Tailoring dielectric properties of ferroelectric-dielectric multilayers

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We develop a nonlinear thermodynamic model for multilayer ferroelectric heterostructures that takes into account electrostatic and electromechanical interactions between layers. We concentrate on the effect of relative layer fractions and in-plane thermal stresses on dielectric properties of Ba0.6Sr0.4TiO3–, BaTiO3–, and PbZr0.2Ti0.8O3 (PZT)-SrTiO3 (STO) multilayers on Si and c-sapphire. We show that dielectric properties of such multilayers can be significantly enhanced by tailoring the growth/processing temperature and the STO layer fraction. Our computations show that large tunabilities (~90%) at 400 kV/cm are possible in carefully designed barium strontium titanate-STO and PZT-STO even on Si for which there exist substantially large in-plane strains. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4861716]

Non-linear dielectric materials have been considered as voltage-controlled frequency-able elements in tunable microwave and millimeter wave devices such as capacitors, phase shifters, resonators, and oscillators.¹ Ferroelectrics (FEs) such as barium strontium titanate (BST, Ba1−xSrxTiO3) have emerged as leading candidates for such applications due to their highly non-linear dielectric response to an applied electric field, especially in the vicinity of the paraelectric (PE)-to-FE phase transformation temperature TC.²⁻⁵ In BST, TC can be controlled via the composition. For example, bulk TC of BST 70/30 (Ba0.70Sr0.30TiO3) is just below room temperature (~15°C).² As such, FEs and, in particular, BST, have been investigated for over a decade as potential candidates in tunable components in telecommunications since the utilization of DC fields for tuning improves the response speed and the power consumption of the device.⁶,⁷ The major challenge in designing materials systems for tunable devices is the simultaneous requirement of high tunability (>40%) over a large temperature interval (~20°C to +85°C), and low dielectric losses (between 3.0 and 4.0 dB in operational bandwidths ranging from several hundred MHz over 30 GHz).⁸⁻¹⁰ It is usually desired in telecommunication applications that FEs are in a PE state to eliminate losses resulting from polarization switching-induced hysteresis, domain wall contributions, and piezoelectric transformations at microwave frequencies.¹⁰,¹¹ Nevertheless, there are reports of acceptable dielectric properties in the FE state as well.¹⁰⁻¹³

Significant efforts have been devoted to maintain high dielectric tunability and to decrease dielectric losses through doping and by constructing a variety of composite structures consisting of FE/PE active materials and low-loss and low leakage oxides and polymers.¹₁,¹₄ Among such composites, carefully designed FE/PE/dielectric multilayers, superlattices, and compositionally graded structures display improved dielectric properties than their bulk and single-crystal counterparts due to electrostatic and electromechanical interlayer interactions. Such materials systems have been shown to be promising candidates in microwave telecommunication applications.¹⁵⁻²⁰

In this letter, the dielectric properties of FE heterostructures with PE buffer layers on IC-compatible Si and c-sapphire substrates are investigated using a non-linear thermodynamic model that takes into account the thermal stresses that develop during cooling from the growth/processing temperature (TC) and the electrostatic coupling between the layers that make up the multilayer construct. We note that the rationale for this study originates from theoretical studies that reveal the existence of a dielectric anomaly in coupled FE-PE bilayers at a critical PE layer fraction resulting from electrostatic interactions that suppress ferroelectricity.¹⁶,²¹ This is considered to be analogous to the dielectric maxima observed near TC in monolithic FEs. This concept has been employed to improve dielectric tunability in microwave and millimeter wave tunable telecommunication devices.¹⁶ The use of a PE layer as a buffer layer in device configuration is also attractive because experimental results show clear improvements in leakage characteristics. For example, ~200 nm thick Mg-doped BST-SrTiO3 (STO) bilayer heterostructures on metallized c-sapphire substrates display enhanced dielectric properties with low losses (~0.02) and leakage currents (7 × 10⁻⁹ A/cm²) when compared to Mg-doped BST films without buffer layers. It was reported that decreasing the thickness of the PE layer (i.e., the layer fraction) from 41 to 19 nm leads to an improvement in the (relative) dielectric constant 𝜀R by nearly 35%.²² It has also been shown that the critical heterostructure composition/configuration corresponding to a dielectric anomaly is quite sensitive to changes in the amount of misfit and thermal stresses.²³⁻²⁵ It is, therefore, of great scientific and technological interest to investigate the effect of strains in multilayers with different multilayer-substrate configurations to tailor desired dielectric properties in detail.
The equilibrium polarizations $P_1^0$ and $P_2^0$ along $z$ in the coupled layer are provided by the equations of state $\partial G / \partial P_1 = 0$ and $\partial G / \partial P_2 = 0$ such that

$$\left[ 2\tilde{a}_1 + \frac{x(1-x)}{\epsilon_0} \right] \cdot P_1 + 4\tilde{b}_1 P_1^3 + 6c_1 P_1^5 = \frac{x(1-x)}{\epsilon_0} P_2 = 0,$$

(5)

$$\left[ 2\tilde{a}_2 + \frac{x(1-x)}{\epsilon_0} \right] \cdot P_2 + 4\tilde{b}_2 P_2^3 + 6c_2 P_2^5 = \frac{x(1-x)}{\epsilon_0} P_1 = 0.$$

(6)

The average dielectric response of the multilayer is

$$\langle \epsilon_k \rangle = \frac{1}{\epsilon_0} \frac{d\langle P \rangle}{dE} = \frac{1}{\epsilon_0} \left[ (1-x) \frac{dP_1^0}{dE} + x \frac{dP_2^0}{dE} \right].$$

(7)

where $P_1^0$ and $P_2^0$ is the average polarization.

A freestanding multilayer configuration in Fig. 1(a) is chosen as the reference state to understand the role of two-dimensional clamping and thermal stresses on the dielectric properties more clearly, see Eqs. (2)–(6). Figs. 2 and 3 plot the small signal $\epsilon_k$ of the multilayers with BTO and BST as the FE layers, respectively, on Si and c-sapphire. As shown in Fig. 2, RT $\epsilon_k$ of unconstrained (bulk) BST is over 2400, whereas the dielectric response of films with $\alpha_{STO} = 0.1$ on Si and c-sapphire for $T_G = 550$°C are 554 and 683, respectively. This is expected since thermally induced in-plane tensile strains and the interlayer coupling both decrease $T_C$ of the FE in such a multilayer configuration. Therefore, such electrical and mechanical boundary conditions are particularly detrimental for the dielectric response if the FE is already in the PE state as it is the case for BST 60/40 at RT, Fig. 2. As $T_C$ moves far below RT in the clamped, in-plane strained condition, an appreciable polarization change cannot be induced upon the application of a biasing field. This is

where $a_i$, $b_i$, and $c_i$ are the bulk dielectric stiffness coefficients. The quadratic coefficient $a_i$ is given by the Curie-Weiss Law, $a_i = (T - T_C)/2\epsilon_0 C$, where $\epsilon_0$ is the permittivity of free space and $C$ is the Curie-Weiss constant. $Q_{ij}$ and $S_{ij}$ are the electrostrictive coefficients and the elastic compliances at constant polarization of layer $i$. The dielectric stiffness and thermal expansion coefficients were obtained from the literature.27–30

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especially critical for films processed at higher $T_G$, since the dielectric maximum, corresponding to the FE-PE phase transition, is shifted to lower temperatures. This is clearly observed in Fig. 2; a lower $T_G$ results in higher $\varepsilon_R$ values on both substrates. For example, if $T_G$ could be decreased from 700 °C to 550 °C for BST on Si with $x_{STO} = 0.1$, we expect that there will be approximately 24% enhancement in $\varepsilon_R$. Fig. 2 also shows that employing STO buffer layers in configurations illustrated in Fig. 1 reduces $\varepsilon_R$ of the heterostructure with increasing $x_{STO}$ since $\varepsilon_R$ of STO is lower than BST. This decrease is non-linear, clearly highlighting the role of electrostatic coupling between BST 60/40 and STO. For the dielectric properties of BTO monolayers ($x_{STO} = 0$), the choice of the substrate and $T_G$ becomes more critical (Fig. 3). This is entirely due to the shift of the bulk $T_C$ (120 °C (Ref. 31)) to lower temperatures. As an example, changing $T_G$ from 625 °C to 475 °C for BTO on c-sapphire results in a 51 °C difference in their transition temperatures ($T_{C,625} = -46$ °C and $T_{C,475} = +5$ °C). Very high dielectric permittivity values can be obtained near the instability from BTO on c-sapphire at a critical $T_C = 475$ °C. Fig. 3 also shows that the dielectric anomaly in unconstrained but electrostatically coupled heterostructures disappears if such bilayers are on c-sapphire and Si due to the in-plane tensile thermal strains and the clamping effect of the substrate. Even at a low $T_G$ such as 400 °C, the magnitude of the thermal strains is sufficient to promote a PE state at RT in the BTO layer on both Si and c-sapphire. Therefore, BTO-STO displays similar behavior to BST 60/40-STO multilayers in that overall $\varepsilon_R$ deteriorates as with increasing $x_{STO}$ as a result of the shift of $T_C$ with respect to RT.

Fig. 4 plots RT small signal $\varepsilon_R$ of PZT 20/80-STO multilayers on Si and c-sapphire as functions of $T_G$ and the STO layer fraction. PZT was chosen as the last example in our analysis because its bulk, unconstrained $T_C$ (459 °C (Ref. 29)) is substantially higher than that of BST 60/40 and BTO. The dielectric response of PZT 20/80 as a function of $x_{STO}$ in both unconstrained and thin film configurations exhibits a similar trend for all $T_G$. When PZT is electrostatically and electromechanically coupled with STO, there is a $\lambda$-type anomaly in the dielectric response as observed in Fig. 4 where the critical $x_{STO}$ varies between 0.2 and 0.4 depending on $T_G$. The monotonic decrease in $\varepsilon_R$ as a function of $x_{STO}$ shown in Figs. 2 and 3 for BST and BTO on Si and c-sapphire is not observed for PZT 20/80 on the same substrates. This means that it is feasible to obtain a very strong dielectric response in PZT-STO heterostructures near the instability at a critical $x_{STO}$ that depends on the processing temperature $T_G$.

The influence of an applied bias along the z-direction on the small signal $\varepsilon_R$ and dielectric tunability ($\eta = (1 - \varepsilon_R, E, E, \varepsilon_R, \varepsilon_R = 0) \times 100$, at $E = 400$ kV/cm) of BTO- ($x_{STO} = 0.1$), BST 60/40- ($x_{STO} = 0.1$), and PZT 20/80-STO ($x_{STO} = 0.35$ and 0.40) multilayers on Si and c-sapphire for $T_G = 700$ °C is illustrated in Figs. 5 and 6, respectively. The justification for the selection of $x_{STO}$ follows from Figs. 2-4. High tunabilities over 60% and 90% at 400 kV/cm can be realized in BTO- ($x_{STO} = 0.1$) and PZT-STO ($x_{STO} = 0.35$ and 0.4) multilayers, respectively, at $T_G = 700$ °C, which is a typical processing temperature for perovskites.

We note that introducing STO buffer layers to improve loss and leakage characteristics of BST films decreases their $\varepsilon_R$, as it has been observed experimentally. Therefore, BST
FIG. 6. Dielectric tunability of BST 60/40 (for $x_{\text{STO}} = 0.1$), BTO (for $x_{\text{STO}} = 0.1$), and PZT 20/80 (for $x_{\text{STO}} = 0.35$ and 0.4) on Si and c-sapphire at $E = 400$ kV/cm for $T_G = 700$ °C.

or BTO multilayer configurations with thin PE buffer layers on IC compatible substrates (Fig. 1(b) or 1(c)) should be understood as a compromise between loss and leakage and dielectric permittivity and tunability. On the other hand, PZT-based FE-PE heterostructures offer an opportunity to tailor desired dielectric response near the instability by varying $x_{\text{STO}}$ at a given $T_G$. Although such an enhanced dielectric response is extremely beneficial, as in the case of the BST and BTO multilayer configurations, to be useful in practical tunable device configurations the exceptionally high dielectric response of the PZT-based heterostructure must also be accompanied by low dielectric loss, low leakage current characteristics, and high breakdown field. Nevertheless, the fact the ferroelectric instability can be tuned as a function of PE buffer layer thickness and process temperatures opens a new region of materials process parameter space to be explored and exploited for voltage-controlled frequency-agile elements in tunable microwave and millimeter wave devices.


