.