Phenomenological model for the dielectric enhancement in compositionally graded ferroelectric films

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The dielectric enhancement observed in compositionally graded ferroelectric films is explained by use of a multilayer model. The finite size effect of the ferroelectric layers has been taken into account. This is tackled by the employment of Landau–Ginzburg thermodynamic theory for each layer. The calculated dielectric susceptibility of the graded film reveals significant enhancement for temperatures below the phase transition point, and is greater in a continuously graded film than in one with a step gradient in composition. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2175496]

In recent years, compositionally graded ferroelectric (CGF) films have attracted great research interest for their unconventional ferroelectric properties that are not observed in nongraded ferroelectric films, which may well lead to worthy new device applications. A phenomenon worth noting is the large polarization offset found in the hysteresis loop measurements under an alternating field.[1–4] Many experimental measurements focus on this property and there have been different theoretical models suggested previously.[4–7] Another useful property observed in CGF is permittivity enhancement, which has started to attract much research interest due to its potential application in microelectronics. Boerasu, Pintilie, and Kosec's measurement revealed the permittivity for a lead lanthanum zirconate titanate graded film was greater than those possessed by single layer structures of nongraded composition.[4] Bao, Zhang, and Yao also found that the permittivity of a three-layer calcium modified lead titanate step-graded film was much higher than the typical values reported for nongraded thin films.[8] Moreover, they obtained a much larger permittivity by smoothing out the stepped composition gradient.[3] Similar finding was also reported by Ranjith *et al.*[9] Bhaskar, Majumder, and Katiyar and Lu *et al.* reported very large permittivity values for CGF films of lead lanthanum titanate and barium strontium titanate (BST) respectively,[10,11] representing significantly enhanced dielectricity over conventional films. Recently, progressive dielectric enhancement was also demonstrated by Wang *et al.* in barium strontium zirconate titanate CGF films by employing an increasing number of layers.[12] The above systems pertain to conventional parallel plate electrode configuration (PPC). High dielectric CGF films with in-plane polarization [e.g., using interdigitated electrode configuration (IDC)] have also attracted attention,[13–15] which may exhibit stronger dielectricity than a PPC does. Lee *et al.*'s results reveal that the permittivities for IDC graded BST are about five times that of a PPC system.[14] Similar phenomenon of significantly enhanced dielectricity in IDC was also reported by Ota *et al.*[15] Summing up, CGF films exhibit not only the anomalous polarization offset behavior, but also the improved dielectric properties for which theoretical investigation has been scanty.

Indeed, very limited theoretical studies are available in the literature for the dielectric properties of CGF. The works of Ban, Alpay, and Mantese and Wang *et al.* may be cited,[6,16] but they only concentrated on the phase transition properties and the flatter temperature characteristic near Curie temperature. The anomalous dielectric enhancement in CGF has not been discussed extensively yet. In this letter, we suggest this phenomenon can be modeled by use of a multilayer structure of ferroelectric films and our discussion will focus on IDC, in which a stronger dielectricity may be achieved. Such is especially useful for the fabrication of memory device. It is known that inhomogeneity and surface/interface effects (e.g., due to misfit strain) may be the origins of finite size effects in ferroelectrics.[17,18] We therefore assume each "layer" in a CGF possesses finite size effect similar to that commonly observed in ferroelectric thin films. The Landau–Ginzburg (LG) model is employed for each layer. We will demonstrate this configuration is capable of reproducing the enhanced dielectricity in CGF.

A CGF film with an IDC can be modeled by a multilayered composite with sufficient number of layers. The dielectric susceptibility is given by

$$\chi = n^{-1}\sum_{i=1}^{n} \chi_i, \tag{1}$$

where n is the number of layers. For a CGF film with a PPC, $\chi^{-1}=n^{-1}\Sigma_{i=1}^{n}\chi_i^{-1}$. In both equations, we have assumed for convenience that all layers have even thickness ℓ (i.e., $\ell=L/n$ where L is the thickness of the graded film). When finite size effects are not considered, each layer i in the CGF film contributes a "bulk" susceptibility χ_i^b given by the Landau parameter α_i of second order phase transition theory: $\chi_i=\chi_i^b=-2\alpha_i$ and α_i for $T<T_{ci}$ and $T>T_{ci}$, respectively, where $\alpha_i=\alpha_{0i}(T-T_{ci})$, α_0 being a positive constant and T_c the critical temperature, respectively.

The variation of composition in a ferroelectric leads to lattice mismatch between layers, spatial variation in thermal expansion coefficient, etc., inducing internal stresses which may have a strong influence on the "surfaces" of each layer in a CGF film, similar to that commonly treated as surface effects in a thin film.[18,19] In this work, we introduce the notion of "internal size effects" of the graded structure by considering each layer in the model as a thin film material

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(i.e., incorporating size effect "internally"). In the modeling of a thin ferroelectric layer of the CGF film, the LG theory is adopted, with the variation of polarization modeled by a gradient term in the free energy expression. For a second order material, the free energy per unit area is[20]

$$F = \int_{-\ell/2}^{\ell/2} [\alpha P^2/2 + \beta P^4/4 + \kappa(dP/dz)^2/2 - EP]dz + \kappa(P_-^2/\delta_- + P_+^2/\delta_+)/2, \tag{2}$$

where $\alpha = \alpha_0(T - T_c)$. P is polarization, E is electric field, β and κ are positive constants. The κ term outside the integral involving the extrapolation lengths $\delta_\pm$ is there to satisfy boundary conditions. We adopt here the well-known Tilley–Žekš approach: $dP/dz \pm P/\delta_\pm = 0$ at $z = \pm \ell/2$.[20]

For a given temperature and electric field, the polarization as well as the susceptibility (via $\chi \equiv dP/dE$) profiles may be obtained by minimizing Eq. (2). The Euler–Lagrange equation is

$$\kappa(d^2P/dz^2) = \alpha P + \beta P^3 - E, \tag{3}$$

where $\kappa(d^2\chi/dz^2) = (\alpha + 3\beta P^2)\chi - 1$. In this work, we only focus on the symmetric condition $\delta_+ = \delta_- = \delta > 0$ and $E = 0$, for simplicity. The calculated susceptibility at $z = 0$ (denoted by χ_i^f) will then be substituted into χ_i of Eq. (1) to calculate the effective susceptibility of the CGF film.

For simplicity, we assume $\alpha_0 = \beta = \kappa = 1$, $\delta = 10$ for all layers in the CGF film with $L = 100$, and T_c varies linearly from 0.5 to 1.5 across the film. Calculated results of the temperature dependence of inverse susceptibility for a CGF film with IDC are shown in Fig. 1 for $n = 4$ and $n = 100$. Both $\chi_i = \chi_i^b$ and $\chi_i = \chi_i^f$ are plotted; the two very different n values are selected to demonstrate the effect of discrete layers (small n) versus that of a "continuum structure" (large n) on the dielectric behavior. In Fig. 1(a), the χ^{-1} curves for bulk materials with $T_c = 0.5$, 0.83, 1.17 and 1.5 are shown (dotted straight lines). For $n = 4$ and assuming all layers in the graded sample possess bulk properties [i.e., $\chi_i = \chi_i^b$ in Eq. (1)], the effective χ^{-1} of the graded sample [solid line in Fig. 1(a)] is essentially the average value of the four χ values of the respective layers such that the calculated χ^{-1} of the graded film always lies in between the maximum and minimum of the χ_i^{-1} values of the constituent layers, which is a result of standard composite theory. This characteristic will not be affected by the introduction of more layers in the calculation. However, the continuous dispersion of layer transition temperature results in the smoothing out of dips in the effective χ^{-1} vs T curve. This feature is consistent with the results demonstrated by Slowak and Ota *et al.*[13,15,21,22] As shown in Fig. 1(a), the calculated result for $n = 100$ with $\chi_i = \chi_i^b$ reveals smooth variation of χ^{-1} within T_{c1} and T_{c100}. At higher or lower temperature away from the region of transition, the susceptibility for $n = 100$ is lower than that for $n = 4$. Suppose the size effect of each layer is introduced into our calculation (i.e., setting $\chi_i = \chi_i^f$), then Eqs. (1) and (3) should be adopted. For $n = 4$ which corresponds to $\ell = 25$ for each layer, the dash-dotted line in Fig. 1(a) shows that the size effect only has minimal effect on the χ^{-1} of the CGF film, being only slightly displaced from the solid line. Actually, as larger n is introduced, a shift in T_c's will become apparent. Hence, a significant increment in χ below T_{c1} will be observed.

Figure 1(b) shows a comparison between the calculated results for $n = 4$ and 100 with $\chi_i = \chi_i^f$. The result for a film

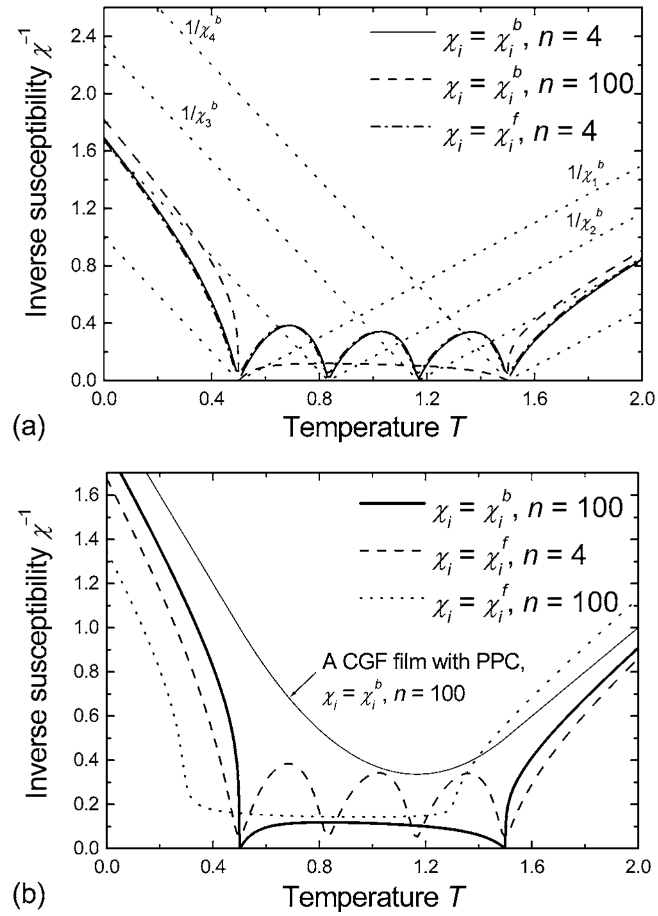

FIG. 1. Inverse susceptibility vs temperature for CGF films. Number of layers $(n) = 4$ and 100. χ_i^f and χ_i^b represent with/without incorporation of size effect for the layers.

with 100 layers of graded bulk materials with IDC (thick solid line) and PPC (thin solid line) is also shown for comparison in which the IDC has a stronger dielectricity. It clearly demonstrates that the whole curve for $n = 100$ with size effect shifts to lower temperature. The susceptibilities of the CGF film reveal considerable enhancement when the film is in ferroelectric phase, but switch to diminution when the film has become paraelectric. In the literature, some experiments had reported the phenomenon of dielectric enhancement in a continuously graded ferroelectric, as compared to a step-graded ferroelectric.[3,8,9,12] We believe that a step-graded structure will effectively function as a "continuously" graded structure when n is set sufficiently large. Thus, a large n in the modeling, which represents a continuously graded structure, is expected to yield enhanced χ values, but only usual values (conformable to predictions by standard composite theory) for a small n. The present model, which includes considerations of size effect does give such an effect and thus provides a possible explanation for this anomalous phenomenon. The same approach should also yield similar anomalous dielectric properties in ferroelectric superlattices, in which the dielectric constant is higher when slab thickness is reduced (i.e., larger slab periodicity).[23]

The phenomenon of dielectric enhancement shown in Fig. 1(b) will actually continue for increasing n. Figure 2 shows the effect of n on the susceptibility of a CGF film with $L = 150$ at $T = 0$. Assuming the maximum and minimum χ values among the graded ferroelectric layers are 0.5 (i.e.,

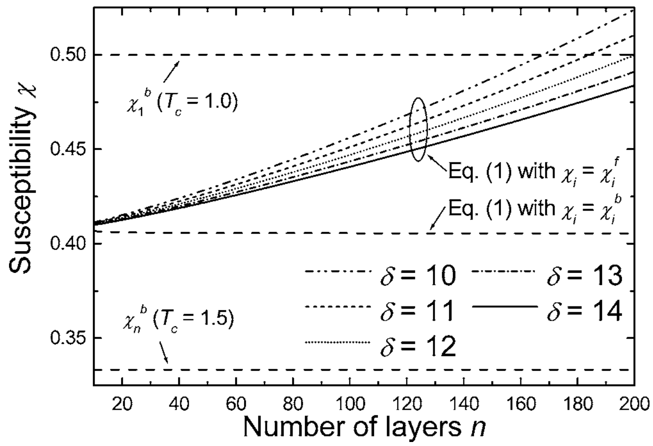

FIG. 2. Effect of the number of layers on the dielectric susceptibility of a CGF at temperature $T=0$. Smaller values of δ represent the stronger surface effect of the layers. Calculated result without incorporation of size effect ($\chi_i=\chi_i^b$) is also shown for comparison.

$T_c=1.0$) and 0.33 (i.e., $T_c=1.5$) respectively, the figure shows that the susceptibility of the CGF film increases monotonically with n for $\chi_i=\chi_i^f$ and may be larger than the maximum χ in the graded layers, which had been reported in experiments.[4,10] However, for each layer there is a critical thickness below which the value of χ decreases with thickness and the ferroelectricity disappears. In the figure, the effect of different δ's has also been examined. In general, as the value of δ decreases, the increment of the calculated χ with n becomes faster. A small δ represents a strong interface/surface effect or a strong coupling between layers.[24] In other words, the present result suggests that a CGF film possesses giant dielectric enhancement if the interfacial coupling between layers is strong.

As we stated previously, our model should be capable of accounting for the observed anomalous dielectric behavior in ferroelectric superlattices. A superlattice slab of two different materials is represented by setting $n=2$ in the present model. A superlattice with larger slab periodicity is effectively realized by reducing the slab thickness. Figure 3 shows the thickness dependence of χ for a bilayer structure with $T_c=0.5$ and 1.5. If the layers are taken as bulk material, χ remains 0.67 for all thicknesses (shown as dashed line). With

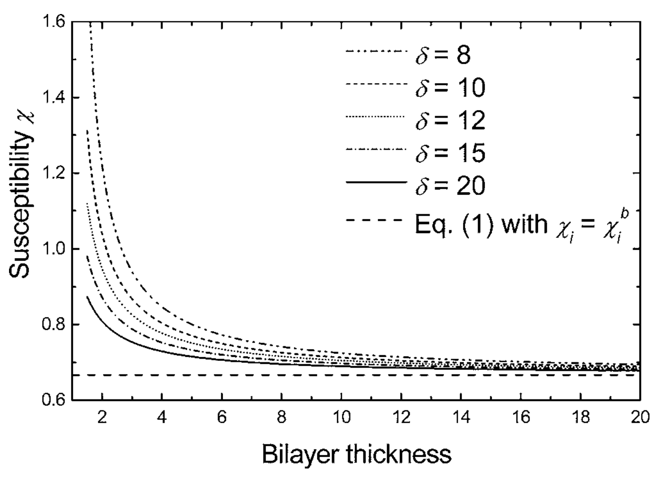

FIG. 3. Thickness dependence of the dielectric susceptibility of a bilayer structure at temperature $T=0$. The dashed line corresponds to the graded structure without size effect.

the size effect introduced, the figure shows the susceptibility increases as the thickness decreases, and more so for smaller thickness. A small δ further promotes the enhancement of χ, similar to the features demonstrated in Fig. 2. However, for the PPC, apart from the coupling arisen from polarization variations (i.e., varying δ), interlayer coupling due to depolarizing field (which can be neglected in this study with IDC) could also contribute the dielectric enhancement as demonstrated by a recent investigation of Roytburd, Zhong, and Alpay.[25] Their model has not yet included a gradient term in the ferroelectric free energy and hence the size effect of slab periodicity has not been discussed there.

In sum, the present multilayer model incorporating layer size effect is capable of reproducing the dielectric enhancement in CGF, as well as the flattened peak characteristic near the transition temperature. Although the effect of increased conductivity had been proposed as a mechanism for the enhancement in superlattices,[23] many experiments on CGF films with enhanced dielectric permittivity reported reasonably low loss.[3,8,10,11,14,22] Therefore, in this work we do not discuss the effect of conductivity.

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