

High dielectric tunability in ferroelectric-paraelectric bilayers and multilayer superlattices

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The dielectric tunability of ferroelectric/paraelectric bilayers and multilayer superlattices are examined theoretically. A numerical analysis is carried out for a pseudomorphic (001) BaTiO₃/SrTiO₃ heteroepitaxial bilayer on (001) SrTiO₃ and a stress-free BaTiO₃/SrTiO₃ bilayer. We show that these structures are capable of tunabilities greater than 90% due to electrostatic and electromechanical coupling between layers. Moreover, we develop the methodology for incorporation conventional integrated circuit silicon dielectrics into heteroepitaxial structures that can reduce current leakage while maintaining high tunability, thereby enabling the device designer flexibility toward the optimization of microwave and millimeter wave elements. © 2006 American Institute of Physics. [DOI: 10.1063/1.2189909]

It has been more than 40 years since ferroelectric (FE) materials were recognized for their potential as high tunability microwave and millimeter wave devices.¹ Since that time, various FE material systems and processing techniques have been employed to simultaneously produce high tunability and low loss structures, crucial properties necessary for microwave and millimeter wave applications. During the last decade, a plethora of deposition techniques have been enlisted toward making the optimum FE materials, including: sol-gel processing, rf-sputtering, pulsed laser deposition, and metalorganic chemical vapor deposition. Ferroelectric ceramics materials have been grown as homogeneous and graded thin films, multilayers, and superlattices with exceptionally good compositional control on various substrates with film thicknesses ranging from a few nanometers up to the micrometer scale. Advances in deposition and patterning techniques have further enabled the formation of miniaturized components and enabled their integration with micro-electronic circuits.

FE multilayers and superlattices show many unique properties and phenomena, such as enhanced remnant polarization, giant dielectric response, and variations in phase transformation characteristics.^{2–12} Recently, Kim *et al.* reported 94% tunability from 100 nm thick BaTiO₃ (BT)-SrTiO₃ (ST) superlattice with a stacking periodicity of 2 unit cells at a potential of 5 V.¹³ This is by far larger than the highest reported tunability of 74% observed in Ba_xSr_{1-x}TiO₃ (BST) thin films.¹⁴ Although it was speculated that the origin of this large tunability could be due to the internal stresses resulting in a lattice distortion,¹⁵ the reasons for this enhancement remains unconfirmed.

In a series of publications,^{16,17} we have developed a thermodynamic model to understand the interlayer coupling in multilayer FE heterostructures. It was shown that the electrostatic interactions between FE layers might lead to a gigantic dielectric response at a critical layer fraction. Building on our prior work,^{16,17} this letter presents a thermodynamic

analysis that shows that the high tunabilities of FE multilayers and superlattices are due to electrostatic and electromechanical coupling between layers. Moreover, we develop the methodology for designing heteroepitaxial structures that may specifically address loss and leakage while maintaining high tunability, thereby giving a great deal of flexibility to the device designer to optimize microwave and millimeter wave elements for the best system performance.

Consider two FE layers with equal lateral dimensions sandwiched between metallic electrodes as shown in Fig. 1(a). In its most general form, the energy density of layer 1 and layer 2 in their uncoupled, unconstrained (freestanding) state can be expressed as

$$F_1 = F_{0,1} + \frac{1}{2}aP_1^2 + \frac{1}{4}bP_1^4 + \frac{1}{6}cP_1^6,$$

$$F_2 = F_{0,2} + \frac{1}{2}dP_2^2 + \frac{1}{4}eP_2^4 + \frac{1}{6}fP_2^6, \quad (1)$$

where $F_{0,i}$ is the energy of layer i in its high-temperature paraelectric state, P_i are the polarizations of layers 1 and 2, and $a, b, c, d, e,$ and f are Landau coefficients. a and d are temperature dependent via the Curie-Weiss law, i.e., $a = (T - T_{C,1})/\epsilon_0 C_1$ and $d = (T - T_{C,2})/\epsilon_0 C_2$, where ϵ_0 is the permittivity of free space, $T_{C,i}$ and C_i are the Curie-Weiss temperature and constant of layer i , respectively. The other coefficients for both materials are assumed to be temperature independent. The spontaneous polarization for each layer ($P_{0,i}$) is given by the condition of thermodynamic equilibrium: $\partial F_i / \partial P_i = 0$.

Suppose layer 1 with thickness h_1 is joined together with layer 2 with thickness h_2 , and the bilayer is sandwiched between metallic electrodes [Fig. 1(a)]. The relative volume fraction of layer 2 is $\alpha = h_2/h$. We will assume that both h_1 and h_2 are much larger than the characteristic correlation length of each layer. This model is equally applicable to a FE superlattice made up of identical bilayers with a periodicity $D = h_1 + h_2$ under the same short circuit conditions. When these layers are coupled, the actual polarization of the layers is different from their “decoupled” values $P_{0,1}$ and $P_{0,2}$. The

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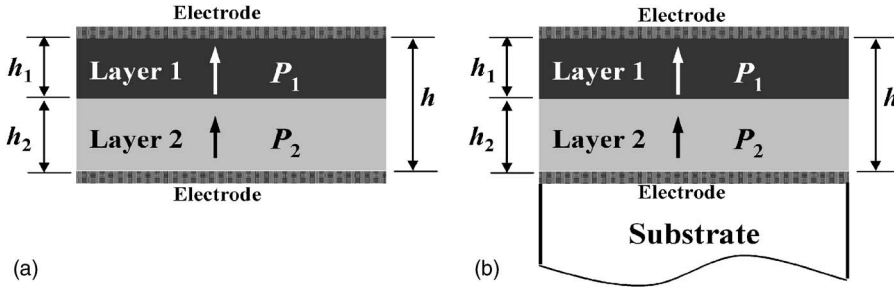


FIG. 1. (a) Freestanding FE bilayer sandwiched between electrodes. (b) Heteroepitaxial FE bilayer deposited on a thick substrate. The thickness of the FE layers are h_1 and h_2 and h is the total thickness.

internal electric fields $E_{D,1}$ and $E_{D,2}$ in layer 1 and layer 2 due to the polarization mismatch establish different polarization states in layer 1 and 2, respectively [Fig. 1(a)]. For perfectly insulating bilayers, the internal fields are given by:^{16,18}

$$E_{D,1} = -\frac{1}{\epsilon_0}(P_1 - \langle P \rangle) = \frac{\alpha}{\epsilon_0}(P_2 - P_1), \quad (2)$$

$$E_{D,2} = -\frac{1}{\epsilon_0}(P_2 - \langle P \rangle) = \frac{1-\alpha}{\epsilon_0}(P_1 - P_2), \quad (3)$$

where $\langle P \rangle = (1-\alpha)P_1 + \alpha P_2$ is the average polarization. While $E_{D,2} > 0$ serves to enhance the polarization of layer 2, $E_{D,1}$ attempts to decrease the polarization of layer 1 since it lies antiparallel to the polarization vector ($E_{D,1} < 0$). Therefore, in equilibrium, it is expected that $P_1 < P_{0,1}$ and $P_2 > P_{0,2}$ as to reduce the initial polarization difference: $\Delta P = P_{0,1} - P_{0,2}$.

The total free energy functional incorporating the potential energies of the internal fields $E_{D,1}$ and $E_{D,2}$, see Ref. 16) is given by

$$F_{\Sigma} = (1-\alpha) \left[F_1(P_1) - \frac{1}{2} E_{D,1} P_1 - E P_1 \right] + \alpha \left[F_2(P_2) - \frac{1}{2} E_{D,2} P_2 - E P_2 \right], \quad (4)$$

where E is an external field parallel to the polarizations of layers 1 and 2 (P_1 and P_2 , respectively).

The (small-signal) average dielectric response of the bilayer is

$$\langle \epsilon_R \rangle (E=0) \cong \frac{1}{\epsilon_0} \frac{d\langle P \rangle}{dE} = \frac{1}{\epsilon_0} \left[(1-\alpha) \frac{\delta P_1}{E} + \alpha \frac{\delta P_2}{E} \right], \quad (5)$$

where $\langle P \rangle = (1-\alpha)P_1 + \alpha P_2$ is the average polarization, $\delta P_i = P_i(E) - P_i(E=0)$ as $E \rightarrow 0$. P_1 and P_2 are given by the simultaneous solution of the equations of state: $\partial F_{\Sigma} / \partial P_1 = 0$ and $\partial F_{\Sigma} / \partial P_2 = 0$. The tunability of the bilayer can thus be expressed as:^{19,20}

$$\eta = \left[1 - \frac{\langle \epsilon_R \rangle (E)}{\langle \epsilon_R \rangle (E=0)} \right] \times 100\%, \quad (6)$$

where $\langle \epsilon_R \rangle (E)$ is the dielectric response in the presence of an external electric field E .

For a heteroepitaxial bilayer grown on a thick cubic substrate as shown in Fig. 1(b), the incorporation of the elastic energy of the internal stresses results in renormalized Landau coefficients:²¹

$$\bar{a} = a - x_1 \frac{4Q_{12,1}}{S_{11,1} + S_{12,1}}, \quad \bar{b} = b + \frac{4Q_{12,1}^2}{S_{11,1} + S_{12,1}}, \quad (7a)$$

$$\bar{d} = d - x_2 \frac{4Q_{12,2}}{S_{11,2} + S_{12,2}}, \quad \bar{e} = e + \frac{4Q_{12,2}^2}{S_{11,2} + S_{12,2}}, \quad (7b)$$

where $S_{ij,i}$ and $Q_{ij,i}$ are the elastic compliances at constant polarization and electrostrictive coefficients of layer i , re-

spectively. $x_i = (a_S - a_i) / a_S$ are the (polarization-free) misfit strains of layer i with respect to substrate, where a_i are the unconstrained equivalent cubic cell constants of layer i and a_S is the lattice parameter of the substrate. For a pseudomorphic bilayer with $h < h_p$, where h_p is the critical thickness for misfit dislocations, these misfit strains are not independent and the relation between them is given by $x_2 = 1 - [a_2(1 - x_1) / a_1]$.

We consider a BT-ST bilayer as an example heteroepitaxial system that has been well studied both as multilayer and superlattice structures. Their Landau coefficients²² and elastic constants²³ are known, allowing us to carry out a numerical analysis. Two cases are considered in this study. One is a freestanding BT-ST bilayer, sandwiched between metallic electrodes [Fig. 1(a)]. The other is a heteroepitaxial BT-ST bilayer grown on a thick (001) ST substrate with pseudomorphic electrodes [Fig. 1(b)] such that $x_{ST} = 0\%$. The lattice parameters of BT and ST are 0.4005 and 0.3905 nm, respectively. Thus, the strain in the BT layer will be $x_{BT} = -2.56\%$. As shown in Fig. 2(a), the dielectric response exhibits an anomaly in the vicinity of a critical fraction ($\sim 14\%$ ST and $\sim 69\%$ ST for the freestanding and heteroepitaxial bilayer, respectively). Detailed analysis of this phenomenon can be found elsewhere.^{16,17}

With the application of an external electric field, we can analyze the dielectric tunability of the bilayer via Eq. (6).

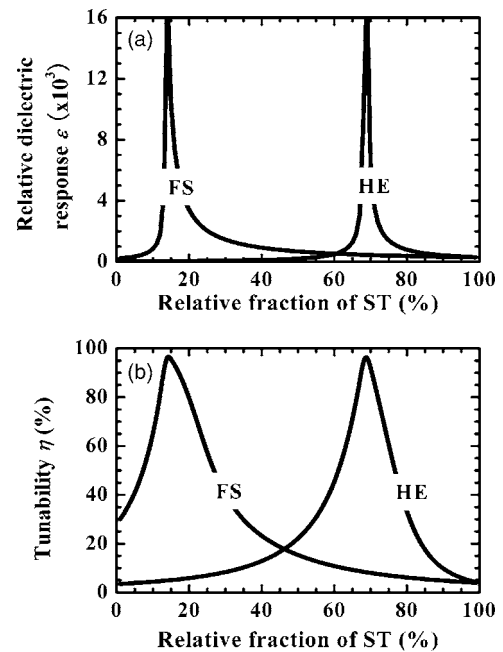


FIG. 2. (a) Relative dielectric responses of freestanding (FS) and heteroepitaxial (HE, $x_{BT} = -2.56\%$ and $x_{ST} = 0\%$) BT-ST bilayers as a function of ST fraction. (b) Dielectric tunabilities of BT-ST bilayers as a function of ST fraction under 100 kV/cm external field.

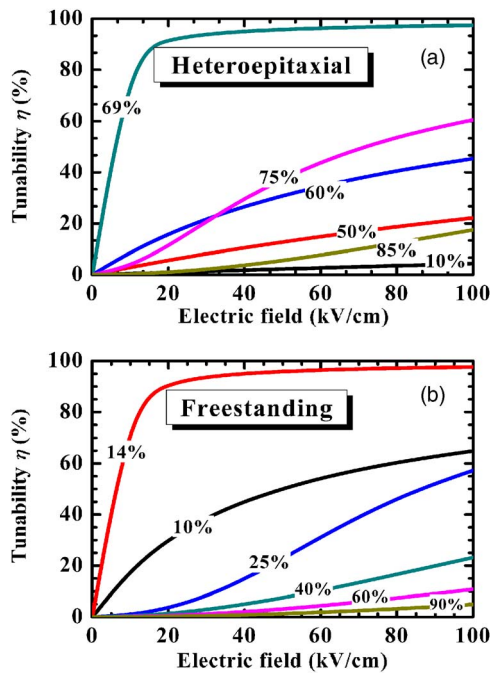


FIG. 3. (Color online) (a) Dielectric tunabilities of freestanding BT-ST bilayers as a function of external field for various ST fractions. (b) Dielectric tunabilities of heteroepitaxial BT-ST bilayers ($x_{\text{BT}}=-2.56\%$ and $x_{\text{ST}}=0\%$) as a function of external field for various ST fractions.

Figure 2(b) plots the tunabilities of both structures at 100 kV/cm as a function of the relative volume fraction of ST layer. Both cases show extremely high dielectric tunabilities, $\eta_{\text{max}} \sim 97\%$, around the dielectric anomaly. Such a high tunability has not been observed from homogeneous thin films primarily because of degradation due to internal stresses.^{24,25} The electric field dependence of the dielectric tunabilities for both cases is shown in Figs. 3(a) and 3(b). For each ST fraction, the tunability increases with the increasing of external field. At the relative critical fraction, it is shown that the bilayers have extremely high tunabilities even in the presence of small external fields; thus further simplifying the silicon integrated circuit (IC) elements necessary to control microwave and millimeter wave tuning devices.

Unlike homogeneous films, which have never achieved the high tunabilities predicted from this analysis because of internal stresses, FE multilayers and superlattices can experimentally achieve near theoretical performance ($>90\%$ tunability) because electrostatic interactions between the layers induce polarization in the paraelectric layer, thus making them ideal for practical applications. Moreover, a straightforward extension of this analysis shows that $>90\%$ tunability may still be achieved when the ST layer is replaced by a linear dielectric such as silicon dioxide or silicon nitride layer. The critical FE volume fraction, however, depends on the room temperature relative dielectric constant of the linear dielectric. For a linear dielectric forming a bilayer with a 100 nm thick BT freestanding film, the critical BT layer fraction around which the high tunability should occur varies from 99.7% to 95% as the dielectric response of the linear dielectric changes from 4 to 40. Such versatility in the structure formation, together with the ability to incorporate standard IC silicon films into the design permit the device designer to construct elements that simultaneously have high

tunability and very low electrical leakage; crucial elements for low power consumption devices.²⁶ In addition, the heteroepitaxial structures described above should have inherently lower loss and temperature variation. The loss should be smaller in the bilayer structures because the polarization in the ST layer is induced, and therefore does not switch under small applied fields, while the temperature dependence should be flattened over that of the homogeneous film as the bilayer structure introduces a dielectric layer into the structure whose permittivity is virtually independent of temperature. These predictions are in qualitative agreement with recent experimental results wherein the loss of ferroelectric memory elements have been shown to be reduced by growing top and bottom paraelectric buffers prior to metallization.²⁷

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