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Modulated internal electric field, dielectric susceptibility and polarization in ferroelectric superlattices

Kok-Geng Lim[a], Khian-Hooi Chew[a,*], Lye-Hock Ong[b], Makoto Iwata[c]

[a]Department of Physics, Universiti Malaya, 50603 Kuala Lumpur, Malaysia
[b]School of Physics, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia
[c]Department of Engineering Physics, Electronics and Mechanics, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

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Abstract

A thermodynamic model for describing interface intermixing in a superlattice combining a ferroelectric and a paraelectric is developed. Formation of intermixed layer at interfaces leads to a periodic modulation of ferroelectric properties in these superlattices. Spatially-varying internal electric field, dielectric susceptibility and polarization of these superlattices are calculated. Effects of modulation period and temperature on the internal electric field, dielectric susceptibility and polarization of these superlattices with inhomogeneous properties are examined. Correlation between these ferroelectric properties is established and discussed.

Keywords: B. Interfaces; C. Ferroelectric properties; Superlattice

1. Introduction

Ferroelectric superlattices present an opportunity for developing artificial structures with fascinating properties for device applications. Superlattices combining a ferroelectric and a paraelectric have been studied extensively both by experiment and theory [1–6]. Induced changes in polarization due to electrostatic coupling can have significant effects on the superlattice properties [2]. Epitaxial strains are well known to have a strong impact on the properties of these superlattices [7]. The properties of these superlattices can be manipulated by changing the ferroelectric volume fraction [8]. Interface coupling [1,9] and intermixing [4,10] effects have also been shown to be important in these superlattices.

In this work, a thermodynamic model for describing a superlattice comprising alternate layers of ferroelectric and paraelectric is developed. The superlattice is modeled by considering them as layers of strained ferroelectric or paraelectric with appropriate electrostatic boundary conditions [3,11]. Torres-Pardo et al. [12] recently studied local structural distortions in PT/ST superlattices and identified the local distortion across the interface. Their work indicates the existence of an inhomogeneous polarization profile in superlattices. Unlike other uniform polarization model [2,4,8], in homogeneous ferroelectric properties are considered. The relationship between these ferroelectric properties including internal electric field, dielectric susceptibility and polarization is examined and discussed.

2. Theory

We consider a periodic superlattice consisting of alternate layers of ferroelectric and paraelectric, which grows on substrate. Hereafter, we denote as ferroelectric/paraelectric superlattices. By assuming that all spatial variation of polarization takes place along the z-direction, the Helmholtz free energy [11,13] per unit area for one period of the superlattice can be expressed as

$$F = \int_{-d_{FE}}^{0} f_{FE} dz + \int_{0}^{d_{PE}} f_{PE} dz + F_i \tag{1}$$

where the first and second terms denote the free energy per unit area of ferroelectric (FE) layer with thickness d_{FE} and the free energy per unit area of paraelectric(PE) layer with

*Corresponding author Tel.: +603 7967 4022; fax: +603 7967 4146.
E-mail address: khchew@um.edu.my (K.-H. Chew).

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thickness d_{PE} respectively. f_j(j: FE or PE) is the free energy densities

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

where p_j corresponds to the polarization of layer j.$\alpha_j^* = \alpha_j + 2(c_{12j}g_{11j}/c_{11j} - g_{12j})u_{mj}$ and $\beta_j^* = \beta_j - g_{11j}^2/2c_{11j}$.$\alpha_j$,$\beta_j$ and γ_j are the Landau coefficients. c_{11j} and c_{11j} are the elastic stiffness coefficients. g_{11j} and g_{12j} denote the electrostrictive constants. $u_{mj} = (a_s - a_j)/a_s$ denotes the in-plane misfit strain induced by the substrate due to the lattice mismatch. a_j is the unconstrained equivalent cubic cell lattice constants of layer j and a_s is the lattice parameter of the substrate. $E_{d,j}$ is the internal electric field of the layer j and E_{ext} is the external electric field.

The interface energy is given by [5,6,11]

$$F_I = \frac{\lambda_0}{2\varepsilon_0}(p_{FE0} - p_{PE0})^2 \tag{3}$$

where $p_{j,0}$ denotes the interface polarizations of layer j. ε_0 is the permittivity in vacuum. Parameter λ_0 describes the intermixing at interfaces [5,6,11]. If $\lambda_0 \neq 0$, an intermixed layer with properties different from its individual layers is formed at the interface region. No intermixed layer is formed, if $\lambda_0 = 0$.

The Euler–Lagrange equations follow from Eqs. (1) and (2) are

$$\kappa_j \frac{d^2 p_j}{dz^2} = 2\alpha_j^* p_j + 4\beta_j^* p_j^3 + 6\gamma_j p_j^5 - \frac{1}{2}E_{d,j} - E_{ext}, \tag{4}$$

and the boundary conditions for the polarization at interfaces are [5,6,11]

$$\begin{aligned}
-\kappa_{FE}\left.\frac{dp}{dz}\right|_{z=-d_{FE}} + \frac{\lambda_0}{\varepsilon_0}[p_{FE}(-d_{FE}) - p_{PE}(d_{PE})] = 0,\\
\kappa_{PE}\left.\frac{dp}{dz}\right|_{z=0} + \frac{\lambda_0}{\varepsilon_0}[p_{FE}(0) - p_{PE}(0)] = 0,\\
\kappa_{FE}\left.\frac{dp}{dz}\right|_{z=0} + \frac{\lambda_0}{\varepsilon_0}[p_{FE}(0) - p_{PE}(0)] = 0,\\
-\kappa_{PE}\left.\frac{dp}{dz}\right|_{z=d_{PE}} + \frac{\lambda_0}{\varepsilon_0}[p_{FE}(-d_{FE}) - p_{PE}(d_{PE})] = 0.
\end{aligned} \tag{5}$$

In the present study, we consider the simple case where there is no free charge. From the Maxwell's equations $\nabla \times D = 0$ and $\nabla \times E = 0$, we obtain the electrostatic equations [3,11].

$$\varepsilon_0 \frac{dE_j}{dz} + \frac{dP_j}{dz} = 0. \tag{6}$$

where $\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P}$ is the electric displacement and $E_j = E_{d,j} + E_{ext}$. Using $E_j = -\nabla\phi_j$, the continuity of electric displacement at interface becomes [11]

$$\begin{aligned}
-\varepsilon_0\left.\frac{d\varphi_{FE}}{dz}\right|_{z=0} + \varepsilon_0\left.\frac{d\varphi_{PE}}{dz}\right|_{z=0} = -(p_{FE}(0) - p_{PE}(0)),\\
-\varepsilon_0\left.\frac{d\varphi_{FE}}{dz}\right|_{z=-d_{FE}} + \varepsilon_0\left.\frac{d\varphi_{FE}}{dz}\right|_{z=d_{PE}} = -(p_{FE}(-d_{FE}) - p_{PE}(d_{PE})),
\end{aligned} \tag{7a}$$

and the continuity of tangential component of electric field gives the following conditions on the electric potentials [11]

$$\begin{aligned}
\varphi_{FE}(0) = \varphi_{PE}(0),\\
\varphi_{PE}(-d_{FE}) = \varphi_{PE}(d_{PE}).
\end{aligned} \tag{7b}$$

By making use of $E_{d,j}(z) = 1/\varepsilon_0(D - p_j(z)) - E_{ext}$ and the permittivity compliance [14] of $\partial D/\partial E_{ext} = \varepsilon_0(1+\overline{\chi})$, the dielectric susceptibility of superlattices can be obtained by the differentiation of Eq. (4) with respect to $E_{ext}(E_{ext} \to 0)$ as

$$\kappa_j \frac{d^2\chi_j}{dz^2} = \left(2\alpha_j^* + 12\beta_j^* p_j^2 + 30\gamma_j p_j^4\right)\chi_j - \frac{1}{2\varepsilon_0}(\overline{\chi} - \chi_j(z)) - \frac{1}{\varepsilon_0} \tag{8}$$

where $\overline{\chi}$ is the mean dielectric susceptibility of the superlattice.

Differentiation of Eq.(5) with respect to E_{ext} yields the boundary conditions for the dielectric susceptibility at interface as

$$\begin{aligned}
-\kappa_{FE}\left.\frac{d\chi}{dz}\right|_{z=-d_{FE}} + \frac{\lambda_0}{\varepsilon_0}[\chi_{FE}(-d_{FE}) - \chi_{PE}(d_{PE})] = 0,\\
\kappa_{PE}\left.\frac{d\chi}{dz}\right|_{z=0} + \frac{\lambda_0}{\varepsilon_0}[\chi_{FE}(0) - \chi_{PE}(0)] = 0,\\
\kappa_{FE}\left.\frac{d\chi}{dz}\right|_{z=0} + \frac{\lambda_0}{\varepsilon_0}[\chi_{FE}(0) - \chi_{PE}(0)] = 0,\\
-\kappa_{PE}\left.\frac{d\chi}{dz}\right|_{z=d_{PE}} + \frac{\lambda_0}{\varepsilon_0}[\chi_{FE}(-d_{FE}) - \chi_{PE}(d_{PE})] = 0.
\end{aligned} \tag{9}$$

The average internal electric field is

$$\overline{E}_d = \int_{-d_{FE}}^{0} E_{d,FE}dz + \int_0^{d_{PE}} E_{d,PE}dz \tag{10}$$

where the periodic thickness $L = d_{FE} + d_{PE}$. The average polarization of superlattice is defined as

$$\overline{P} = \int_{-d_{FE}}^{0} p_{FE}dz + \int_0^{d_{PE}} p_{PE}dz, \tag{11}$$

and the mean dielectric susceptibility $\overline{\chi}$ of the superlattice is given by

$$\frac{1}{1+\overline{\chi}} = \frac{1}{L}\int_{-d_{FE}}^{d_{PE}} \frac{1}{1+\chi_j(z)}dz. \tag{12}$$

In this work, Eqs. (4) and Eqs. (6) are solved numerically subject to the boundary conditions of Eq. (5), Eq. (7a) and Eq. (7b). After that, by inserting the result of polarization and electrostatic potential into Eqs. (8), the configuration of dielectric susceptibility can be calculated numerically subject to the boundary conditions Eq. (9).

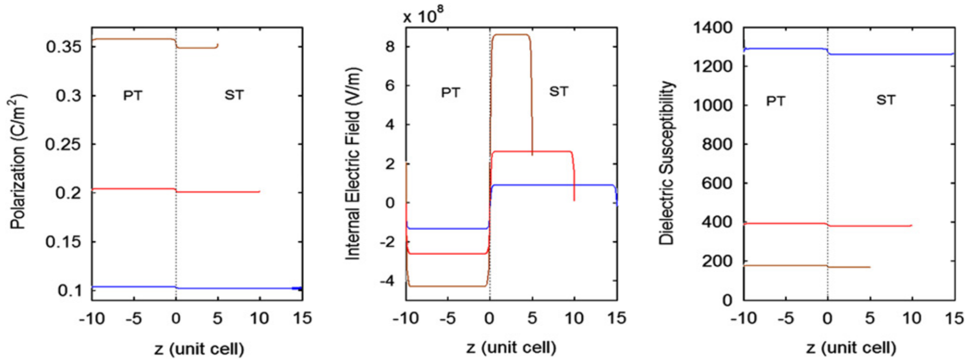

Fig. 1. Profiles of polarization, internal electric field and dielectric susceptibility of PT/ST superlattice at $T=298$ K.The three lines represent different period thickness with ratio d_{FE}/d_{PE} (in *u.c.*): 10/15 —, 10/10 — and 10/5 —.

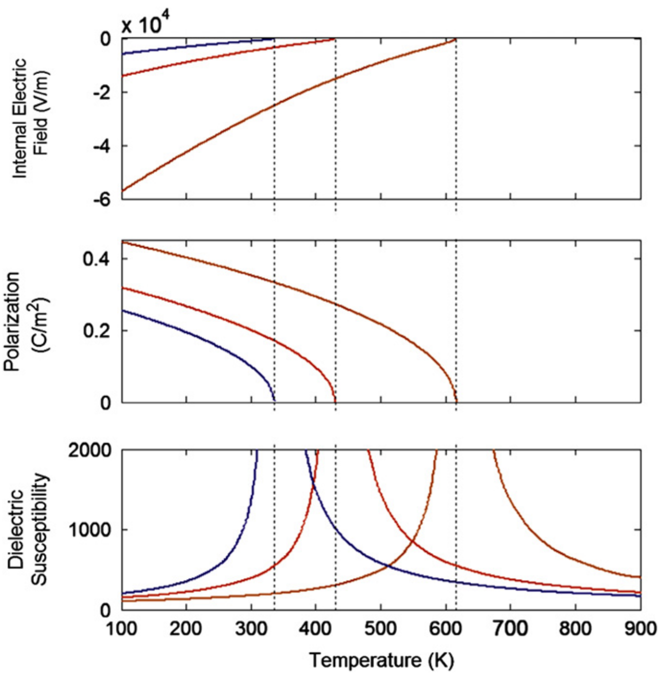

Fig. 2. Internal electric field, polarization and dielectric susceptibility as a function of temperature for PT/ST superlattice with thickness ratio d_{FE}/d_{PE} (in *u.c.*): 10/15 —,10/10 — and 10/5 —. Dotted-lines represent the transition temperature.

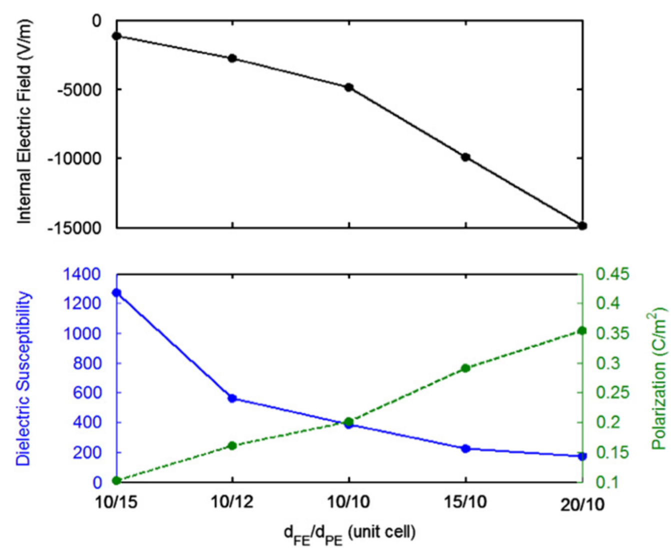

Fig. 3. Internal electric field, dielectric susceptibility and polarization as a function of d_{FE}/d_{PE} at $T=298$ *K*.

3. Results and discussion

In this section, the numerical parameters representing a superlattice combining of $PbTiO_3$ (PT) as FE and $SrTiO_3$ (ST) as PE on ST substrate are listed in Ref. [14]. We assume 1 unit cell $(u.c.)\sim 0.4$ nm,and the length $\xi_0 = \sqrt{\kappa_{FE}/(\alpha_{0FE}T_{0FE})} \sim 0.6nm$ denotes the domain wall half width [3,15]. The lattice constants in the PE state are 3.969 Å and 3.905 Å for PT and ST, respectively [8]. From the lattice constants, the lattice strains are obtained as $u_{mA}=-0.0164$ and $u_{mB}=0$. In this work, the interface intermixing parameter is set as $\lambda_0 = \xi_0$, implying that an intermixed layer with inhomogeneous properties are formed at interface region [11].

Fig. 1 shows the profiles of polarization, internal electric field and dielectric susceptibility in PT/ST superlattices for different thickness ratio. It is seen that intermixed layers with properties difference than that of both layers are formed at interfaces $z=0$ [11]. The formation of intermixed layer leads to inhomogeneity in polarization, internal field and dielectric susceptibility near the interfaces. The internal field in PT layer acts as the depolarization field $E_{\mathrm{d,FE}}<0$, whereas $E_{\mathrm{d,PE}}>0$ tends to induce the polarization in ST layer [2,12]. The internal field in ST layer originates from the electrostatic coupling between different PT layers (across the ST layer), and it plays an important role in determining the ferroelectricity of these superlattice. The spatial profiles of polarization, internal electric field and dielectric susceptibility depend sensitively on the layer thickness of superlattice.

The dependence of average internal electric field, polarization and dielectric susceptibility of superlattice on temperature for different thickness ratio is shown in Fig. 2. Internal electric field and polarization disappear at the transition temperature, whereas the dielectric susceptibility diverges. It can be seen that the phase transition temperature of superlattices increases with increasing the thickness ratio.

In Fig. 3, we show the internal electric field, dielectric susceptibility and polarization as a function of d_{FE}/d_{PE}. As the thickness ratio increases from 10/15 to 20/10, the polarization and depolarization field of superlattice increases. On the hand, the dielectric susceptibility decreases from ~1200 to ~200. From Figs. 2 and 3, it is seen that the control of thickness ratio or volume fraction allows the tuning of ferroelectric properties in these superlattices [8].

Conclusion

We have developed a thermodynamic model for a ferroelectric/paraelectric superlattice with interface intermixed layer. Correlation between internal electric field, dielectric susceptibility and polarization is discussed. Unlike other uniform polarization model [2,4,8], our model allows the study of inhomogeneous ferroelectric properties in these superlattices.

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