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Influence of dielectric stiffness, interface, and layer thickness on hysteresis loops of ferroelectric superlattices

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We examined the influence of dielectric stiffness, interface, and layer thickness on the hysteresis loops, including the remanent polarization and coercive field of a superlattice comprising alternate layers of ferroelectric and dielectric, using the Landau-Ginzburg theory. An interface energy term is introduced in the free energy functional to describe the formation of interface "dead" layers that are mutually coupled through polarization (or induced-polarization). Our studies reveal that the hysteresis loop is strongly dependent on the stiffness of the dielectric layer, the strength of the interface coupling and layer thickness. The intrinsic coupling at the interface between two neighboring layers reduces the coercive field, though the corresponding remanent polarization is significantly enhanced by a soft dielectric layer. © *2011 American Institute of Physics*. [doi:10.1063/1.3630016]

I. INTRODUCTION

Ferroelectric superlattices, comprising alternate layers of ferroelectric and dielectric, are currently a topic of active research[1] because of their potential applications[2,3] and fundamental scientific interest.[4–6] Recent advances in film fabrication have made it possible to study the properties of well-controlled interfaces in perovskite ferroelectrics. The presence of symmetry-breaking elements such as surfaces/interfaces in layered ferroelectrics might be the underlying structures that provide the fundamental mechanism of the new behaviors that are so different from those of the bulk.[7–10] When the ferroelectric system has superlattice or multilayer structure, there is an additional coupling that originates from the interaction at the interface between the ferroelectric layers, which may affect the ferroelectric properties of the structure. Indeed, the coupling at the interface between the two constituent layers has been demonstrated in experiments[11–15] to play an important role in governing their properties.

Christen and co-workers studied ferroelectric superlattices consisting of $KTaO_3$ and $KNbO_3$ layers.[11–13] Their studies show evidence of antiferroelectric behaviors in the superlattice, indicating the existence of strong coupling across the interface between the two layers.[13] A transition from ferroelectric to antiferroelectric orderings was also observed in short-period $BaZrO_3/SrTiO_3$ (Ref. 14) and $BaTiO_3/SrTiO_3$ (Ref. 15) superlattices, as well as structures involving relaxors such as $PbTiO_3/PbMg_{1/3}Nb_{2/3}O_3$.[16] The origin of antiferroelectric ordering was suggested due to the imposition of a *B*-site ordering in the ABO_3 perovskite oxides.[13] On the other hand, a recent study using first principle calculations reports that the internal electric field plays an important role in the appearance of antiferroelectricity (ground state) in ferroelectric/dielectric superlattices.[17]

During recent years, numerous experimental studies have been devoted to investigate the ferroelectric properties of various superlattice or multilayer structures such as $BaTiO_3/SrTiO_3$,[18] $BaTiO_3/CaTiO_3$,[19] $SrTiO_3/BaTiO_3/CaTiO_3$,[20,21] $BaTiO_3/LaAlO_3$,[22] $BiFeO_3/SrTiO_3$,[23] $PbTiO_3/SrTiO_3$,[24–26] as well as system involving relaxor ferroelectrics.[16,27,28] Majority of these works reported the observation of completely new or enhanced behaviors that are absent in the individual constituent. Among these works, Dawber *et al*.[24–26] reported an interesting recovery of ferroelectricity in $PbTiO_3/SrTiO_3$ superlattices at thickness ratio less than [1/2] in $PbTiO_3$ to $SrTiO_3$.[24] First principle calculations[26] proposed that the unusual recovery of ferroelectric polarization in the superlattice is due to the polarization coupling at the interface between the polar ground state of $PbTiO_3$ and antiferrodistortive ground state of $SrTiO_3$, leading to the notion of interface-induced improper ferroelectricity. Effect of polarization coupling between two constituent layers was also reported to play an important role in governing the ferroelectric properties of superlattice composed of relaxors.[16,27,28]

Many theoretical studies of ferroelectricity in superlattices were carried out using the phenomenological Landau-type theory.[29–33] Landau theory with antiferroelectric interlayer coupling was developed to study the hysteresis loop of ferroelectric bilayers and superlattices.[30] Stephanovich and co-workers[31] studied the phase transition of ferroelectric/paraelectric superlattice using the Landau-Ginzburg theory with interlayer coupling. The influence of ferroelectric interlayer coupling on the polarization and dielectric properties of ferroelectric/dielectric superlattice was studied on the basis of the Landau theory.[32] Urtiev *et al*.[33] developed a misfit strain-temperature phase diagram for a ferroelectric/dielectric superlattice using a thermodynamic model. Those works,[29–33] however, do not consider the effect of interface or interface coupling.

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Qu *et al.*[29] (hereafter, we denote as the Qu's model) studied the effect of interface coupling in ferroelectric superlattices using the Landau-like formulation, which was obtained by taking the continuum approximation of transverse Ising model. In the model (for 1D case), two-surface parameters (namely, the extrapolation lengths[34–36]) are required to describe the inhomogeneity of polarization near the surfaces of two constituent layers, and another interface coupling parameter is needed to account for the polarization coupling at the interface. While the transverse Ising model was first proposed by Gennes[37] to study the phase transitions of order-disorder ferroelectrics, the Qu's model[29] was proposed to study the influence of interface polarization coupling in $PbTiO_3/BaTiO_3$ superlattices. Their work, however, did not address how the interface polarization coupling affects the local polarization across the interface.

While several authors[38–41] investigated the influence of interface coupling on ferroelectricity of superlattice using the Qu's model,[29] the spatial distribution of polarizations was not reported and discussed.[38–41] Zheng and Woo[40] studied the polarization and dielectric susceptibility of ferroelectric superlattices by assuming that the polarization is continuous across the interface. A phase-field simulation of domain structure for $PbTiO_3/SrTiO_3$ was studied by assuming that the interface between the two layers is coherent without considering the interface coupling effect.[41] Our recent studies on the switching behaviors in ferroelectric superlattices[42,43] show that the Qu's model[29] with interface polarization coupling can only describe polarization discontinuities at the interface between the two constituents.

We have recently proposed a model to study the ferroelectricity of a superlattice using the Landau-Ginzburg model by introducing an interface energy term,[42,44–51] which describes the formation of "dead" layers at the interface region and their mutual polarization interaction. The unique feature of our proposed model is that only an interface-related parameter is required (for 1D case) to address the issue associated with the inhomogeneity of polarization near surface/interface and their mutual polarization coupling at the interface. Despite its simplification, we have demonstrated that the model can capture the essential physics associated with the polarization continuities or discontinuities at the interface, interface "dead" layer and phase transitions in ferroelectric heterostructures[44–46] and superlattices.[42,47–51]

In those studies, however, the effect of an applied electric field on the ferroelectric hysteresis loops was not considered. In this paper, we focus on the effects of dielectric stiffness, intrinsic interface coupling, and layer thickness on the hysteresis loop behaviors of a superlattice form out of alternating ferroelectric layer and dielectric layer. The changes in the coercive field and remanent polarization associated with the hysteresis loops are also investigated. In Sec. II, the Landau-Ginzburg model of ferroelectric superlattices is described in detail, with a particular focus on the physical origin of the interface energy term. The results and discussion are presented in Sec. III. In Sec. IV, the conclusion is given.

II. THEORY

We consider a periodic superlattice—*ABABAB*—composed of two different ferroelectric layers, as shown in Fig. 1. The two constituent layers interact with each other via the polarizations located at the interfaces. We first construct the model using a dipole lattice model, as proposed by Ishibashi.[52] The dipole lattices model has been used to study the polarization reversal in ferroelectric thin films,[53] as well as the polarization and dielectric properties of ferroelectric superlattices.[47] Based on the dipole lattice model, each constituent layer is an ensemble of dipole lattices characterized by polarization, which has double potential wells. For simplicity, we consider the simple case of one-dimensional ferroelectric superlattices consisting of alternating layer A and layer B with total number of M and N lattices, respectively. P_m and Q_n represent dipole lattices located at the mth and nth site of layer A and layer B, respectively. Each dipole interacts with its nearest-neighboring dipole. κ_1 and κ_2 denote the interaction parameter between the nearest-neighboring dipoles within layer A and layer B, respectively.

The free energy for the ferroelectric layer A with total dipole lattices M, is[47]

$$F_1 = \sum_{m=1}^{M}\left[\frac{\alpha_1}{2}P_m^2 + \frac{\beta_1}{4}P_m^4 - EP_m\right] + \sum_{m=2}^{M}\left[\frac{\kappa_1}{2}(P_m - P_{m-1})^2\right], \tag{1}$$

and the free energy for the dielectric layer B with total lattices N is

$$F_2 = \sum_{n=1}^{N}\left[\frac{\alpha_2}{2}Q_n^2 - EQ_n\right] + \sum_{n=2}^{N}\left[\frac{\kappa_2}{2}(Q_n - Q_{n-1})^2\right], \tag{2}$$

where the higher order Q terms are truncated. E denotes the applied electric field. In the ferroelectric phase, $\alpha_1 < 0$ and $\beta_1 > 0$, whereas $\alpha_2 > 0$ for the dielectric layer.

The dipoles at the interfaces of layer A ($m = 1$ and M) and layer B ($n = 1$ and N) are given by $P_1 = P_M$ and $Q_1 = Q_N$, respectively. It is easily seen that the interaction energy between the dipoles at the interface of the two constituent layers is given by[47]

$$F_i = \frac{\lambda'}{2}[(P_M - Q_1)^2 + (P_1 - Q_N)^2], \tag{3}$$

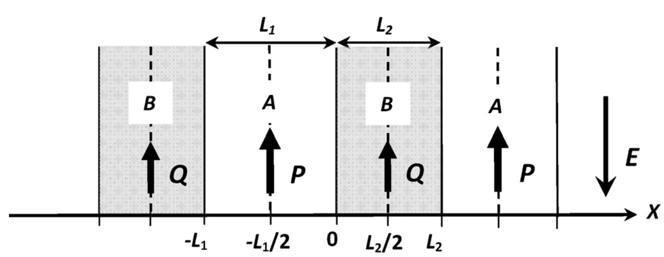

FIG. 1. Schematic illustration of a periodic superlattice composed of ferroelectric and paraelectric layers with the thicknesses L_1 and L_2, respectively. The direction of polarization P, induced-polarization Q, and applied electric field E are indicated in the figure.

where the interaction parameter between the interface dipole lattices is given by λ'. Note here that if the variation of the order parameter within each layer is smooth and each layer consists of a large number of dipoles, the interaction energy of layer A (second summation in Eq. (1)) can be approximated as follows

$$\sum_{m=2}^{M}\left[\frac{\kappa_1}{2}(P_m - P_{m-1})^2\right] \approx \int_0^{L_1}\frac{\kappa_1}{2}\left(\frac{dP}{dX}\right)^2 dX,$$

where $L_1 = Ma_1$ and a_1 are the thickness and the lattice constant of layer A, respectively. Similarly, the interaction energy of layer B with thickness $L_2 = Na_2$ and its lattice constant a_2 (second summation in Eq. (2)) is given by

$$\sum_{n=2}^{N}\left[\frac{\kappa_2}{2}(Q_n - Q_{n-1})^2\right] \approx \int_0^{L_2}\frac{\kappa_2}{2}\left(\frac{dQ}{dX}\right)^2 dX,$$

where the periodic thickness is $L = L_1 + L_2$. Since there are only two dipoles at each interface that contribute to the interface coupling energy, the interface energy Eq. (3) remains unchanged. Thus, it is clear that the interface energy has the same form as the interaction energy term of the dipole lattice model or the gradient term of the continuum Landau-Ginzburg theory, which describes the inhomogeneity of polarization within the constituent layer.

Let us now cast the free energies Eqs. (1), (2), and (3) into a continuum Landau-Ginzburg theory by putting the superlattice in the coordinate system, as shown in Fig. 1. By symmetry, the total free energy per unit area of the one-period superlattice F with the periodic thickness is $L = L_1 + L_2$ is

$$F = \frac{2}{L}(F_1 + F_2 + F_i), \tag{4}$$

where the total free energy densities of A and B are

$$F_1 = \int_{-L_1/2}^{0}\left[\frac{\alpha_1}{2}P^2 + \frac{\beta_1}{4}P^4 + \frac{\kappa_1}{2}\left(\frac{dP}{dX}\right)^2 - EP\right]dX, \tag{5}$$

and

$$F_2 = \int_0^{L_2/2}\left[\frac{\alpha_2}{2}Q^2 + \frac{\kappa_2}{2}\left(\frac{dQ}{dX}\right)^2 - EQ\right]dX, \tag{6}$$

respectively. For ferroelectrics with second order transition, the correlation length ξ_1' characterizing the domain wall thickness is $\sqrt{-\kappa_1/\alpha_1}$, whereas $\sqrt{\kappa_2/\alpha_2}$ is the correlation length ξ_2' in the paraelectric layer.

The interface energy is[42,44–46,48–51]

$$F_i = \frac{\lambda'}{2}(P_i - Q_i)^2 = \frac{\lambda'}{2}\left(P_i^2 + Q_i^2\right) - \lambda' P_i Q_i, \tag{7}$$

with the periodic boundary condition gives $P_M = P_1 = P_i$ and $Q_N = Q_1 = Q_i$. Here, the boundary conditions at the interfaces are given by

$$\left.\begin{aligned} \frac{dP}{dX} &= -\frac{\lambda'}{\kappa_1}(P_i - Q_i) \\ \frac{dQ}{dX} &= \frac{\lambda'}{\kappa_2}(P_i - Q_i). \end{aligned}\right\} \tag{8}$$

We now take a closer look at the interface energy term Eq. (7), which is characterized by the interface parameter λ'. In particular, we attempt to interpret the interface energy term Eq. (7) from the perspective of interface "dead" layer effect.[54–56] For clarity of illustration, we divide the interface energy term Eq. (7) into two parts: (i) non-ferroelectric part (first two terms) and (ii) polarizations coupling part (last term). The former term is analogous to the formation of "dead" layers at the interface region, i.e., the surfaces of layer A ("$\lambda' P_i^2/2$") and layer B ("$\lambda' Q_i^2/2$"). The dead layers are linear dielectrics, and their dielectric stiffnesses are determined by the interface parameter $\lambda' > 0$. Hence, it is not necessary to consider explicitly the interface polarizations or induced-polarizations (i.e., P_i and Q_i) in those layers. The strength of polarization interaction between the "dead" layers is given by the last term "$\lambda' P_i Q_i$", which has the same form as the coupling term (the linear term) in the Qu's model.[29] Under a sufficiently large applied electric field E, P_i, and Q_i can be switched or non-switched. In the present study, we assume that both P_i and Q_i are switchable. It is important to note here that we consider the simple case of polarization parallel to surfaces or interfaces, and thus the depolarization field can be ignored. Hence, when an external electric field is applied, there is no surface charge at the electrodes and at the interfaces, thus the internal electric field in each layer is constant. The effect of misfit strain is also neglected.

If $\lambda' = 0$, no dead layers form at the surfaces of the two constituent layers. No depletion layer (due to the degradation of polarization) forms near the interfaces/surfaces of the ferroelectric layer A is expected, and no polarization is induced near the surfaces of the dielectric layer B. Therefore, the polarization in the ferroelectric layer A is homogenous and no induced-polarization is expected in the dielectric layer. $\lambda' \neq 0$ indicates that the dead layers are formed at the interfaces. The presence of dead layers at the interface leads to the degradation of polarization near the interfaces of ferroelectric layer A. In addition, polarization may induce at the layer B interface, depending on the properties of dielectric layer B.

In our early works, we have confirmed that the interface parameter λ' and the extrapolation lengths govern the inhomogeneity of polarization near the interface though the physical origins are different.[45] We have also shown that the continuity or discontinuity of polarizations across the interface depends upon the interface parameter λ'.[42,44,45,47,50] For the particular case of $\lambda' \gg 0$, we find $P_i \approx Q_i$. This indicates that an interface "dead" layer with the intermixed properties of the two constituents is formed at the interface.[44] We have demonstrated that the present model and the Qu's model[29] give a similar qualitative description of switching dynamics, including switching current and switching time, as well as the evolution of polarization profile during switching process.[42] Exact expression for describing the transition point of a ferroelectric superlattice is obtained.[50,51] It is found that the phase transition point is governed by the interface parameter and the physical properties of the two layers, as expected.

In the present study, the average polarization of the superlattice is given by

$$\bar{P} = \frac{2}{L}\left[\int_{-L_1/2}^{0} P dX + \int_{0}^{L_2/2} Q dX\right]. \tag{9}$$

If $\lambda' = 0$, there is no interface coupling at the interface, we have $P_i = P_b$ and $Q_i = 0 = Q_b$ where the bulk polarization of the ferroelectric is $P_b = \pm\sqrt{-\alpha_1/\beta_2}$ and that of paraelectric layer is $Q_b = 0$. Without the interfacial coupling, the two layers are independent of each other; hence the coercive field of the superlattice E_C is the same as the coercive field for the ferroelectric layer E_{1C}, which can be obtained from $dE/dP = 0$ as

$$E_C = E_{1C} = \pm\frac{2\alpha_1}{3}\left(-\frac{\alpha_1}{3\beta_1}\right)^{1/2}. \tag{10}$$

For the case with $\lambda' \neq 0$, the coupling at the interface may form an interface-ordered state in the dielectric layer and an inhomogeneous polarization near the interface of the ferroelectric layer. Thus, the coercive field of Eq. (10) will no longer be valid in the presence of interface coupling and this will be studied in detail numerically.

For numerical studies, we rescale the variables in Eqs. (4)–(7) into dimensionless form using the following scaling: $p = P/p_0$, $q = Q/p_0$, $p_i = P_i/p_0$, and $q_i = Q_i/p_0$ with $p_0^2 = |\alpha_1|/\beta_1$; $x = X/X_0$, $\ell = L/X_0$, $\ell_1 = L_1/X_0$, $\ell_2 = L_2/X_0$ with $X_0 = \kappa_1/|\alpha_1|$; $\alpha_r = \alpha_2/|\alpha_1|$; $\kappa_r = \kappa_2/\kappa_1$; $e = E/E_0$, and $e_C = E_C/E_0$ with $E_0^2 = \beta_1 p_0^3$; $\lambda = \lambda'/\beta_1 p_0^2$; $f = F/F_0$; $f_1 = F_1/F_0$; $f_2 = F_2/F_0$, and $f_i = F_i/F_0$ with $F_0 = \beta_1 p_0^4/X_0$. The free energy per unit area of the superlattices in dimensionless form becomes

$$f = \frac{2}{\ell}\left(\int_{-\ell_1/2}^{0}\left[-\frac{p^2}{2}+\frac{p^4}{4}+\frac{1}{2}\left(\frac{dp}{dx}\right)^2 - ep\right]dx + \int_{0}^{\ell_2/2}\left[\frac{\alpha_r}{2}q^2+\frac{\kappa_r}{2}\left(\frac{dq}{dx}\right)^2 - eq\right]dx\right) + \frac{\lambda}{2}(p_i - q_i)^2, \tag{11}$$

with the boundary condition at interfaces

$$\left.\begin{aligned}\frac{dp}{dx} &= -\lambda(p_i - q_i),\\ \frac{dq}{dx} &= \frac{\lambda}{\kappa_r}(p_i - q_i).\end{aligned}\right\} \tag{12}$$

The average polarization in dimensionless form becomes

$$\bar{p} = \frac{2}{\ell}\left[\int_{-\ell_1/2}^{0} p dx + \int_{0}^{\ell_2/2} q dx\right]$$

and the dimensionless coercive fields are $e_C = E_C/E_0$ and $e_{1C} = E_{1C}/E_0$. $\xi_1 = \xi_1'/X_0$ and $\xi_2 = \xi_2'/X_0$ denote the rescaled coherence lengths for the ferroelectric layer and dielectric layer, respectively.

III. RESULTS AND DISCUSSION

In this section, the influence of the dielectric stiffness, interface, and layer thickness on the hysteresis loop of the superlattice is investigated in details using a relaxation method.[57] Periodic boundary conditions are used in the numerical calculations. We first examine the thickness ℓ_1 dependences of coercive field e_C and average polarization $\bar{p}$ when $e = 0$ with $\ell_2 = 2$ for various interface couplings λ, as shown in Fig. 2. Hereafter, we denote $\bar{p}$ as the remanent polarization of the superlattice. In general, $\bar{p}$ reduces with decreasing thickness of ferroelectric layer ℓ_1, and e_C exhibits the expected dependence on ℓ_1. The dependence of $\bar{p}$ and e_C on ℓ_1 is stronger when $\ell_1 \tilde{<} 2\xi_1$. Here, the factor "2" in the term $2\xi_1$ associates with the two interfaces in thin film.[47]

The interface coupling-dependent behaviors of the remanent polarization $\bar{p}$ and e_C in the superlattice are more interesting. $\lambda \neq 0$ indicates the formation of "dead" layer at the interface region, and polarization coupling at the interface leads to the induced-polarization near the interface of dielectric layer. Therefore, $\bar{p}$ enhances with increasing interface coupling λ. The changes in $\bar{p}$ depend strongly on λ and ℓ_1. When $\lambda = 0$, no "dead" layers form at interfaces and $\bar{p}$ is mainly contributed by the polarization p in the ferroelectric layer (no polarization is induced in the dielectric layer $q = 0$). For an intermediate coupling strength of $\lambda = 0.5$, $\bar{p}$ is enhanced from ~1.2% to ~8.8% when the ferroelectric layer thickness reduces from $\ell_1 = 20$ to 1, as compared with the superlattice with $\lambda = 0$. On the other hand, the enhancement of $\bar{p}$ in a superlattice with a strong interface coupling $\lambda = 50$ is not as significant as compared to the superlattice with $\lambda = 0.5$, and $\bar{p}$ is significantly suppressed when

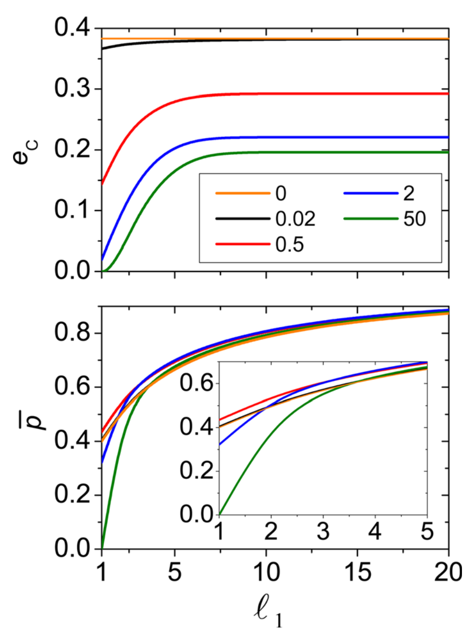

FIG. 2. (Color online) Coercive field and polarization as a function of ferroelectric layer thickness ℓ_1 of a superlattice with different interface couplings λ. The parameter values are adopted as $\alpha_r = 1$, $\kappa_r = 1$, and $\ell_2 = 2$.

approaching its characteristic length $\ell_1 < 5$, as compared with the superlattice with $\lambda = 0$. This is not surprising because the polarization p of the ferroelectric layer is strongly suppressed, if $\lambda = 50$. In this case, an interface "dead" layer with intermixing properties of two constituents is formed and the superlattice behaves like a hybrid structure.[44]

The coercive field e_C of the superlattice with no interface coupling $\lambda = 0$ is similar to the bulk ferroelectric layer $e_C = e_{1C} \sim 0.385$ and it is independent of layer thickness ℓ_1. It is seen that e_C decreases with increasing λ. Even a weak coupling across the interface (e.g., $\lambda = 0.02$), leads to a reduction in the coercive field $e_C \leq e_{1C}$, particularly if $\ell_1 \tilde{<} 2\xi_1$. $\lambda = 0.02$ implies that the "dead" layers at interfaces are dielectrically "soft". In this case, the structure at the interface exhibits a high nonlinearity in dielectric susceptibility when $e = 0$.[46] As λ increases, the coercive field of the superlattice reduces and the reduction in e_C is more marked for stronger coupling. The results in Fig. 2 suggest that the effect of interface coupling assists the polarization reversal by reducing the coercive field, though the presence of interface coupling may lead to an enhancement in the remanent polarization $\bar{p}$.

In Fig. 3, we show the typical hysteresis loops of a superlattice with $\ell_1 = 3$ and $\ell_2 = 2$ with different λ. The inset (in the $\bar{p}$-e hysteresis loop of Fig. 3) indicates the polarization profiles of different λ at $e = 0$. The polarization profiles clearly show the continuity or discontinuity of polarization across the interface due to interface coupling λ,[42,44,45,47,50] as well as the depletion region due to the formation of interface "dead" layers. For the case with $\lambda = 0$, q_i depends linearly on e, which is the typical behavior of a dielectric. Both the $\bar{p}$- and p_i-e hysteresis loops are rectangular with $e_C = e_{1C} \sim 0.385$, as discussed earlier. The thin $q_i - e$ hysteretic-like loop exhibits in the superlattice with $\lambda = 0.02$, implying the presence of "switchable" induced-polarizations at the interface of dielectric layer. As the interface coupling is increased, e_C decreases and the hysteresis loop tends to be more squared. The value of p_i at $e = 0$ decreases with increasing λ, indicating that the degradation of polarization due to the formation of the "dead" layers as the interface coupling increases. On the other hand, q_i at $e = 0$ enhances with increasing λ. Both the p_i- and $q_i - e$ hysteresis loops of the superlattice with $\lambda = 50$ are similar when the interface coupling is strong. This is because an interface "dead" layer with intermixing properties of the two constituents is formed.[44]

Figure 4 illustrates how the dielectric stiffness α_r affects $\bar{p}$ and e_C in a strongly coupled superlattice $\lambda = 50$. It is seen that the superlattices with soft dielectric layers $\alpha_r = 0.02$ lead to strong enhancement in $\bar{p}$. As the rigidity of the dielectric layer increases, $\bar{p}$ reduces. A strong interface coupling between a ferroelectric layer and a very rigid dielectric layer (e.g., $\alpha_r = 50$) result in the disappearance of ferroelectricity at a critical thickness. Let us now look at the effect of dielectric stiffness α_r on the coercive field of the superlattice. For the case with $\ell_1 < 5$, the coercive field e_C of the superlattice decreases with increasing α_r. For the superlattice with a thick ferroelectric layer $\ell_1 > 5$, an unusual dielectric stiffness α_r dependence of coercive field is predicted. The coercive field of a superlattice decreases with increasing rigidity of the dielectric layer α_r from 0.02 to 1.02. On the contrary, upon further increasing α_r from 1.02 to 50, it is found that e_C is increased. The peculiar dependence of e_C on α_r can be understood from the presence of interface "dead" layers and their mutual polarization interaction, which leads to the formation of (i) the induced-polarization and (ii) the "domain wall-like structure" at the interface in the superlattice.[42,46] A larger e_C is required for the superlattice with a soft dielectric

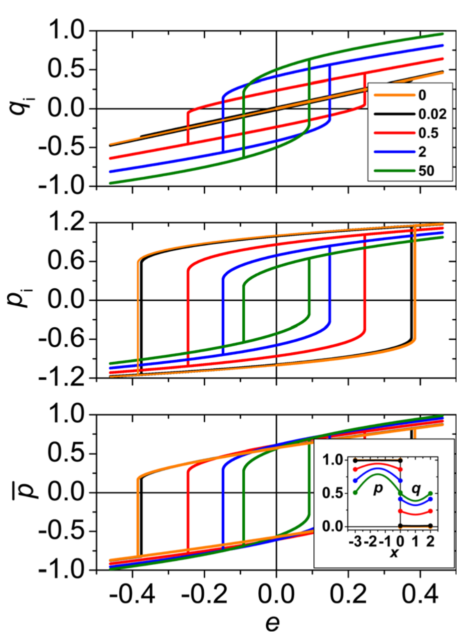

FIG. 3. (Color online) $\bar{p}-$, p_i-, and $q_i - e$ hysteresis loops of a superlattice with different interface coupling λ. The parameter values are adopted as $\alpha_r = 1$, $\kappa_r = 1$, $\ell_1 = 3$, and $\ell_2 = 2$. Inset shows the spatial dependence of polarization profile at $e = 0$.

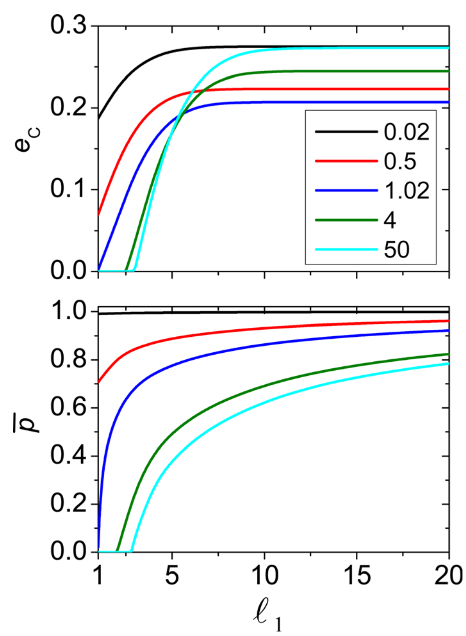

FIG. 4. (Color online) Coercive field and polarization as a function of ferroelectric layer thickness ℓ_1 of a superlattice with different dielectric stiffnesses α_2. The parameter values are adopted as $\alpha_r = 1$, $\kappa_r = 1$, $\ell_2 = 1$, and $\lambda^{-1} = 0.02$.

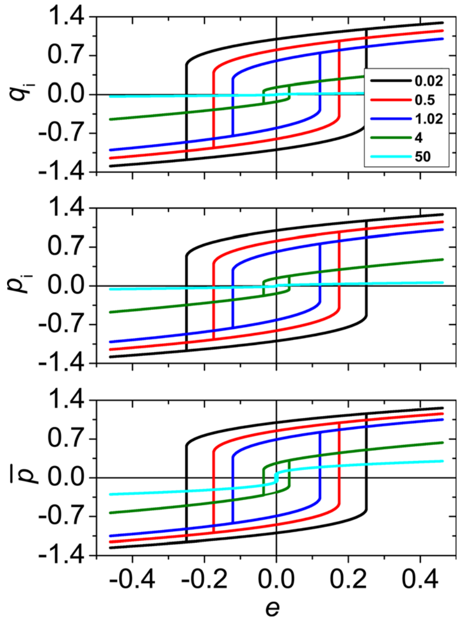

FIG. 5. (Color online) $\bar{p}-$, p_i-, and $q_i - e$ hysteresis loops of a superlattice with different dielectric stiffnesses α_r. The parameter values are adopted as $\kappa_r = 1$, $\lambda^{-1} = 0.02$, $\ell_1 = 3$, and $\ell_2 = 1$.

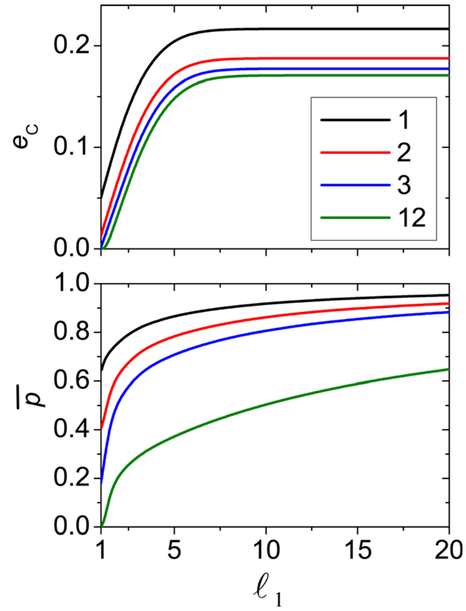

FIG. 6. (Color online) Coercive field and polarization as a function of ferroelectric layer thickness ℓ_1 of a superlattice with different dielectric layer thicknesses ℓ_2. The parameter values are adopted as $\alpha_r = 0.6$, $\kappa_r = 1$, and $\lambda^{-1} = 0.02$.

layer $\alpha_r = 0.02$ since the induced-polarization is stronger than the superlattice with $\alpha_r = 0.5$ or 1.02. On the other hand, the coercive field of the superlattice with a rigid dielectric $\alpha_r = 50$ is relatively larger than the superlattice with $\alpha_r = 0.5$ or 1.02 because the domain wall-like structure is strongly pinned by the rigid "dead" layer at the dielectric interfaces with $p_i \sim q_i \sim 0$. The results further provide evidence that the interface coupling leads to a reduction in the coercive field, though the correlated remanent polarization $\bar{p}$ is strongly enhanced.

In Fig. 5, we show the dielectric stiffness α_r dependence of polarization hysteresis loops for a strongly coupled superlattice with $\ell_1 = 3$ and $\ell_2 = 1$. It is seen that the coercive field and the remanent polarization decrease with increasing the rigidity of dielectric layer α_r. For the superlattice with $\alpha_r = 0.05$, a large q_i at $e = 0$ indicates that the induced-polarization (of the "dead" layer) in the dielectric layer is strong. Since the ferroelectricity is significantly weakened in the superlattice with a rigid dielectric layer $\alpha_r = 50$, the coercive field and the remanent polarization are very small. Finally, we examine the effect of dielectric layer thickness ℓ_2 on $\bar{p}$ and e_C, as shown in Fig. 6. We see that $\bar{p}$ and e_C are reduced with decreasing ℓ_1 and increasing ℓ_2. Figure 7 shows the typical $\bar{p}$–, p_i-, and $q_i - e$ hysteresis loops of a superlattice with different ℓ_2.

In summary, we have used the Landau-Ginzburg theory to investigate the influence of dielectric stiffness, interface, and layer thickness on the hysteresis loop in superlattices composed of alternating layers of ferroelectric and dielectric. Within the framework of the dipole lattices model,[52,53] we show that the model[47] can be constructed based on the concept of interaction of dipole lattices, which are characterized by polarization with double potential wells. The interacting coefficient of the dipole lattices at the interface is given by an interface parameter λ, which is different from that of the nearest-neighboring dipole lattices within the ferroelectric or dielectric layer. As the model is constructed based on the interaction of dipole lattices[47,52,53] constrained by double potential energy wells, the concept should be general to all ferroelectric layered structures involving surfaces or interfaces. In the continuum model, the interface parameter λ appears in the interface energy term in the free energy functional. The interface energy term describes the formation of interface "passive" layers that are mutually coupled via polarizations. The "passive" layers form at the interface region can be analogous to interface "dead" layer.[54–56]

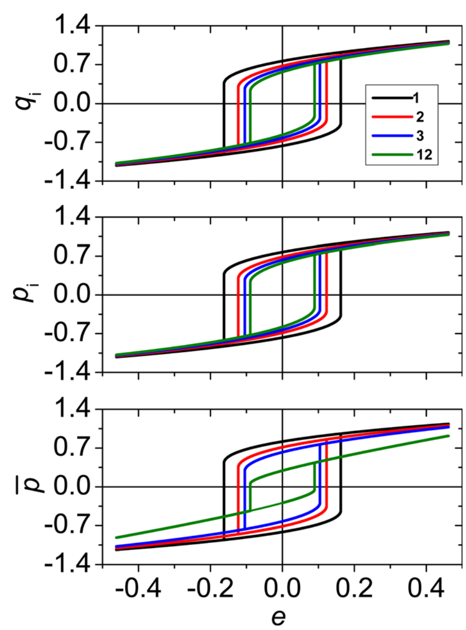

FIG. 7. (Color online) $\bar{p}-$, p_i-, and $q_i - e$ hysteresis loops of a superlattice with different dielectric layer thickness ℓ_2. The parameter values are adopted as $\alpha_r = 0.6$, $\kappa_r = 1$, $\lambda^{-1} = 0.02$, and $\ell_1 = 3$.

A thermodynamic model describing the surface effect on phase transition in semi-infinite ferroelectrics was first developed by Kretschmer and Binder[34] using the Landau-Ginzburg theory. The extension of the model to ferroelectric films was performed by Tilley and Zeks (hereafter, the Tilley-Zeks model).[35] The Tilley-Zeks model has been explored extensively by many authors.[36] The essence of this method is the introduction of the so-called "extrapolation length" at surface. Nevertheless, they are still undergoing constant discussion and improvement.[58,59] Bratkovsky and Levanyuk[58,59] successfully illustrated the strong smearing of phase transition in ferroelectric thin films by considering the surface as a defect coupled to the order parameter. In their model,[58] the surface energy term consists of a dead layer (which is a linear dielectric) and its field component. We would like to stress here that the dead layers in our model (appear in the interface energy term of Eq. (7)) are also linear dielectrics. The stiffness of the dielectric is determined by an interface parameter λ.

Recently, first-principle calculations demonstrated that the interface bonding at the ferroelectric-metal interface of ultrathin ferroelectric capacitors affects strongly the interface ferroelectricity via the formation of intrinsic dipole moments at the interfaces (or dead layer).[55,60,61] The interface dipole moments can be of two types: switchable or non-switchable, depending on the stiffness of the interface bonding. Their works[60,61] on thin-film ferroelectrics demonstrate that spatial distribution of polarization is significantly inhomogeneous across film thickness and produces an "interface domain wall" if the interface bonding is sufficiently strong and if the intrinsic interface dipole moments are comparable to the bulk polarization. Those works[55,60,61] clearly indicate the importance of considering the coupling of polarization at the interface between a ferroelectric layer and its neighboring layer in system involving surfaces or interfaces. In our study, we assume that the polarizations (or induced-polarizations) in the dead layers are "switchable". In fact, the formation of such "interface domain walls" due to interface polarization coupling (in our case, we denote as "domain wall-like structures") has been predicted and discussed in ferroelectric heterostructures[46] and superlattices.[42]

While most theoretical studies on ferroelectric superlattices using a thermodynamic model were established by assuming a coherent interface,[40,41,62] it was recently predicted using first-principle calculations that interfaces with continuity or discontinuity polarizations can be constructed out of ferroelectric and dielectric layers, with different composition and choices of polar/non-polar combinations.[63,64] In this study, the coupling at the interface between the switchable induced-polarization of dielectric layer and the electrically switchable spontaneous polarization of ferroelectric layer leads to polarization continuities or discontinuities at interface. We have shown how the changes in hysteresis loop behaviors in ferroelectric superlattices can be related to the formation of "dead" layer and polarization continuities/discontinuities at interfaces. The "dead" layers form at the interface region consist of intermixing properties of the two constituent layers in the superlattices,[44] and their physical relationship can be explained through a discussion of interacting polarizations. It is interesting to note here that Cooper and co-workers[65] also discuss the effect of interface intermixing on the polarization enhancement in short-period superlattices through the consideration of interacting polarizations using first-principle calculations. Our study demonstrates that the change of local properties at the interface region (i.e., interface structures[44–46]) in superlattices is responsible for the deviation of ferroelectric behaviors from the bulk. This is physically consistent with recent predications from first-principle calculations, indicating the modification of local soft modes at the interface region leads to a suppression of polarization in superlattices.[66]

While the model can explain many fundamental aspects of physics associated with interface ferroelectricity in heterostructures and superlattices, it is still primitive at the current stage and still not suitable to make any quantitative analysis by fitting experimental results. This is because we consider for the simple case of the effect of interface on polarization parallel to the surface or interface with the applied electric field homogenous throughout the constituent layers. We do not discuss the effect of interface on polarization perpendicular to surface or interface, in which the depolarization field or internal electric field cannot be neglected, and it plays an additional role in governing the ferroelectricity in superlattices. In reality with polarization perpendicular to surface or interface, the inhomogeneity of polarization due to the effect of interface means that the depolarization field effect is essential. The two constituent layers in the superlattice act as potential dividers, indicating that the applied electric field is no longer homogenous throughout the superlattices. The internal electric fields form in the superlattices may distribute inhomogenously, and may or may not act as a depolarization field, depending on the polarization behaviors of the constituent layer. Further research will obviously be required to investigate in detail the case of polarization perpendicular to surface or interface.

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