Effect of Asymmetrical Interface Charges on the Hystereses, Domain Configuration and Phase Transition Characteristics of Ferroelectric Thin Films

I. B. Misirlioglu 1, M. B. Okatan 2 and S. P. Alpay 2

1Faculty of Engineering and Natural Sciences, Sabancı University, Tuzla-Orhanlı, 34956, İstanbul, Turkey

2Department of Chemical, Materials, and Biomolecular Engineering, Materials Science and Engineering Program, and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, USA

We simulate the hystereses and phase transition properties of ferroelectric films with space charges in thick (~200 nm) and thin structures (~20 nm). Epitaxial (001) PbZr0.3Ti0.7O3 thin films sandwiched between metallic electrodes on (001) SrTiO3 substrate is taken as a model system. We show that space charge accumulated near the metal-ferroelectric interfaces gives rise to a very strong imprint where only one polarization orientation is favored regardless of the sign of the external field. The space charges, when asymmetrically distributed, also lead to a smearing of the phase transition. Single-domain approximation for asymmetrical distributions of planar space charges are discussed.

Keywords: Ferroelectric thin films, thermodynamics, phase transitions, defects, interfaces, electrical domains.

1. INTRODUCTION

Developments in the integrated circuit technologies have created new demands for capacitive materials that sustain functionality at reduced thicknesses on dissimilar substrates. Ferroelectrics (FEs) have become a strong candidate in this regard owing to their switchable electric polarization below the Curie point, high dielectric, piezoelectric and pyroelectric properties. The sensitivity of ferroelectric systems to defects is well known since several decades and formation of defects during thin film fabrication is an evitable aspect that can significantly alter the properties. Defects could be that of strain-field inducing or electric field inducing type that often lead to inhomogeneities [1]. Defect fields can couple to the eigen strains or the electric dipole moment magnitudes at relatively large distances depending on the boundary conditions. These materials are also wide band-gap semiconductors that produce Schottky-type interfaces when brought in contact with metallic electrodes. [2-6]

Among the defect-induced changes in properties that are often considered as loss of functionality, an important degradation type often observed in FEs is imprint. The most common characteristic of imprint is the displacement of the polarization versus the
applied electric field hysteresis loop along the electric field axis. This gives rise to an asymmetry in the remnant polarization and also an effective variation in the coercive field defined by an off-set, \( \Delta E = E_{c_+} - E_{c_-} \), where \( E_{c_+} \) and \( E_{c_-} \) are the coercive fields on the right and left side of the hysteresis loop, respectively. Imprinted hysteresis loops can emanate from variations in deposition conditions of thin film materials that are often far from ideal. Hence, kinetic factors play an important role in the ultimate spatial stoichiometry of the film. [7-10] As perovskite FEs have a mix of ionic and covalent interatomic bonding, local deviations from the exact stoichiometry can create frozen dipoles and electrostatic fields emanating from these complexes. Furthermore, it has often been discussed that these “defects” can then trap carriers and become \( p \)- or \( n \)-type centers in the deep-trap limit. [3-6, 11] As an example, the surfaces of FE thin films are highly susceptible to creation of oxygen vacancies during processing and an electrode-FE film interface is often thought to be forming a Schottky contact accompanied by a depletion layer. While the effect of the internal electric fields due to surfaces, structural variations, and trapped charges, and other defect microstructures on the properties of FEs is well-understood, theoretical studies of the imprint phenomenon have focused on charge injection and frozen average electrostatic fields. [4,5,12,13,14-20] The motivation behind exploring the charge effects is that these formations could reduce the polarization stability and the dielectric response. [21, 22, 23]

In a recent article, we showed that internal voltage off-sets and imprint can result from asymmetrically distributed trapped space charges described through a constant planar space charge density in a simple FE capacitor structure using a non-linear thermodynamic analysis coupled with electrostatics. [24] In that work, we accounted for the space charge in discrete 2D planar layers. Our current work focuses on FE films sandwiched between metallic electrodes and we introduce position-dependent, continuous distribution of space charge along the thickness of the film. These charges are thought as fixed-field defects and are distributed inside the film as a function of position. We find that hysteresis characteristics of FE films can be altered dramatically under asymmetric spatial variations of the space charge density. It is also shown that space charges in FE thin films result in variation in the FE-paraelectric phase transition (PT) behavior, commensurate with a reduction in the transition temperature and a smearing of the transition over a temperature range instead of the sharp dielectric anomaly at the bulk Curie temperature compared to defect-free “ideal” FEs of the same composition. Following the analysis of the single domain state films with perfect electrodes, we simulate thin films structures with dead layers and check whether asymmetrically distributed space charges could favor single domain states in films with thin dead layers.

2. THEORY AND METHODOLOGY

Before we proceed with the thermodynamics of a FE film with an arbitrary volumetric variation of space charges, we first focus on the distribution of these in vacuum between two planar electrodes and their potential. To study the single domain FE film with space charges, we form a one-dimensional system where there could either be a discrete or a continuous distribution of charges. The system analyzed here has its boundaries along the \( z \)-axis and is infinite along other directions. A simple sandwich-type
capacitor structure with a sheet charge situated at a point \( k \) will have an internal potential at a point \( j \) given by:

\[
\phi_{j,k} = \frac{\rho A z_j (L - z_k)}{\varepsilon_0 L} \quad \text{for} \quad 0 \leq z_j < z_k
\]

(1)

\[
\phi_{j,k} = \frac{\rho A z_j (L - z_j)}{\varepsilon_0 L} \quad \text{for} \quad z_k < z_j \leq L
\]

(2)

which correspond to the analytical solutions of the Poisson’s equation at all other points other than the charge location when the electrodes are kept at zero potential. In Eqs. (1) and (2), \( \rho \) is the charge density, \( A \) is the area of the capacitor, \( L \) is the distance between the electrodes, \( \varepsilon_0 \) is the permittivity of free space. The indices serve to distinguish the position of the sheet charge and its potential at a given location such that \( \phi_{j,k} \) stands for the potential at \( j \) due to a charge density situated at a point \( k \). For example, it is clear that there will be two different fields in +\( z \) and −\( z \) whose magnitudes are equal (but of opposite sign) when the sheet charge is in the middle of the capacitor. We note that in the presence of a material between the electrodes, \( \varepsilon_0 \) should be replaced with \( \varepsilon_r \cdot \varepsilon_0 \) where \( \varepsilon_r \) is the background dielectric constant that is basically a measure of electronic polarizability of the ions. For a sheet of charge \( \rho \) fixed in the center, the fields pointing along +\( z \) and −\( z \) will be \( \pm \rho / 2 \varepsilon_0 \) when there is no material and \( \pm \rho / 2 \varepsilon_0 \varepsilon_r \) in the presence of a dielectric. For this study, \( \varepsilon_r \) is taken as 10, corresponding to an optical frequency refractive index of ~3.16. [25]

In a periodic or random distribution of space charge, there can be a bias field along either +\( z \) or −\( z \) directions depending on the charge density as a function of position. We assign each discrete point \( k \) a planar charge density that is infinite along \( x \)- and \( y \)-axes, i.e., in the plane of the film-substrate interface. Hereafter, we approximate the total potential at each point inside the capacitor as a sum of all potentials due to all charges in the system at that point (excluding the particular point itself). Using this superposition principle of electrostatic potential due to a charge distribution in the space between two electrodes, we can discrete-wise approximate the total potential, \( \phi \) at a point \( j \) due to the space charges situated at all \( k \) in our system as:

\[
\phi_j = \sum_k \phi_{j,k}.
\]

(3)

Thus, \( \phi_j \) defines the total potential at a point \( j \) due to all charges at points \( k \). We consider three cases corresponding to the following distributions:

i) exponentially but asymmetrically decaying charge density to zero from interfaces 1 (bottom electrode-FE) and 2 (FE-top electrode) towards the interior of the film [Figure 1 (a)] along with the induced built-in fields due to these distributions given in Figure 1 (b),

ii) symmetrical charge at both interfaces decaying to zero in the middle of the film [Figure 1 (c)] with the corresponding built-in field in Figure 1 (c)

iii) random distribution of space charge throughout the entire film, and,

iv) no space charge as the reference state.
The first and second distributions are chosen to simulate interfaces that either have high concentration of traps at the FE-electrode interfaces or are due to a Schottky-behavior resulting from band bending. The third case corresponds to film with high density of charge trapping defects throughout the volume. The total number of discrete points in the system is 500 and each cell length is taken as 0.4 nm, close to the unit cell parameter of prototypical perovskite FEs such as barium titanate \([\text{BaTiO}_3 \text{(BT)}]\) or lead zirconate titanate \([\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3 \text{(PZT \_x/1-x)}]\) with Ti-rich stoichiometries. Once the total built-in potential at each point in the system is established, the local internal field \(E\) can simply be computed from the gradient of the potential \(\phi\) along the \(z\)-axis via:

\[
E_j = -\nabla \phi_j
\]  

(4)

We should also mention here that the above approach is for a capacitor whose electrodes are kept at zero potential. In the presence of an externally applied potential, where experimentally one electrode often attains a particular sign while the other is kept at ground, the internal total potential due to the space charge distribution might vary as the boundary conditions change for the solution of the Poisson’s equation. Throughout the current work, we consider that the interaction of the applied potential with the space charge is via a straightforward vectorial addition of the electric fields at each point.

We now proceed with the thermodynamics of the ferroelectric film sandwiched between two electrodes and how space charge is introduced to the system energy. The Landau-Ginzburg-Devonshire (LGD) free energy for an epitaxial monodomain (001) ferroelectric film on a (001) cubic substrate can be expressed as:

\[
F_T = \int_0^L [F_0 + F_P + F_E + F_G - F_{ES}]dz
\]  

(5)

where \(L\) is the film thickness, \(F_0\) is the energy of the paraelectric state, \(F_P = \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) + \alpha_{12}(P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2)
\]

\[+ \alpha_{111}(P_1^6 + P_2^6 + P_3^6) + \alpha_{112}[P_1^4(P_2^2 + P_3^2) + P_2^4(P_1^2 + P_3^2) + P_3^4(P_1^2 + P_2^2)] + \alpha_{123}P_1^2 P_2^2 P_3^2\]

(6)

is the energy due to the polarization \(P_i (i=1,2,3)\) in the ferroelectric state, and \(\alpha_i, \alpha_{ij},\) and \(\alpha_{ijk}\) are the dielectric stiffness coefficients [26]. \(F_E\) in Eq. (5) is the internal elastic energy due to epitaxy given by:

\[
F_E = \frac{1}{S_{11} + S_{12}}(u_m - Q_{12}P_3^2)^2,
\]  

(7)

where \(u_m\) is the in-plane polarization-free misfit strain, \(Q_{12}P_3^2\) is the self-strain in the plane of the film due to polarization along the film thickness, and \(Q_{ij}\) and \(S_{ij}\) are the electrostrictive coefficients and the elastic compliances at constant polarization, respectively, in the contracted notation.

The gradient energy in Eq. (5) is given by:

\[
F_G = G_{33}\left(\frac{dP_3}{dz}\right)^2 + G_{13}\left(\frac{dP_1}{dz}\right)^2 + G_{23}\left(\frac{dP_2}{dz}\right)^2,
\]  

(8)

where \(G_{ij}\) are the gradient energy coefficients.

The last term entering Eq. (5) is the electrostatic energy. In its most general form, it can be expressed as:
\[ F_{ES} = \left[ E_{APP} + E(z) - \frac{1}{2} E_D(z) \right] P_3, \quad (9) \]

and the total field \( E_3 \) at a position \( j \) due to the electrostatic interactions is given as:

\[ E_3 = E_{APP} + E(z) - E_D(z) \quad (10) \]

In Eqs (9) and (10), \( E_{APP} \) is the external applied field, \( E(z) \) is the built-in field due to the space charges attaining its value from Eq. (4), and \( E_D \) is the depolarization field arising due to the polarization variations at the interfaces resulting in bound charges. \( E(z) \) and \( E_D \) are both functions of position and the latter is given as:

\[ E_D(z) = \frac{1}{\varepsilon_0} \left[ P_3 - \frac{1}{L} \int_0^L P_3 dz \right] \quad (11) \]

For thin layers (at the order of a few nanometers) and highly inhomogeneous structures, the gradient energy may have a significant effect on polarization and cannot be neglected. In our calculations, we shall assume that the gradient energy is isotropic, and thus \( G_{33} = G_{13} = G_{23} = G \). Furthermore, the in-plane biaxial internal stress state with equal orthogonal components due to epitaxy require that \( P_1 = P_2 \). Thus we obtain the following Euler-Lagrange relations from the equations of state \( \partial F_T / \partial P_3 = 0 \) and \( \partial F_T / \partial P_1 = 0 \):

\[ G \frac{d^2 P_3}{dz^2} = 2\alpha_3^m P_3 + 4\alpha_{13}^m P_3 P_1^2 + 4\alpha_{33}^m P_3^3 + 6\alpha_{111} P_3^5 \]
\[ + \alpha_{112}(4P_3 P_1^4 + 8P_3^2 P_1^2) + 2\alpha_{123} P_3 P_1^4 - \left[ E_{APP} + E_B - \frac{1}{\varepsilon_0 L} \int_0^L P_3 dz \right] \quad (12) \]

\[ G \frac{d^2 P_1}{dz^2} = 2\alpha_1^m P_1 + 2(2\alpha_1^m + \alpha_{12}^m) P_1^3 + 2\alpha_{13}^m P_1 P_3^2 + 6\alpha_{111} P_1^5 \]
\[ + 2\alpha_{112}[3P_3^5 + 3P_1^2 P_3^3 + P_1 P_3^4] + 2\alpha_{123} P_3^5 \quad (13) \]

where the \( \alpha_3^m \), \( \alpha_{13}^m \), \( \alpha_{33}^m \) are the renormalized dielectric stiffness coefficients, modified by the misfit strain, the depolarizing field, and the two-dimensional clamping of the film. [27] We note that the only dielectric stiffness coefficient that is renormalized due to the depolarizing field is \( \alpha_3^m \) and is given by:

\[ \alpha_3^m = \alpha_1 - u_m \frac{2Q_{12}}{S_{11} + S_{12}} + \frac{1}{\varepsilon_0} \quad (14) \]

as a result of the emergence of the \( P_3^5 / \varepsilon_0 \) term coming from the depolarization field energy [Eq. (9-11)]. The boundary conditions at the interfaces employed for the films are:

\[ P_1 + \lambda \frac{dP_1}{dz} \bigg|_{z=0,L} = 0 \quad (15a) \]
\[ P_3 + \lambda \frac{dP_3}{dz} \bigg|_{z=0,L} = 0 \quad (15b) \]

and \( \lambda \) is the extrapolation length. Eq. (15b) implies that there are no surface fields at the FE-electrode interfaces. Therefore, the only depolarizing field contribution in the system

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are due to the local variations of $P_3$ induced by space charges, which are weakly screened by the background dielectric constant. The materials system considered in this study is a 200 nm thick heteroepitaxial (001) PZT 30/70 on a (001) SrTiO$_3$ (ST) substrate with pseudomorphic top and bottom metallic electrodes. The equations of state given in Eq. (12) and (13) have to be solved simultaneously with the boundary conditions given in Eqs. (15a) and (b). To obtain the polarizations at different space charge and applied fields and different temperatures, we use a Gauss-Seidel iterative scheme where we start with random polarization distributions in the system that converges to the real solution after a number of iterations.

The temperature-polarization ($T$-$P_3$) curves reflect the equilibrium polarization at each temperature interval in the presence and absence of space charge distribution. The quasi-static $P_3$--$E_{APP}$ hysteresis curves are at room temperature (RT=25°C) obtained by applying a triangular field that has a maximum amplitude of $5 \times 10^8$ V/m and incremental values of $2.5 \times 10^7$ V/m, adding up to a total of 100 steps. At each field, the polarization as a function of position is computed using the iterative method detailed above. In both the temperature dependence of the polarization and the hysteresis loop computations, the values of polarization obtained for a given state are fed as initial values for the next iterative run, ensuring high convergence precision. The small signal average dielectric constant of the system along $z$ is found from:

$$\varepsilon(T, \rho) = \frac{D_3(T, \rho, E_s) - D_3(T, \rho, E_{APP} = 0)}{E_s}$$

(16)

where $D_3$ is the dielectric displacement of the film along the $z$-axis obtained at the end of the numerical iteration for zero field followed by for a small signal field, $E_s = 1$ V/m.

The in-plane misfit strain considered in all computations corresponds to a pseudomorphic (001) PZT 30/70 film on a (001) ST substrate (-1.66 % at room temperature). During the numerical iteration, although we took into account the possible presence of an in-plane polarization in PZT 30/70, the solution of the in-plane components comes out as zero for the considered strain state. In the $T$--$P$ plots, to be able clearly judge the effect of space charge and avoid complications due to thermal strain effects on the PT characteristics, we assumed both the substrate and the ferroelectric film have the same thermal expansion coefficients. The reason for this assumption is that while thermal strains as well as stress relaxation due to the formation of interfacial dislocations can easily be incorporated into the current analysis, these might mask space charge related changes in the polarization and dielectric response.

For the sake of clarity and completeness, we also would like to indicate here the modifications to the above model when one wants to consider the formation of electrical domains. To do so, we first construct a two dimensional grid with a sandwich type capacitor geometry that is 200n x kn cells where $k$ (200) is the number of cells along the film thickness (width) and each cell, $n$, has a dimension of 0.4 nm, imitating the unit cell dimensions of PZT. The LGD volumetric free energy for an epitaxial single domain (001) ferroelectric film on a (001) cubic substrate now has to be modified to take into account dead layers and can be expressed as:

$$F_T = \int \left[ w(F_0 + F_p + F_k + F_G - F_{ES}) + (1 - w)F_{DL} \right] dV$$

(17)
where \( w \) becomes zero (0) in the dead layer and is one (1) in the ferroelectric film. \( F_0 \) is the energy of the paraelectric state and \( F_P \) is the energy due to the polarization \( P_i \) \((i=1,2,3)\) in the ferroelectric state as in Eqn. (6). \( F_E \) is the internal elastic energy both due to the misfit between the film and the substrate as well as the self-strain given by:

\[
F_E = \frac{1}{2} C_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^0)(\varepsilon_{kl} - \varepsilon_{kl}^0)
\]  

which is a more general form of Eqn. (7) where \( C_{ijkl} \) is the elastic stiffness for a cubic crystal, \( \varepsilon_{11}=\varepsilon_{22} \) is the film-substrate misfit strain in the pseudocubic limit, \( \varepsilon_{ij} \) is the self-strain energy due to the paraelectric-ferroelectric phase transition in the pseudocubic film. The gradient energy has to now also take into account the variations in \( P_i \) in all directions given by:

\[
F_G = G_{33} \left( \frac{dP_3}{dz} \right)^2 + G_{31} \left( \frac{dP_1}{dx} \right)^2 + G_{13} \left( \frac{dP_1}{dz} \right)^2 + G_{11} \left( \frac{dP_1}{dx} \right)^2 + G_{23} \left( \frac{dP_2}{dz} \right)^2 + G_{21} \left( \frac{dP_2}{dx} \right)^2
\]

where \( G_{ij} \) are the gradient energy coefficients and we shall assume that it is isotropic for convenience, namely \( G \). We also neglect the variations along \( P_2 \) along \( y \) in the 2D limit. \( F_{ES} \) is the electrostatic energy of the system, \( F_{ES} = -E_iP_i \) where \( E_i \) is found from the Maxwell equation \( \text{div}D_i = 0 \) and \( D_i \) are the dielectric displacement components. Note that Eqn. (11) is also a solution for \( \text{div}D_i = 0 \) for a single domain FE film. \( F_{DL} \) is the energy of the dead layer that is assumed to be a linear dielectric. Equation (17) is minimized and the corresponding Euler-Lagrange equations are obtained from where we find the \( P \) components in the system. The dead layer, when present, is assumed to be a high-k dielectric whose dielectric constant is chosen as 20 with thicknesses as either one \((s=1)\) or two \((s=2)\) unit cells when specified. The boundary conditions we employed for \( P_{3,1} \) are \( dP_3/dz \) and \( dP_3/dx \) at the top and bottom electrode-film interface of the ferroelectric layer, consistent with Eqn. (15). The periodic boundary conditions used along the sides \((x\text{-axis})\) are:

\[
P_1(z,x = 0) = P_1(z,x = L), \quad P_3(z,x = 0) = P_3(z,x = L)
\]

\( P_i \) are coupled with the electric fields both via the equation of state and the Maxwell equation. Dirichlet boundary conditions are applied at the dead layer-electrode interface. The equations of state and the Maxwell equation are solved simultaneously employing a Gauss-Seidel iterative scheme subject to boundary conditions mentioned above. We again limit ourselves to 5000 iterations converging to a difference of \( 10^{-8} \) between consecutive iterative \( P \) solution steps when ferroelectricity exists. We only check the stability of a FE phase when interfacial space charges are present and do not attempt to reveal the domain contributions to the electrical properties.
3. RESULTS AND DISCUSSION

3.1. FE Hysteresis Loops

As one of the prominent observations in FE thin films compared to their bulk counterparts is the asymmetry in the $P$–$E_{\text{APP}}$ ($P=P_3$) hysteresis loops, we first focus on the effect of charge distributions at interfaces that decay exponentially towards the interior of the film. Such an accumulated charge density near interfaces will induce asymmetric potentials in the film resulting in internal electric fields that might favor an asymmetric variation of $P(z)$. An example of the charge distribution at interface 1 with a maximum planar density amplitude of $0.05$ C/m$^2$ at interface 1 and $1/10^{th}$ of this value at interface 2 (denoted as distribution 1 or d1), and vice versa (distribution 2, d2) are given in Figure 1(a). The built-in fields associated with d1 and d2 are plotted in Figure 1(b). The gradient of the potential is steeper towards interfaces, creating the highest internal fields in this region for both of the two cases. The maximum amplitude of the charge density can be adjusted or a random distribution could also be defined. We did so for maximum asymmetric local density amplitudes of $0.05$ C/m$^2$ and $0.075$ C/m$^2$ for both d1 and d2. Such a spatial density of space charge accumulating on either side of the capacitor structure should be expected to pin the polarization when the bias field it creates is comparable to the thermodynamic coercive field.

Figure 1. (Color online) (a) The space charge distribution for the case of asymmetric exponential decay from both film-electrode interfaces towards the interior of the film. d1 and d2 correspond to exponential charge injection from the top and bottom electrodes, respectively; (b) the built-in field due to charge distributions d1 and d2 in (a); (c) a symmetric distribution of space charges and the corresponding built-in field.
Assuming perfect electrodes and infinite extrapolation length at the interfaces, together with incorporation of the small screening contribution from the background dielectric constant to the depolarizing field term, we find the spontaneous polarization at zero field and RT the same as the analytically computed value (~ 0.7 C/m², T_c ~ 900ºC) for a mono-domain pseudomorphic (001) PZT 30/70 film on (001) ST. For a perfect film with perfect electrodes and infinite extrapolation length, there is no depolarization as the polarization is homogeneous. The $P^−E$ hysteresis in Figures 2(a) and (b), respectively are computed for the charge density distributions given in Figure 1 with the form of d1 and d2 for maximum planar densities of 0.05 C/m² and 0.075 C/m².

![Figure 2](image.png)

Figure 2. The displacement of the polarization-applied electric field hysteresis curves due to asymmetrically exponential decay of space charge distributions with a maximum amplitude of (a) 0.05 C/m² and (b) 0.075 C/m² with charge distribution d1 and d2, respectively; and (c) fully symmetric charge distribution with 0.05 C/m² at each interface. The hysteresis curves outlined by solid squares in (a), (b), and (c) correspond to films with no space charges.

As shown in Figure 2, the shift of the hysteresis loops depends on the way space charge is distributed as well as its local concentration in the film. We note that we only exchange the amplitudes of planar space charges to obtain d1 and d2 but not the sign of charge. Furthermore, another important finding is that the $P^−E_{APP}$ loops under asymmetrically distributed high space charge densities near the interfaces (such as in the case of 0.075 C/m² local planar density) can be shifted along the applied field axis such that
$E_c, E_c^*, > 0$ or $E_c, E_c^*, < 0$ compared to charge-free films for which $|E_c| = E_c$ and $\Delta E = E_c - |E_c| = 0$ [also shown in Figures 2 (a)-(c) as a reference]. Similar behavior was discussed in Ref. [1] where irradiated triglycine sulphate (TGS) samples were shown to display strongly shifted or deformed hysteresis response.

To elucidate the formation of space charges even in nearly defect-free films where behavior similar to that in Figure 2 might be observed, we provide the following example. Epitaxial growth of FE films on metallized single-crystal substrates is usually carried out at relatively high temperatures (typically in the range of 500-800°C) in controlled oxygen atmospheres followed by cooling. The sample is then taken out of the chamber for the placement of a mask to enable the growth of top electrodes, typically achieved via rf-sputtering or thermal evaporation. The diameter of the top electrodes may vary from a few hundred nanometers to a few tens of microns. This processing sequence may actually promote an asymmetric charge injection at the two FE-electrode interfaces just because a different deposition method at a different temperature was used to grow the bottom electrode, the FE film, and the top electrode. Moreover, the formation of asymmetrical space charges may result from the termination of different atomic planes of the FE film. One must also note that an average negative bias due to asymmetric surface effects or near-interface charges displaces the hysteresis loop towards the positive $E_{APP}$-axis and vice versa.

In order to provide a complimentary view of the effect of distribution of the space charges throughout the film, we give in Figure 2(c) the hysteresis loop of a FE film when there are equal concentrations of fixed space charges that decay exponentially from both interfaces. Due to the symmetry of the internal electric field distribution in the film, there is no displacement of the hysteresis loops but there is a considerable reduction in the coercive field, consistent with our recent findings\textsuperscript{17}. This is due to the the depolarization field that arises from the inhomogeneous variation of the polarization along the film thickness as well as the commensurate gradient energy. As such, the phase transition temperature $T_C$ is reduced. The behavior of the total polarization as a function of the temperature is discussed in the next section.

### 3.2. Phase Transition Temperature and Dielectric Properties

Using the methodology described in the previous section, we calculated the total polarization and the dielectric response of the FE film as a function of the temperature for a perfect film with no space charges and a film with asymmetric distribution of space charge densities. Figure 3 plots the temperature dependence of the polarization and the dielectric constant of the (001) PZT 30/70 film on (001) ST with no space charges and a space charge distribution $d_1$ with a maximum amplitude of 0.05 C/m$^2$. For the case for $\rho=0$, the spontaneous polarization in the film vanishes above $T_C$, and, as expected, there is a $\lambda$-type anomaly in the dielectric response at $T_C$. However, if there is an inhomogeneous distribution of the space charges, the phase transformation is “smeared” over a temperature interval rather than a singular transition point as it is the case for $\rho=0$. Furthermore, there is also a significant reduction in the dielectric properties near $T_C$ for films with asymmetric space charge distributions (Figure 3).
Figure 3. (Color online) Total polarization and the dielectric constant as a function of temperature in the absence of space charges and with space charges (d1, with a maximum of 0.05 C/m²).

For asymmetric variations of the space charge, there is a nearly temperature-insensitive polarization above the effective $T_C$ that is essentially the built-in polarization due to the space charges. In the case of higher values of the space charge density, the transition becomes a very gradual one, almost a linear variation of polarization with temperature with no apparent phase transformation point. While there is a small reduction in the polarization values and $T_C$, the latter is considerably more pronounced for a system with a random distribution of space charges. We note here the space charge concentrations may not necessarily remain constant as it is assumed in our analysis at temperatures near $T_C$ and could be expected to be reduced (or entirely neutralized) via thermally excited carriers. Such a process may thus reduce (or completely eliminate) the built-in fields at temperatures near the $T_C$ of strained PZT 30/70.

In Figure 4, we provide the temperature dependence of the total polarization and the dielectric response for the case of a random space charge variation throughout the film thickness. Such a distribution introduces almost a linearly varying built-in field that changes sign near the middle of the film. This field results in a drastic reduction in $T_C$ while there is a sharper dielectric anomaly at $T_C$ compared to the conditions corresponding to asymmetric distribution of space charges discussed in connection with Figure 3. We also note that the dielectric constant of the film with random variation of high density space charges at RT given in Figure 4 is higher than the films with $\rho=0$ because of the significant reduction in $T_C$. Above the effective $T_C$, there is nearly no net built-in polarization due to the opposite but nearly equal polarization profile in the two halves of the film with respect to the middle of the film at zero field.
In Figure 5, we give the temperature dependence of the total polarization and the dielectric response in the case of a symmetrical charge distribution given in Figure 1(c). A symmetrical variation in the planar space charge concentration removes any net internal bias in the system and the dielectric anomaly at $T_C$ is nearly the same as that of the perfect film with no net built-in polarization except a slight reduction in $T_C$ and $P$. From Figure 5, one can observe a near zero net built-in polarization above $T_C$ as a consequence of the nearly equal internal field due to space charges in the two halves of the film. Due to the absence of a net bias field, the induced polarization due to space charges is weak and there is no smearing of the dielectric response at $T_C$.

The fields due to space charges are mostly confined to the near-interface regions with exactly equal but opposite signs, giving rise to a symmetrical polarization variation below $T_C$. Thus, the small reduction in the remnant polarization at all temperatures below $T_C$ compared to the charge-free film is mostly due to the inhomogeneous variation of the local polarization near the film-electrode interfaces. The changes in the polarization near
the electrode interfaces also increases the gradient energy increase in the film. Therefore, the combination of both the depolarization and the gradient energy act to slightly reduce $T_C$.

As a result, the gradual nature of the transition in the presence of asymmetric space charge dramatically reduces the dielectric anomaly that is a characteristic of the charge-free film in addition to a considerable drop in $T_C$. For thinner films, the same charge density distribution whose potential will become steeper (for zero potential at the electrodes), creating larger internal built-in fields can be expected to render a stronger $P$ pinning highly probable. The strongly inhomogeneous fields acting at distances at the order of a few nanometers due to space charge lead to greater spatial variation of the polarization and hence yield higher depolarizing fields, resulting in a larger reduction in $T_C$, similar to the finite size effect. This decrease should certainly be much more dramatic for highly asymmetrical distributions of space charges. We note that even if the switchable FE polarization disappears at temperatures above $T_C$, the space charge induced temperature-independent polarization will remain. In addition, a stronger smearing of the transition temperature could also be expected as discussed in Ref. 28. This is, of course, possible for materials with low $T_C$ wherein thermally excited neutralization mechanisms of space charges will not be significant. For films with high $T_C$, thermally excited carriers from the traps could take effect in neutralization of the space charges at elevated temperatures, reducing the smearing effects.

3.3. Impact on electrical domain formation

In this section, we discuss the RT results for electrical domain stabilities when one of the interfaces in a thin PZT 30/70 film has a high concentration of charge. We take into account the presence of space charge as a “sheet potential” that correspond to a weak charge density of around $1 \times 10^{-19} \text{ /nm}^2$. Note that this sheet potential is placed at the dead layer-FE film interface. We realize that a thin dead layer at the order of one or two unit cell thickness is not sufficient to trigger electrical domains in a 200 nm thick film and therefore we focus on a 20.8 nm thick film (52 unit cells). The 20.8 nm thick film splits into domains when $s=2$ that creates imperfect screening of the polarization charges at the interfaces as seen in Figure 6a. The dielectric constant of the dead layer is taken as 20 for demonstrative purposes. It must be kept in mind that the domain period is a function of the dielectric constant of the dead layer and that very high values can even stabilize a single-domain state. The latter option, however, is kept outside the scope of this section for a compact and focused discussion.
Clearly, rather low densities of asymmetrical space charge can overcome the depolarizing fields through altering the potential distribution in the films. The position of the charges with respect to the electrode-film interfaces plays an important role in the way the charge-induced fields interact with the depolarizing fields. To check with this, we placed the sheet of potential imitating a sheet of space charge in the middle of the film and ran our simulations. After 5000 iterations, we obtained a nearly monodomain, negatively polarized system with the two halves with respect to the sheet potential in the centerline having a step-wise difference. Keeping in mind that the FE film has dead layers, this case demonstrates the probable impact of localized charges on domain stabilities. It is straightforward to notice that the FE film does not get polarized in +z and –z respectively but along –z only due to the large electrostatic energy cost as well as the gradient energy cost at the center where \( P_z \) would change sign. Quite large densities of local charges might change this picture but to stay focused, we refrain ourselves from analyzing extreme cases which is possible otherwise. In addition, we present here a 20.8 nm thick film: The competition between the depolarizing effects and the space charge fields should be expected to become more prominent in structures that are just a few nanometers thick, namely ultrathin films.

4. CONCLUSIONS

In this work, using the LGD formalism coupled with an electrostatic analysis, we have investigated the effects of a continuous distribution of planar space charges along
the film thickness on the phase transition characteristics, hysteresis response, and dielectric properties of epitaxial (001) PZT 30/70 films between metallic electrodes on (001) STO substrates. Asymmetrically distributed space charges result in displacements in the $P-E_{\text{APP}}$ hysteresis curves along the applied field axis and may even give rise to coercive fields $E_{C^-}, E_{C^+} > 0$ or $E_{C^-}, E_{C^+} < 0$ compared to charge-free films for which $|E_{C^-}| = E_{C^+}$ and $\Delta E = E_{C^+} - |E_{C^-}| = 0$. These trapped charges residing at deep levels may significantly smear out the FE phase transition and reduce $T_C$. If the space charges are symmetrically distributed, the FE hysteresis loops shrink along both the polarization and the applied field axes but remain centered at the origin. For relatively high charge densities, we find that a monodomain FE film cannot be switched from one polarization state to another under typical cyclic (e.g., completely reversed sinusoidal) electrical bias with an amplitude $2E_{\text{APP}}$. A polydomain structure may form in FE films with dead layers to minimize internal depolarizing fields originating from local variations in the polarization. However, the strong internal bias due to an asymmetric charge distribution may preclude the generation of electrical domains. The latter should certainly be a strong function of film thickness, especially for the ultrathin structures. Our analysis presented herein is in the limit of thermodynamics and future time-dependent studies should focus on nucleation and growth kinetics of domains during switching in the presence of a spatial space charge distribution.

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