Hysteretic Dynamics of Polarization and Internal Field in Ferroelectric Superlattices

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Abstract. Based on the time-dependent Landau-Khalatnikov theory, we study the dynamics of polarization switching in the ferroelectric superlattices comprising alternate layers of ferroelectric and paraelectric. The effects of interface intermixing are considered where the intermixed layer is formed at the interface with properties different from its constituent layers. In addition to the polarization hysteresis, the internal electric field also exhibits a hysteresis behaviour in response to a time-dependent driving applied electric field. The influence of thickness ratio and temperature on the hysteretic dynamics of ferroelectric superlattices are examined.

Keywords: Ferroelectric, Superlattices, Landau-Khalatnikov theory

I. INTRODUCTION

Ferroelectrics are polar materials that exhibit a spontaneous polarization that can be reversed by an applied electric field [1], for example, perovskite-oxide ferroelectric such as $PbTiO_3$. The ferroelectric superlattice is a periodic structure of layers of two or more different materials. In fact, ferroelectric superlattice is a potential replacement of ordinary ferroelectric bulk or thin-film in a wide range of electronics applications, due to its enhanced ferroelectric properties and the flexibility to tune its physical properties which are unachievable in its parent compounds [2].

In ferroelectric superlattices or multilayer structures, the intermixed layers may form at interfaces between the multilayers [3, 4]. These interface intermixed layers with properties different from those of parent compound layers may affect the properties of superlattices. We recently proposed a thermodynamic model based on the Landau-Ginzburg theory to study the phase transitions in ferroelectric superlattices [5-7]. An interface energy term is introduced in the free energy to describe the formation of an intermixed layer with properties different from its parent compounds. These intermixed layers are mutually coupled through the local polarization at interfaces [8]. The polarization discontinuity and screening charge in ferroelectric superlattices were studied based on our model [9, 10]. We found that the properties of ferroelectric superlattice can be strongly influenced by the alternative appearance of accumulated screening charge at interface. We extended our work to study the hysteresis behaviours in ferroelectric superlattices. In addition to the usual polarization hysteresis loop, the internal electric field also demonstrates a hysteresis loop behaviour [11, 12].

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II. THEORY

We consider a periodic ferroelectric superlattice composed of alternating layers of $PbTiO_3$ (PT) as ferroelectric and $SrTiO_3$ (ST) as paraelectric which grown on an ST substrate as shown in Fig. 1. Since the polarization is perpendicular to the interface, the depolarization field can't be ignored. Hence, the Helmholtz free energy per unit area of the PT/ST superlattice with periodic thickness $d = d_{PT} + d_{ST}$ is given as [5]:

$$F = \int_{-d_{PT}}^{0} f_{PT} dz + \int_{0}^{d_{ST}} f_{ST} dz + F_I \tag{1}$$

where the free energy density of PT and ST are given as:

$$f_j = \alpha_j^* p_j^2 + \beta_j^* p_j^4 + \gamma_j p_j^6 + \frac{\kappa_j}{2}\left(\frac{dp_j}{dz}\right)^2 + \left(\frac{c_{11,j}^2 + c_{11,j}c_{12,j} - 2c_{12,j}^2}{c_{11,j}}\right)u_{m,j}^2 - \frac{1}{2}E_{int,j}p_j - E_{ext}p_j \tag{2}$$

p_j denote the polarization of layer j (j: PT or ST). $\alpha_j^* = \alpha_j + 2\left(c_{12,j}g_{11,j}/c_{11,j} - g_{12,j}\right)u_{m,j}$ and $\beta_j^* = \beta_j - g_{11,j}^2/2c_{11,j}$. α_j (temperature dependent), β_j and γ_j are the Landau parameters. $c_{i,j}$ and $g_{i,j}$ are the elastic stiffness coefficients and electrostrictive constants. $u_{m,j} = \left(a_s - a_j\right)/a_s$ represent the in-plane misfit epitaxial strain due to lattice mismatch between layers and substrate [13]. a_s and a_j are the lattice parameter of the substrate and the cubic cell lattice constant of layer j. κ_j is the gradient coefficient, E_{ext} is the external applied electric field and $E_{int,j}$ is the internal electric field in layer j.

The interface energy F_I is:

$$F_I = \frac{\lambda_0}{2\varepsilon_0}\left[\left(p_{PT}(0) - p_{ST}(0)\right)^2 + \left(p_{PT}(-d_{PT}) - p_{ST}(d_{ST})\right)^2\right], \tag{3}$$

where λ_0 is the temperature-independent interface intermixing parameter and ε_0 is the dielectric permittivity in the vacuum. In particular, λ_0 describes the interface intermixing effect in superlattices. If $\lambda_0 \neq 0$, intermixed layers with properties different from those of both constituents is formed at the interface region. No intermixed layer is formed, if $\lambda_0 = 0$.

In order to simulate the hysteresis loop, the Landau-Khalatnikov equation is employed:

$$\Gamma_j \frac{\partial p_j}{\partial t} = -\frac{\delta F_j}{\delta P_j} \tag{4}$$

where j: PT or ST, t is the time taken, Γ_j is the viscosity coefficient of layer j. The switching dynamics are studied by applying a sinusoidal external applied electric field:

$$E_{ext} = E_0 \sin(2\pi f t)$$

where E_0 is the amplitude of the external applied electric field, f is the frequency.

The average polarization is given as:

$$P = \frac{1}{L}\left(\int_{-d_{PT}}^{0} p_{PT} dz + \int_{0}^{d_{ST}} p_{ST} dz\right).$$

Likewise, the average internal electric field is defined as:

$$E_{int}=\frac{1}{L}\left(\int_{-d_{PT}}^{0}E_{int,PT}dz+\int_{0}^{d_{ST}}E_{int,ST}dz\right),$$

where the periodic thickness is $d = d_{PT} + d_{ST}$.

III. RESULTS AND DISCUSSION

In the present study, the thermodynamic coefficients and elastic constants of PT and ST used in the calculation are adopted from Ref [5]. 1 unit cell (*u.c.*) is taken approximately as 0.4 *nm* and the correlation length is defined as $\xi_0 = \sqrt{\kappa_f/(\alpha_{0f}T_{0f})} \sim 0.6nm$. The lattice constants in the paraelectric state for PT and ST are a_{PT} = 3.969 Å and a_{ST} = 3.905 Å, respectively. The interface intermixing parameter is set as $\lambda_0 = \xi_0$ indicating an intermixed layer with inhomogeneous properties is formed at the interface. The dimensionless frequency and time are introduced as $\tilde{f} = f \times t_0$ and $\tilde{t} = t/t_0$, where $t_0 = \Gamma_{PT}/(T_{0,PT}\alpha_{0,PT})$. In the calculation, the following parameter values are used: $\tilde{f} = 0.04$, and $\Gamma_r = \Gamma_{PT}/\Gamma_{ST} = 1$.

Fig. 2 shows the profiles of polarization and internal electric field of PT/ST superlattice with different thickness ratios at $T = 298$K without an external applied electric field. Since the interface intermixing parameter is $\lambda_0 = \xi_0$, the intermixed layer is formed at the interface of the PT/ST superlattice. Hence, it gives rise to the inhomogeneity of polarization and internal electric field near the interface. Overall, the polarization is enhanced with an increasing thickness ratio d_{PT}/d_{ST} from $5/8 \rightarrow 5/5 \rightarrow 8/5$ (in *u.c.*). Note that the negative sign of the internal electric field in the PT layer indicates that it is acting a depolarization and suppresses the polarization in that layer. On the other hand, the positive sign of the internal electric field in the ST layer means it induces the polarization in the ST layer although it is paraelectric with no spontaneous polarization at room temperature.

Fig. 3 illustrate the effect of thickness ratio d_{PT}/d_{ST} (in *u.c.*) on the polarization-applied electric field ($P - E_{ext}$) hysteresis loop of PT/ST superlattice. As the thickness ratio increase from $5/8 \rightarrow 5/5 \rightarrow 8/5$ (in *u.c.*), the area of $P - E_{ext}$ hysteresis loop increases. The remnant polarization (the value of P when $E_{ext} = 0$) for the thickness ratio $5/8$, $5/5$, $8/5$ are: $P_r = 0.1937\text{C/m}^2$, $P_r = 0.2568\ \text{C/m}^2$ and $P_r = 0.3368\ \text{C/m}^2$ respectively. The coercive fields E_c (the required E_{ext} to bring the P to zero) increase with increasing the thickness ratio from $5/8 \rightarrow 5/5 \rightarrow 8/5$, and their values are: 7.259×10^7 V/m, 9.193×10^7 V/m and 11.779×10^7 V/m.

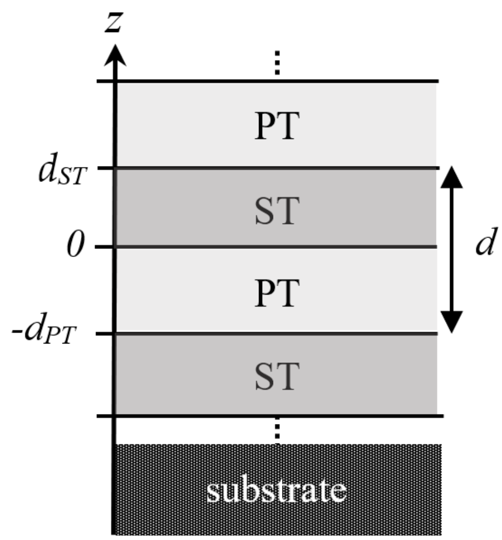

FIGURE 1. Schematic illustration of a periodic PT/ST superlattices on a ST substrate. The thickness of PT layer and ST layer are d_{PT} and d_{ST}.

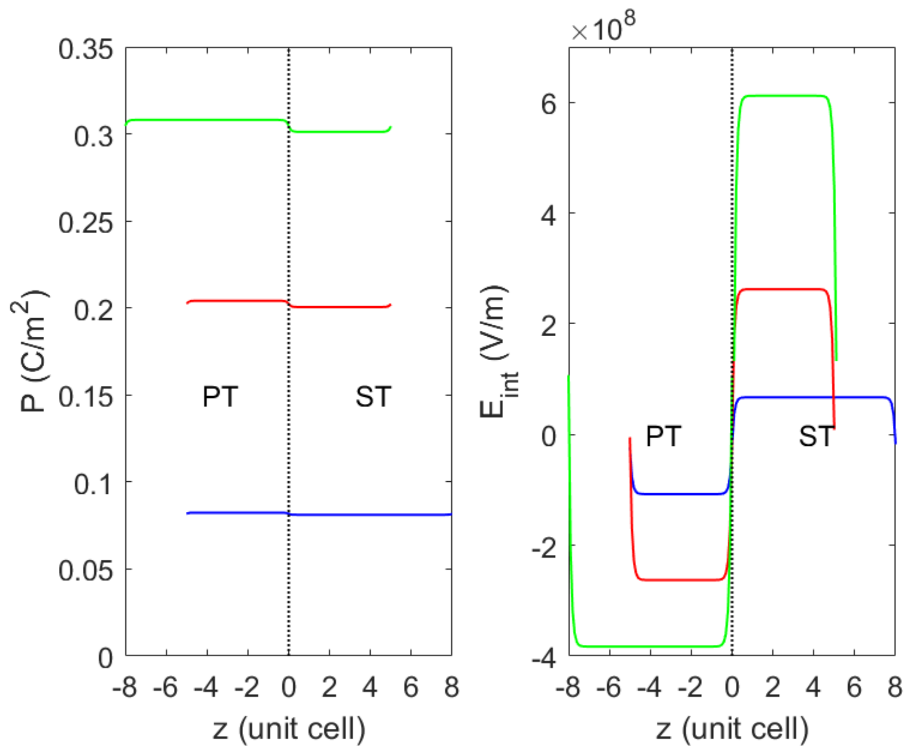

FIGURE 2. The profiles of polarization and internal electric field of PT/ST superlattices with $\lambda_0 = \xi_0$ at $T = 298$K. The thickness ratio d_{PT}/d_{ST}: 5*u.c*/8*u.c* (blue line), 5*u.c*/5*u.c* (red line), 8*u.c*/5*u.c* (green line).

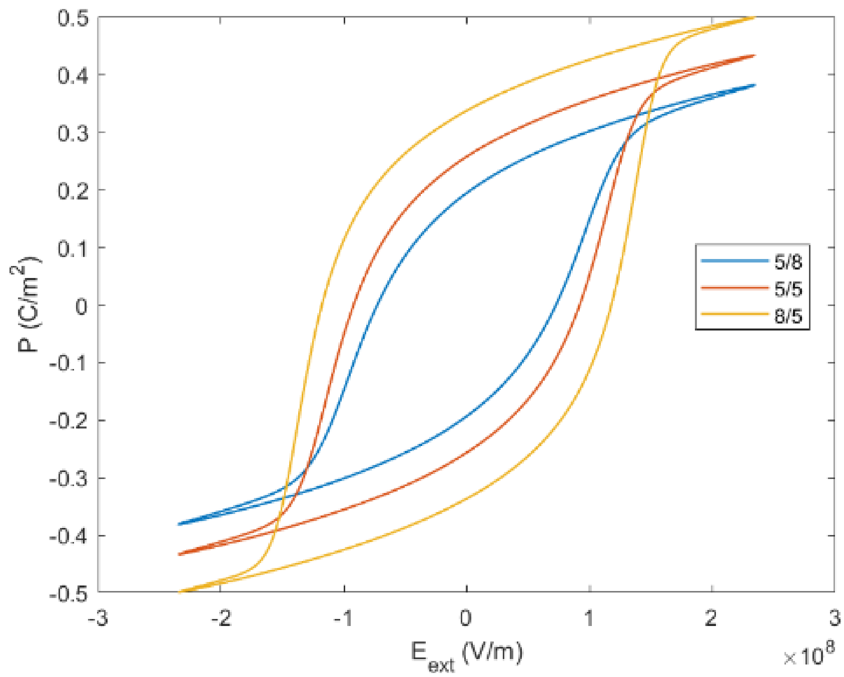

FIGURE 3. Polarization-applied electric field ($P - E_{ext}$) hysteresis loops of PT/ST superlattices with $\lambda_0 = \xi_0$ at $T = 298$K.

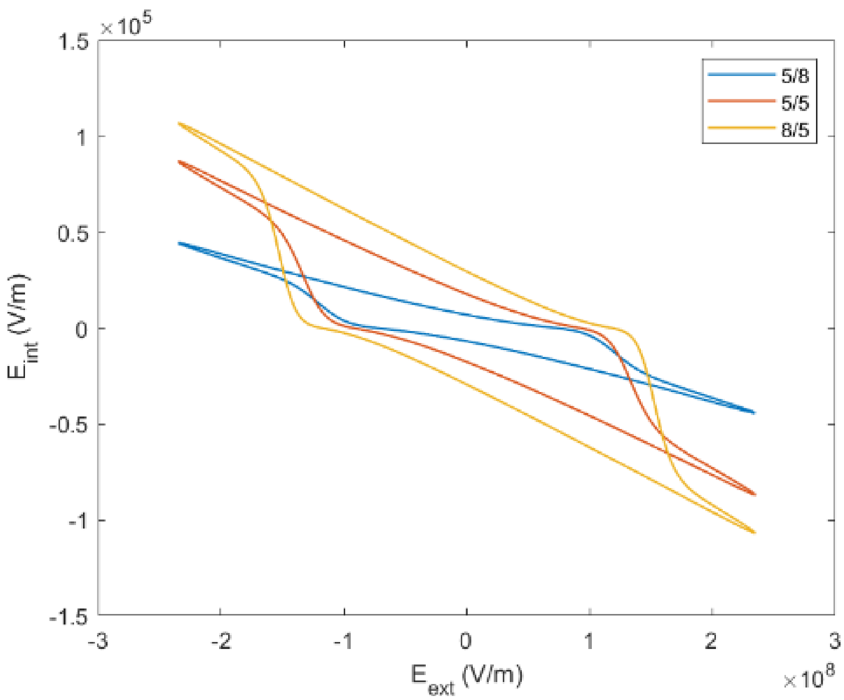

FIGURE 4. Internal electric field-applied electric field ($E_{int} - E_{ext}$) hysteresis loops of PT/ST superlattices with $\lambda_0 = \xi_0$ at $T = 298$K.

Interestingly, the internal electric field-applied electric field ($E_{int} - E_{ext}$) hysteresis loop is observed as shown in Fig. 4. Overall, the area of $E_{int} - E_{ext}$ loop increases with increasing thickness ratio d_{PT}/d_{ST}. Similar to remnant polarization, we introduce the remnant internal electric field which is the value of E_{int} when $E_{ext} = 0$ [12]. As the thickness ratio increases from $5/8 \rightarrow 5/5 \rightarrow 8/5$, the remnant internal electric fields E_r rise from 0.689×10^4 V/m $\rightarrow 1.771 \times 10^4$ V/m $\rightarrow 2.944 \times 10^4$ V/m. It is important to note that the increase of thickness ratio d_{PT}/d_{ST} will enhance the ferroelectricity (P and E_{int}) of the PT/ST superlattice due to the high proportion of the ferroelectric component $PbTiO_3$ in the superlattice.

The influence of the temperature on the $P - E_{ext}$ hysteresis loop of PT/ST superlattice with thickness ratio $d_{PT}/d_{ST} = 5/5$ (in *u.c.*) for different temperatures are illustrated in Fig. 5. Basically, the area of $P - E_{ext}$ loop decreases with increasing temperature. As temperature rises from $200\text{K} \rightarrow 298\text{K} \rightarrow 400\text{K}$, the remnant polarization P_r drops from $0.2986\text{C/m}^2 \rightarrow 0.2568\text{C/m}^2 \rightarrow 0.2118\text{C/m}^2$. Likewise, the coercive field E_c declines from 10.90×10^7 V/m $\rightarrow 9.193 \times 10^7$ V/m $\rightarrow 7.651 \times 10^7$ V/m as well.

The effect of the temperature on the $E_{int} - E_{ext}$ hysteresis loop of PT/ST superlattice with thickness ratio $d_{PT}/d_{ST} = 5/5$ (in *u.c.*) for different temperatures are shown in Fig. 6. As temperature increases from $200\text{K} \rightarrow 298\text{K} \rightarrow 400\text{K}$, there has been a gradual fall in the area of $E_{int} - E_{ext}$ loops. The remnant internal electric fields E_r fell from 2.517×10^4 V/m $\rightarrow 1.771 \times 10^4$ V/m $\rightarrow 1.196 \times 10^4$ V/m. In general, an increase in temperature will cause a decrease in the polarization of ferroelectric materials. Likewise, the polarization and internal electric field of PT/ST superlattice are suppressed by the increase in temperature.

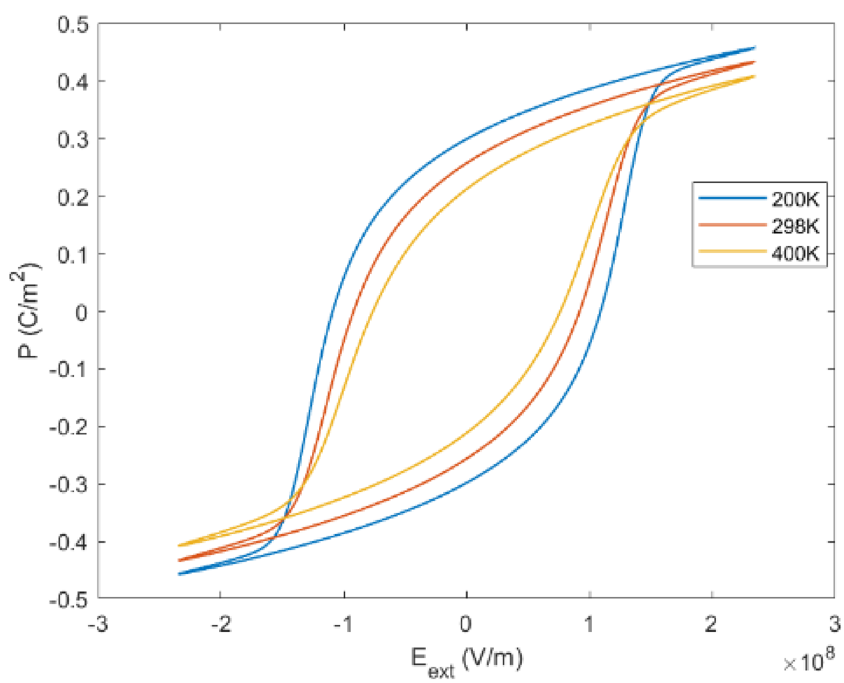

FIGURE 5. Polarization-applied electric field ($P - E_{ext}$) hysteresis loops of PT/ST superlattices with $\lambda_0 = \xi_0$ for thickness ratio $d_{PT}/d_{ST} = 5/5$.

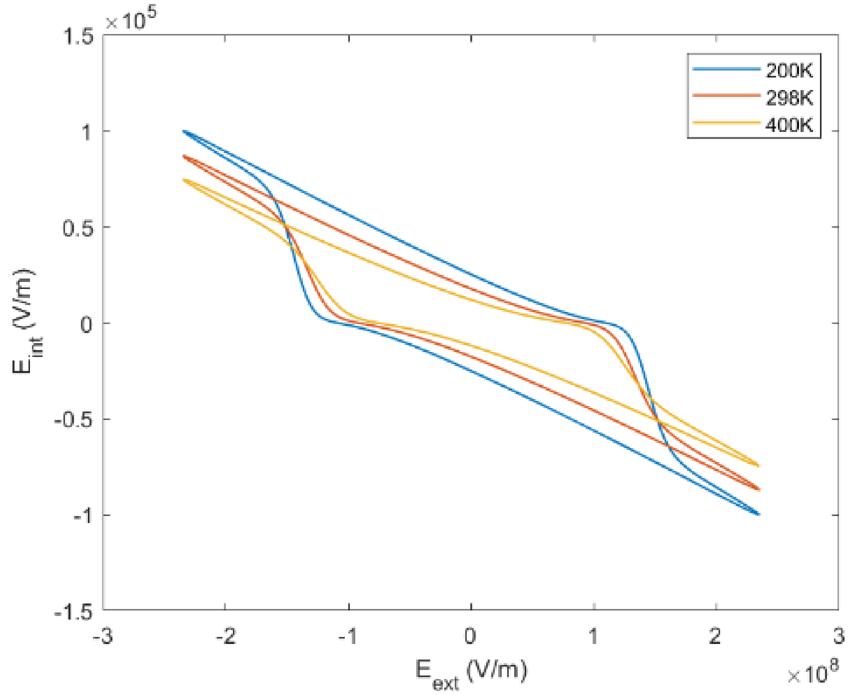

FIGURE 6. Internal electric field-applied electric field ($P - E_{ext}$) hysteresis loops of PT/ST superlattices with $\lambda_0 = \xi_0$ for thickness ratio $d_{PT}/d_{ST} = 5/5$.

CONCLUSION

In conclusion, we have studied the hysteretic dynamics of polarization and internal electric field in ferroelectric superlattices consist of alternating layers of ferroelectric and paraelectric using the Landau-Khalatnikov equation. In addition to the polarization-applied electric field ($P - E_{ext}$) hysteresis loop, the internal electric field-applied electric field ($E_{int} - E_{ext}$) hysteresis loop is also observed in our calculations. Our results reveal that the thickness ratio and temperature have a strong influence on the properties of $P - E_{ext}$ and $E_{int} - E_{ext}$ hysteresis loops.

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