Domain engineering in compositionally graded ferroelectric films for enhanced dielectric response and tunability

M. B. Okatan,1 A. L. Roytburd,2 J. V. Mantese,3 and S. P. Alpay1,a)

1Materials Science and Engineering Program and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, USA
2Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA
3United Technologies Research Center, East Hartford, Connecticut 06108, USA

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Functional materials with nonlinear dielectric response are ideally suited for telecommunications applications and threat detection in beam-steering and frequency tuning devices. Developing the theory of wedge domain in graded ferroelectrics, we present herein a quantitative model of domain evolution and dielectric response of compositionally graded ferroelectric multilayers. We show that the domain structure adapts itself to the applied electric field via domain modification. As the applied field rises, the domains are swept away layer by layer resulting in a strong nonlinear field dependence of the dielectric constant and tunability of the multilayers. There is approximately a fivefold improvement in the small-signal dielectric response and threefold enhancement in the dielectric tunability at 400 kV cm−1 in compositionally graded (001) Ba0.6Sr0.4TiO3 [BST x/ (1−x)] compared to homogeneous BST layers on (001) SrTiO3 substrate. We also demonstrate that by controlling the relative thicknesses of the layers that make up the graded heterostructure, one could further enhance the dielectric response and tunability. © 2009 American Institute of Physics. [DOI: 10.1063/1.3142385]

I. INTRODUCTION

The electromagnetic spectrum utilized for wireless communication and detection is said to span more than nine orders of magnitude in frequency, ranging from less than a hundred hertz for extremely low frequency submarine antenna systems to hundreds of gigahertz for mobile communications, thus reaching into the near optical regime. The line between what has been traditionally been viewed as wireless and optical communications has been further blurred by the emergence of micro-optoelectromechanical systems, which combine the on-chip manipulation of optical signals with nonlinear dielectric and/or magnetic response such as ferroelectrics, ferromagnetics, and multiferroics have gained considerable interest in recent years.1–6

Ferroelectric and ferromagnetic domains arise in dielectric and magnetic media as a means of minimizing the energy associated with the stray (fringing) electrostatic or magnetostatic field due to the presence of a spontaneous polarization or magnetization. In monolithic perovskite ferroelectric materials, 180° domains (or electrical domains) as shown in Fig. 1(a) are formed. The opposing domains antialign head-to-tail, reducing the net polarization of the system to near zero. Structural (or elastic) domains in ferroelectrics may also form. These latter domains enable lower collective system free energy by minimizing the internal stress fields. The reversible motion of the structural domain walls is responsible for the large (extrinsic) piezoelectric response of ferroelectric materials, yielding much larger mechanical deformation than that due to ion displacements in the presence of an external electric field (intrinsic piezoelectric response).7,8

Ferroelectric domain structures and their associated mechanisms have often been studied relative to their effects as

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1Author to whom correspondence should be addressed. Electronic mail: p.alpay@ims.uconn.edu.

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device performance limiters including their switching speed, cycle life, fatigue, remnant polarization, creation of Barkhausen noise, nonlinear dielectric effects, and loss characteristics.19,20 Recently, Catalan et al.11 pointed to the importance of domain structures in the scaling of three-dimensional ferroelectric columnar architectures wherein ferroelectric capacitors technology approaches the single-domain limit both laterally and vertically. More rarely has domain engineering been exploited as a means of creating wholly unique mechanisms for enhanced performance, although examples do exist. For instance, it has been shown that the morphology of the structural domains in epitaxial Pb(Zr, Ti)O3 films can be manipulated by changing the substrate orientation resulting in enhanced piezoelectric properties.12 Furthermore, the effect of the misfit with the substrate in epitaxial ferroelectric films on the domain architecture that determines the film properties has been demonstrated by several simulations.13–16 In this paper, we explicitly show how an electrical domain structure in the form of “wedges” may be realized in compositionally graded heteroepitaxial ferroelectric multilayers. Moreover, we theoretically demonstrate that such materials will display a colossal dielectric permittivity that can be electrically tuned, thereby creating application opportunities in communications (e.g., phase variable devices) and related fields.

Ferroelectric multilayers and compositionally graded structures exhibit a wide spectrum of intriguing properties.17–27 These include an offset in the polarization-electric field hysteresis with applied periodic electric field excitation, an enhancement of spontaneous polarization, and a gigantic dielectric response. It has been experimentally shown that the dielectric properties can be tailored to create a nearly temperature independent relative dielectric permittivity by adjusting the layer thicknesses of a ferroelectric multistack.20,25 Compared to homogeneous BaTiO3 films, an enhancement of 50% in polarization was achieved in “tricolor” superlattices made up of BaTiO3, SrTiO3, and CaTiO3 layers.28 In (001) KTaO3/KNbO3 superlattices on (001) KTaO3 substrate, the paraelectric to ferroelectric phase transformation temperature was varied from 475 to 825 K via adjusting the superlattice periodicity.29 The polarization of superlattices of relaxor ferroelectrics 0.2Pb(Zn1/3Nb2/3)O3 −0.8BaTiO3 and Pb(Mg1/3Nb2/3)O3 exhibits a functional coupling between layers, which is thought to be related to the structural coupling in KTaO3/KNbO3 superlattices.30

There exists a depolarizing field due to the polarization mismatch at the interlayer interface(s) in ferroelectric bilayers and multilayer heterostructures. While a monodomain ferroelectric state in each layer of a ferroelectric-ferroelectric or a ferroelectric-dielectric bilayer can be maintained if the relative thickness of the “softer” ferroelectric or dielectric layers is less than a certain critical thickness,31,32 a polydomain state consisting of electrical domains may occur as well. Indeed, thermodynamic analysis has shown that the electrostatic energy of the depolarizing field in ferroelectric multilayers is minimized as a result of the formation of special type domains called wedge domains.33 The theory of wedge domains has shown that upon the application of an external electric field, the polarization of graded multilayers should proceed by movement of wedgelike domains as a result of the progressive transformation of polydomain layers to a single-domain state. This theory explains the principal properties of graded ferroelectrics: offset of the polarization and strong field dependence of the dielectric permittivity. However, the analytical solution presented by Roytburd and Slutsker33 is based on a quadratic approximation of Landau–Devonshire potential and, therefore, does not allow one to obtain a quantitative description of dielectric properties of graded multilayers. Building upon these findings, in this study we develop the domain wedge theory to obtain a quantitative model of domain evolution and polarization in compositionally graded ferroelectric multilayers. The computational model described herein may use any Landau–Devonshire potential and is thus capable of calculating the dielectric properties of any real ferroelectric multilayer system for which this potential and its coefficients have been determined. As an example, we consider a heteroepitaxial barium strontium titanate compositionally graded multilayer on a SrTiO3 substrate and demonstrate that highly tunable dielectric devices may be realized by carefully engineering the domain structure in multilayer ferroelectrics.

II. THEORY

In this analysis, we consider an n-layered compositionally graded (001) heteroepitaxial ferroelectric multilayer with wedge-shaped electrical domains on a (001) cubic substrate as shown schematically in Fig. 1(b). The free energy density of this heterostructure can be expressed through

\[ F_{\Sigma} = \sum_{i=1}^{n} \alpha_i (\Phi_i - E^{ext} P_i) - \frac{1}{2} \sum_{i=1}^{n} \alpha_i E_{D,i} P_i, \]  \tag{1}

where \( \alpha_i \) is the volume fraction of layer \( i \) and

\[ \Phi_i = \Phi_{0,i} + \frac{1}{2} a'_i p_i^2 + \frac{1}{4} b'_i p_i^4 + \frac{1}{6} c_i p_i^6 + \frac{x_i^2}{s_{11,i} + s_{12,i}} \]  \tag{2}

is the Landau expansion of the free energy of the \( i \)th layer with the polarization \( p_i \) as the order parameter. Here, we employ renormalized coefficients \( a'_i \) and \( b'_i \) to take into account the epitaxial strain and the two-dimensional clamping of the substrate34 such that,

\[ a'_i = a_i - x_i \frac{4Q_{12,i}}{s_{11,i} + s_{12,i}}, \]  \tag{3}

\[ b'_i = b_i + \frac{4Q_{12,i}^2}{s_{11,i} + s_{12,i}} \]  \tag{4}

where \( a_i, b_i, \) and \( c_i \) are the unconstrained bulk dielectric stiffness coefficients of layer \( i \). The temperature dependence of the \( a_i \) is given by the Curie–Weiss law such that \( a_i = (T - T_{C,i}) / \varepsilon_0 C_i \) where \( \varepsilon_0 \) is the permittivity of free space, and \( T_{C,i} \) and \( C_i \) are the Curie temperature and constant of layer \( i \), respectively. In Eqs. (2)–(4), \( x_i = (\xi_i - \xi_s) / \xi_s \) is the pseudocubic polarization-free misfit (epitaxial) strain34 in layer \( i \) and \( \xi_s \) and \( \xi_i \) are the lattice constants of the substrate and layer \( i \) in its cubic paraelectric state, respectively. \( Q_{mn,i} \) and \( s_{mn,i} \) are the electrostrictive coefficients and elastic com-
pliances of layer $i$, respectively. $\Phi_{0,i}$ in Eq. (2) is the free energy density of the polarization-free high temperature paraelectric phase.

We note that $p_i$ is the micropolarization in $i$th layer corresponding to the polarization of an individual domain in layer $i$. The spontaneous micropolarization $p_{oi}$ of a domain is given by the equation of state $d\Phi_i/dp_i=0$. Taking into account the formation of the domain pattern shown in Fig. 1(b), the electrostatic equilibrium between layers should be defined through $P_i$ corresponding to the overall (or macro) polarization of each layer rather than just the polarization in each domain defined via the Landau expansion given in Eq. (2). Hence, $P_i$ entering Eq. (1) is given by $P_i=(1-2\beta_p)p_i$, where $\beta_p$ is the domain fraction of $i$th layer. Using this notation, the second term of Eq. (1) is the electrostatic energy due to an externally applied electric field $E^{\text{ext}}$ and the last term is the energy of the depolarizing field in layer $i$ ($E_{D,i}$). This internal field follows from the short-circuit boundary conditions, i.e., the potential drop along the multilayer must vanish along with the necessity of continuity of the electric displacement field at the interfaces. These result in

$$
\sum_{i=1}^{n} \epsilon_i E_{D,i} = 0, \tag{5}
$$

$$(P_iP_{i+1}) + e_0(E_{D,i} - E_{D,i+1}) = 0 \quad i = 1, 2, \ldots, (n - 1), \tag{6}
$$

where $\epsilon_i$ is the thickness of layer $i$. The above set of relations yield the depolarizing field in each layer as

$$
E_{D,i} = -\frac{1}{e_0} \left( P_i - \sum_{j=1}^{n} a_j p_j \right), \tag{7}
$$

where $a_i = \epsilon_i/\sum_{k<i} \epsilon_k$.

Inserting Eqs. (2) and (7) into Eq. (1) and then making the substitution $P_i=(1-2\beta_p)p_i$, the equilibrium state of heterostructure is found by minimizing the total free energy with respect to $p_i$ and $\beta_i$, which yield

$$
\frac{\partial F_s}{\partial p_i} = 0; \quad \frac{\partial \Phi_i}{\partial p_i} = (1 - 2\beta_p) \left[ E^{\text{ext}} - \frac{1}{e_0} (P_i - \bar{P}) \right], \tag{8}
$$

$$
\frac{\partial F_s}{\partial \beta_i} = 0; \quad E^{\text{ext}} = \frac{1}{e_0} (P_i - \bar{P}), \tag{9}
$$

where $\bar{P} = \sum_{j=1}^{n} a_j p_j$ is the average polarization.

It is easy to see that in layers where there are electrical domains, there is no electric field. Thus, for the layer(s) of a graded heterostructure in a monodomain state, $E^{\text{ext}}$ is confined to that particular layer(s). The equilibrium state of polarization in a monodomain layer is obviously given just by Eq. (8). For $E^{\text{ext}} = 0$, Eqs. (8) and (9) have solutions corresponding to cases (i) $p_i = p_{oi}$ and the trivial solution $\beta_i = 1/2$, thus no macropolarization in $i$th layer, and (ii) $p_i = p_{oi}$ and $P_i = P_{i+1} = \ldots = P_n$. For $E^{\text{ext}} \neq 0$, Eqs. (8) and (9) have solutions $p_i = p_{oi}$ and $E^{\text{ext}} -(P_i - \bar{P})/e_0 = 0$.

Concentrating on the nontrivial solution, we consider a case where there are $s$ single domain layers. Rearranging Eq. (8), one can find for $i = s+1, \ldots, n$ (polydomain layers),

$$
\beta_i = \frac{1}{2} \left[ 1 - \frac{1}{(1 - \alpha_i)p_{oi}} \left( e_0 E^{\text{ext}} + \sum_{j=1}^{s} a_j p_j ight) + \sum_{j=1}^{n} a_j (1 - 2\beta_p)p_{oj} \right]. \tag{10}
$$

Solution of the system of equations given above yields

$$
\beta_i = \frac{1}{2 \left( \sum_{j=1}^{s} a_j \right)} \left( e_0 E^{\text{ext}} + \sum_{j=1}^{s} a_j p_j \right), \tag{11}
$$

$$
i = s+1, \ldots, n. \tag{11}
$$

The details of the methodology are given in the Appendix. Upon increasing $E^{\text{ext}}$, the polydomain ($s+1$)th layer transforms to a single-domain state with $\beta_{s+1}=0$ at an electric field $E^{\text{ps}}_{s+1}$ that can be determined from Eq. (11) as

$$
E^{\text{ext}} = E^{\text{ps}}_{s+1} = \frac{1}{e_0} \left( \sum_{j=1}^{s} a_j (p_{0(j+1)} - p_j) \right). \tag{12}
$$

Therefore, the electric displacement, $D$, of the graded heterostructure given as

$$
D = \bar{P} + e_0 E^{\text{ext}} = \sum_{i=1}^{n} a_i p_i + \sum_{i=s+1}^{n} a_i (1 - 2\beta_p)p_{oi} + e_0 E^{\text{ext}},
$$

and can be rewritten using of Eq. (11) within the range $E^{\text{ps}}_{s} \leq E^{\text{ext}} < E^{\text{ps}}_{s+1}$ as

$$
D = \frac{1}{\sum_{j=1}^{s} a_j} \left( e_0 E^{\text{ext}} + \sum_{j=1}^{s} a_j p_j \right). \tag{13}
$$

The state of the polarization, i.e., micropolarization $p_{ii}$ in single-domain, $\beta_i = 0$ and thus $P_i = p_i$, layers are determined by solving system of equations given in Eq. (8) for $i = 1, 2, \ldots, s$,

$$
\frac{d\Phi_i}{dp_i} = E^{\text{ext}} - \frac{1}{e_0} (p_i - \bar{P})
$$

$$
= -\frac{p_i}{e_0} + \frac{1}{e_0 \sum_{j=1}^{s} a_j} \left( e_0 E^{\text{ext}} + \sum_{j=1}^{s} a_j p_j \right). \tag{14}
$$

The equilibrium value of polarization, i.e., micropolarization $p_{ii}$ in polydomain layers for $i = s+1, \ldots, n$ are determined from

$$
\frac{d\Phi_i}{dp_i} = 0 \Rightarrow p_i = p_{oi}. \tag{15}
$$

Inserting Eq. (12) into Eq. (14), it can be found that at an electric field strength of $E^{\text{ps}}_{s+1}$, the critical micropolarization, $p_{c}^{i}$, prevailing in the single-domain $i$th layer is given by the solution of equations for $i = 1, 2, \ldots, s$. 


For the initial analysis, we assume that the equations given above is found as

\[ T_c (°C) \]
\[ 120 \]
\[ -253 \]
\[ \begin{array}{ll}
C (°C) & 1.7 \times 10^5 \\
& 8 \times 10^4 \\
b (N m^4/C^4) & 1.44 \times (175) \times 10^7 \\
& 8.4 \times 10^9 \\
c (N m^3/C^2) & 3.96 \times 10^{10} \\
\end{array} \]
\[ \begin{array}{ll}
\alpha_1 (m^2/C^2) & -0.045 \\
& -0.013 \\
c_{11} (N/m^2) & 1.76 \times 10^{11} \\
& 3.18 \times 10^{11} \\
c_{12} (N/m^2) & 8.46 \times 10^{10} \\
& 1.025 \times 10^{11} \\
\xi (Å) & 4.001 \\
& 3.905 \\
\end{array} \]

\[ \frac{d\Phi_i}{dp_j} = -\frac{p_i}{e_0} \frac{p_{0(i+1)}}{e_0} \Rightarrow p_i = p_j^c. \]  

(16)

Therefore the upper bound, i.e., \( E^{ext} = E^{ps}_{s+1} \), of validity of equations given above is found as

\[ E^{ext} = E^{ps}_{s+1} = \frac{1}{e_0} \sum_{i=0}^{s} \alpha_i (p_{0(i+1)} - p_j^c). \]  

(17)

The relative dielectric permittivity of the graded heterostructure is then determined from the relation

\[ e_r = \frac{1}{e_0} \frac{dD}{dE^{ext}}, \]  

(18)

and the dielectric tunability of the graded heterostructure is defined as

\[ \% \eta = \left( e_r @ E^{ext} = 0 \right) / \left( e_r @ E^{ext} = 0 \right) \times 100. \]  

(19)

### III. RESULTS AND DISCUSSION

We considered in our simulations several five-layered heteroepitaxial multilayer thin film structures with various compositional gradients. The ferroelectric materials system was chosen to be barium strontium titanate, \( Ba_xSr_{1-x}TiO_3 \) \( [BST \_x/(1-x)] \). BST solid solutions have received significant interest for applications in tunable devices since the relative dielectric permittivity and its tunability are very high in the vicinity of the paraelectric-to-ferroelectric phase transformation temperature \( T_C \), which can be controlled via the composition (e.g., the bulk \( T_C \) of BST 70/30 is around room temperature). For the initial analysis, we assume that the thicknesses of the individual layers that make up multilayer heterostructures are the same. Furthermore, to understand the role of the compositional variations we have chosen to maintain the same compositional gradient in the multilayer construct but changed the composition of the very first layer and maintained a constant compositional increment from layer to layer. As an example, the abbreviation BST 60/40–80/20 stands for a multilayered film consisting of five layers with compositions BST 60/40, BST 65/35, BST 70/30, BST 75/25, and BST 80/20. The thermodynamic parameters of the BST layers were assumed to vary linearly as a function of the composition between those values of bulk BaTiO_3 and bulk SrTiO_3 tabulated in Table I. SrTiO_3 was selected as the substrate material as it induces compressive in-plane epitaxial strains and thus stabilizes the ferroelectric phase in all the BST layers.

To initiate the computations, first the spontaneous micropolarization \( p_{0i} \) of each layer is calculated at \( E^{ext} = 0 \) as mentioned above, see condition (ii), from \( d\Phi / dp_j = 0 \). Then for \( s \neq 1 \), the critical micropolarization, \( p^c_j \), is calculated from Eq. (16). The next step is finding the upper bound of externally applied electric field \( E^{ext} = E^{ps}_{s+1} \) from Eq. (17). After that one can find the micropolarization \( p_j \) from Eq. (14) at certain values of \( E^{ext} \) such as starting from 0 kV cm\(^{-1}\) in increments of 1 kV cm\(^{-1}\) used in this study. Following this, micropolarization \( p_j \) values are inserted into Eq. (13) to give the value of electric displacement \( D \) at \( E^{ext} \) of interest. This way of calculation is continued until \( E^{ps}_{s+1} \) is reached but not at \( E^{ps}_{s+1} \). When \( E^{ps}_{s+1} \) is reached \( s \) attains the value 2 and computations are carried out to \( E^{ps}_{s+1} \) as described above. The corresponding values of the relative dielectric permittivity and the dielectric tunability are calculated from Eqs. (18) and (19), respectively.

The electric displacement, \( D \), relative dielectric permittivity, \( e_r \), and the percent tunability, \( \% \eta \), of four different graded heteroepitaxial multilayers are plotted in Figs. 2(b)–2(d), respectively, as a function of the external electric field. The schematic representation in Fig. 2(a) shows the variation in the equilibrium domain configuration of the multilayers with increasing \( E^{ext} \). For comparison purposes, we also present the variation in the corresponding electric displacement, relative dielectric permittivity, and tunability of monolithic epitaxial monolayer films with different BST compositions in Figs. 2(e)–2(g).

The domain structure shown in Fig. 1(b) and in Fig. 2(a) corresponds to a minimum free energy that relaxes the internal electric field due to the polarization gradient. This equilibrium structure indicates that the heterostructure is self-poled, i.e., it consists of a single-domain starting layer, which is the “softest” ferroelectric composition followed by poly-domain layers with “harder” ferroelectric compositions. At first, when \( E^{ext} = 0 \), all layers possess a finite micropolarization due to the compressive epitaxial misfit strain induced by the substrate, although the stable state of most of the layers (BST 60/40, BST 65/35, and BST 70/30) is paraelectric in bulk form at room temperature. Upon the application of the external electric field \( E^{ext} \) along the positive \( z \)-direction as defined in Fig. 1, the electric displacement of multilayers as shown in Fig. 2(b) exhibits a strong nonlinear response with “kinks” at certain values of the applied electric field corresponding to \( E^{ps}_{s+1} \). The domain structure in the multilayer ferroelectric adjusts itself to the increase in the applied electric field by varying the domain period such that the ratio of the up-oriented \( \text{positive} z \)-direction in Fig. 1(b)) to down-oriented \( \text{negative} z \)-direction) domains increases in all layers. This process proceeds until a critical field is reached at which the polydomain pattern completely disappears in the second layer. It is this value of the applied electric field at which there is a kink in the dielectric displacement; a resulting domino effect that continues until all the domains oriented in the negative \( z \)-direction in Fig. 1(b) are swept away layer by layer in succession with increasing \( E^{ext} \). The transi-
FIG. 2. (Color online) (a) The schematic drawing shows the variations in the wedge domain morphology as a function of the applied field. Theoretical (b) electric displacement, (c) dielectric permittivity, and (d) electric tunability as a function of the applied electric field and the “strength” of the compositional grading of a thin five-layer (001) heteroepitaxial BST on (001) SrTiO$_3$ substrate. For comparison purposes, theoretical (e) electric displacement, (f) dielectric permittivity, and (g) electric tunability as a function of the applied electric field for a variety of monolithic epitaxial (001) BST films on (001) SrTiO$_3$ substrate are also included.
tion from a polydomain state to a monodomain state in a layer results in a commensurate variation both in the relative dielectric permittivity [Fig. 2(c)] and in its tunability [Fig. 2(d)] as a function of the applied electric field; the discontinuities correspond to the disappearance of polydomain structures with increasing $E^\text{ext}$.

There are dramatic enhancements in both the relative dielectric permittivity and in the tunability of compositionally graded ferroelectric layers over monolithic epitaxial monolayers. These enhancements are obvious when one compares Figs. 2(e) and 2(d) with Figs. 2(f) and 2(g). At low electric field strengths, the heteroepitaxial multilayers display a much higher dielectric response compared to epitaxial monolayer thin films [Fig. 2(e)] due to the fact that in multilayered films the applied electric field is confined only to the portion of the multilayer that is in a single-domain state. This internally amplifies the applied electric field and hence permittivity; for example, at $E^\text{ext}=0$ kV cm$^{-1}$, the relative dielectric permittivity of polarization graded BST 60/40–80/20 heterostructure is 475, five times more than that of a homogeneous epitaxial BST 60/40 layer having a permittivity of 95. As more and more polydomain layers progressively collapse into a single-domain state, the thickness of the region confining the electric field increases so that the effective electric field strength within the heteroepitaxial multilayered film decreases gradually toward the value of the externally applied electric field $E^\text{ext}$. Therefore, the enhancement in the dielectric response is maximum at very small external fields and decreases nonlinearly with increasing $E^\text{ext}$.

It is clear that the reason for the large nonlinearity in the dielectric response in the case of a graded ferroelectric multilayer is extrinsic in nature as it is controlled by the domain structure that adapts itself to the external stimulus. It is also apparent from Fig. 2 that this extrinsic response is much larger than the intrinsic nonlinearity caused by relative ionic displacements as is the case for the single-domain compositionally homogeneous epitaxial BST. Therefore, all the heteroepitaxial multilayered thin films analyzed here exhibit a large improvement in the dielectric tunability compared to monolayer monolithic BST films. For instance, at an external field of $E^\text{ext}=400$ kV cm$^{-1}$, multilayered heterostructures attain a tunability as high as 85%, at least three times higher than the tunability of epitaxial compositionally homogeneous BST [between 16%–28% depending on the BST composition, see Fig. 2(f)].

As the first layer is in a single-domain state, it is possible to adjust the small-signal dielectric permittivity of the entire heterostructure by varying the relative layer thickness $\alpha_1$ of the first layer as small electric fields will be confined to this layer with no electrical domains. To better understand this, we have also investigated the variation of the dielectric properties of a heteroepitaxial multilayer BST 60/40–80/20 as a function of the volume fraction of the layer with the softest ferroelectric composition BST 60/40 ($\alpha_1$). The volume fractions (or the relative thicknesses) of the remaining four layers were taken as equal to each other. At a constant value of $E^\text{ext}$, the electric displacement of BST 60/40–80/20 multilayer increases with decreasing $\alpha_1$ (Fig. 3). In addition, it is clearly seen that the electric field required for maintain-
to 85%) can be realized in graded ferroelectrics with $\alpha_1$ values less than 0.2 even at electric field strengths as low as 14 kV cm$^{-1}$.

We note that it is possible that the energy barrier preventing the transition of an individual layer from a monodomain to the polydomain state results in partial hysteresis loops. These loops describe the field dependence of the polarization at a fixed boundary between polydomain and single-domain part of the crystal.33 This barrier can be negligible if the electrical and mechanical discontinuity between layers is small. In this case, easy penetration of wedge domains from one layer to another resulting in a fast nucleation process and the high mobility of domain walls.

IV. CONCLUSIONS

In this study, we presented a quantitative computational analysis based on the theory of wedge domains in compositionally graded ferroelectric multilayers. Wedge domains form in ferroelectric multilayers to minimize the internal electrostatic field energy that arises from the polarization mismatch between the layers. A nonlinear thermodynamic model was formulated that takes into account electrostatic and electromechanical interactions in heteroepitaxial ferroelectric multilayers with a compositional gradient. The results show that the dielectric response and its tunability can be significantly enhanced in multilayered ferroelectric thin films via engineering the domain structure. The numerical analysis provides the necessary theoretical tools to guide experimental studies in order to obtain large dielectric response and tunability. These findings also describe how domain engineering may be exploited to create a different class of electromagnetic conditioning devices. It should also be noted that much of the above analysis is not only germane to compositionally graded ferroelectrics, but may extend to the entire class of graded ferroics; thus ushering in an emerging area of device design and classification that has not been fully explored nor exploited in the past.

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APPENDIX: CALCULATION OF THE DEPOLARIZING ELECTRIC FIELD AND DOMAIN FRACTIONS

The solution given in Eq. (7) for the depolarizing field in terms of the macro-polarization follows from Eqs. (5) and (6). The details of this derivation are provided in Ref. 44.

The system of equations given by Eq. (10) can be written in terms of macro-polarizations as:

$$(1 - \alpha_i) P_i - \sum_{j=i+1}^{n} \alpha_j P_j = \epsilon_0 E_{\text{amt}}^{\text{exi}} + \sum_{j=1}^{i} \alpha_j P_j ,$$

where $i = s + 1, \ldots, n$.

Writing in matrix notation, Eq. (A1) is given as:
Arranging for Okatan et al. can be rewritten after a simple Gaussian elimination as:

\[
\begin{bmatrix}
1 - \alpha_{s+1} & - \alpha_{s+2} & - \alpha_{s+3} & - \alpha_{s+4} & \cdots & - \alpha_{n-1} & - \alpha_n \\
- \alpha_{s+1} (1 - \alpha_{s+2}) & - \alpha_{s+3} & - \alpha_{s+4} & \cdots & - \alpha_{n-1} & - \alpha_n \\
- \alpha_{s+1} & - \alpha_{s+2} (1 - \alpha_{s+3}) & - \alpha_{s+4} & \cdots & - \alpha_{n-1} & - \alpha_n \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
- \alpha_{s+1} & - \alpha_{s+2} & - \alpha_{s+3} & - \alpha_{s+4} & \cdots & - \alpha_{n-1} & - \alpha_n \\
- \alpha_{s+1} & - \alpha_{s+2} & - \alpha_{s+3} & - \alpha_{s+4} & \cdots & (1 - \alpha_{n-1}) & - \alpha_n \\
- \alpha_{s+1} & - \alpha_{s+2} & - \alpha_{s+3} & - \alpha_{s+4} & \cdots & - \alpha_{n-1} & (1 - \alpha_n)
\end{bmatrix}
\begin{bmatrix}
P_{s+1} \\
P_{s+2} \\
P_{s+3} \\
\vdots \\
P_{n-2} \\
P_{n-1} \\
P_n
\end{bmatrix}
= \begin{bmatrix}
\Gamma \\
\Gamma \\
\Gamma \\
\vdots \\
\Gamma \\
\Gamma \\
\Gamma
\end{bmatrix}.
\] (A2)

The augmented matrix of Eq. (A2),

\[
\begin{bmatrix}
1 -1 0 0 \cdots 0 0 0 \\
0 1 -1 0 \cdots 0 0 0 \\
0 0 1 -1 \cdots 0 0 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 0 0 0 \cdots -1 0 0 \\
0 0 0 0 \cdots 1 -1 0 \\
0 0 0 0 \cdots 0 \left(1 - \sum_{j=s+1}^{n} \alpha_j\right) 1
\end{bmatrix}
\begin{bmatrix}
P_{s+1} \\
P_{s+2} \\
P_{s+3} \\
\vdots \\
P_{n-2} \\
P_{n-1} \\
P_n
\end{bmatrix}
= \begin{bmatrix}
\Gamma \\
\Gamma \\
\Gamma \\
\vdots \\
\Gamma \\
\Gamma \\
\Gamma
\end{bmatrix}.
\] (A3)

can be rewritten after a simple Gaussian elimination:

\[
\begin{bmatrix}
1 & -1 & 0 & 0 & \cdots & 0 & 0 & 0 \\
0 & 1 & -1 & 0 & \cdots & 0 & 0 & 0 \\
0 & 0 & 1 & -1 & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & \cdots & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & \cdots & 1 & -1 & 0 \\
0 & 0 & 0 & 0 & \cdots & 0 & \left(1 - \sum_{j=s+1}^{n} \alpha_j\right) 1
\end{bmatrix}
\begin{bmatrix}
P_{s+1} \\
P_{s+2} \\
P_{s+3} \\
\vdots \\
P_{n-2} \\
P_{n-1} \\
P_n
\end{bmatrix}
= \begin{bmatrix}
\Gamma \\
\Gamma \\
\Gamma \\
\vdots \\
\Gamma \\
\Gamma \\
\Gamma
\end{bmatrix}.
\] (A4)

or

\[
\begin{bmatrix}
1 & -1 & 0 & 0 & \cdots & 0 & 0 & 0 \\
0 & 1 & -1 & 0 & \cdots & 0 & 0 & 0 \\
0 & 0 & 1 & -1 & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & \cdots & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & \cdots & 1 & -1 & 0 \\
0 & 0 & 0 & 0 & \cdots & 0 & \left(1 - \sum_{j=s+1}^{n} \alpha_j\right) 1
\end{bmatrix}
\begin{bmatrix}
P_{s+1} \\
P_{s+2} \\
P_{s+3} \\
\vdots \\
P_{n-2} \\
P_{n-1} \\
P_n
\end{bmatrix}
= \begin{bmatrix}
\Gamma \\
\Gamma \\
\Gamma \\
\vdots \\
\Gamma \\
\Gamma \\
\Gamma
\end{bmatrix}.
\] (A5)

Now solving for \( P_n \), one finds

\[
\left(1 - \sum_{j=s+1}^{n} \alpha_j\right) P_n = \Gamma,
\] (A6)

\[
P_n = \frac{\Gamma}{\left(1 - \sum_{j=s+1}^{n} \alpha_j\right)} = \frac{1}{\left(\sum_{j=1}^{s} \alpha_j\right)} \left(e^{E_{\text{ext}}^s} + \sum_{j=1}^{s} \alpha_j p_j\right) = (1 - 2\beta_n) p_{0n}.
\] (A7)

Arranging for \( \beta_n \) yields

\[
\beta_n = \frac{1}{2} \cdot \frac{1}{2} \left(\sum_{j=1}^{s} \alpha_j\right) p_{0n} \left(e^{E_{\text{ext}}^s} + \sum_{j=1}^{s} \alpha_j p_j\right).
\] (A8)

Considering the fact that in the polydomain layers macro-polarization is same, i.e., \( P_{s+1} = P_{s+2} = \ldots = P_n \), one finds

\[
\beta_i = \frac{1}{2} \cdot \frac{1}{2} \left(\sum_{j=1}^{s} \alpha_j\right) p_{0i} \left(e^{E_{\text{ext}}^s} + \sum_{j=1}^{s} \alpha_j p_j\right),
\] (A9)

\[i = s + 1, \ldots, n.
\]