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COHERENT COUPLING IN FERROELECTRIC SUPERLATTICES*

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Coherent Coupling in Ferroelectric Superlattices

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Abstract—The phase transition and dielectric behavior of ferroelectric multilayers have been discussed. The coherent interaction between ultra-thin layers can be significantly strong, resulting in a broad difffuse phase transition. The thicknesses of layers and their spatial distributions hold the keys of enhancing dielectric properties in a broad temperature range.

I. INTRODUCTION

There is a fundamental interest in the study of ferroelectric superlattices because their mesoscope structures drastically differ from bulk homogeneous materials. It has been expected that dielectric characteristics of ferroeletrics could be manipulated by controlling material's heterogeneity at the mesoscopic level(5-80nm)[1] , leading to artificially engineering ferroelectric phase transitions and obtaining ferroelectric dielectrics with exceedingly larger dielectric coefficients.

Recently the experimental efforts of synthesizing ferroelectric superlattices or nanocomposites have been initiated by several groups[2] in order to produce ferroelectrics with novel dielectric properties through controlling their heterogeneities. While, on the other hand, the dielectric properties of ferroelectric superlattices and ferroelectric multilayers have also been theoretically examined in serveral aspects[3,4]. Schwenk et al. first employed the Ginzburg-Landau theory[3] to examine the dielectric properties of ferroelectric superlattices, such as $PbTiO_3/BaTiO_3$ superlattice with the first-order phase transition. More recently, Qu et al.[4] also analyzed the polarization and static dielectric susceptibility in ferroelectric superlattices for some special case. However, all these efforts overlooked a critical aspect: the heterogeneity in ferroelectrics with the diffuse phase transition is inhomogeneous in nature. From the phase transition point of view, the inhomogeneous heterogeneity is crucial for causing the dielectric anomalies in ferroelectrics. As well known, in the normal systems, the spatial correlation length of order parameters (such as polarization) diverges at the Curie point, resulting in the dielectric singularity in ferroelectrics. While in inhomogeneous systems, the situations are quite different. The phase transitions in these situations tend to be confined in the localized regions from few nanometers upto a submicon level in scale. Additionally, the correlation lengths of local order parameters are limited by the physical sizes or dimensions of heterogeneities. More precisely, the soft modes will not propagate beyond the physical scale of heterogeneities. Another important feature in these cases is that localized transition points are virtually determined by the physical sizes of heterogeneities. Thus the phase transition in the system with mesoscopic inhomogeneities will be no longer a temperature point but a continuum temperature range as the physical sizes of heterogeneities form a continuum distribution.

Although it has long been postulated that most of inhomogeneous systems exhibit the diffuse phase transitions, it is still lacking a quantitative connection between the heterogeneity and dielectric coefficient in inhomogeneous systems. In this paper, we for the first time report a theoretical evaluation of dielectric phase transition behavior for a multilayer system with designed heterogeneity, based on an extended Ginzburg-Landau model. Our numerical results predict that a giant dielectric susceptibility may be obtained in ferroelectric superlattices or ultra-thin multilayer structures with the desirable heterogeneity.

II. MODEL

The Landau theory has long been successfully used to explain the phase transition behavior of ferroelectrics, and it has been proved to be a good description of the phase transition behaviour in ferroelectrics because the smmoothy varing coulomb force is responsible for establishing the polar phase. Recently it has been extended to study the surface and size effect on nanostructured ferroelectrics[5].

Following the expressions of the free energy in the literature[3,5], we now consider a O_h-C_{4v} proper ferroelectric phase transition in a superlattice system with different localized polarizations as order parameters. For simplicity, by assuming that the polarizations are always oriented along the z-axis, i.e., P={0, 0, P(z)}, and the superlattice dimensions along x-axis and y-axis are infinite, the free energy of the superlattice system with alternating slabs of a_n and b_n can be written as

$$\Phi = \frac{F}{S} = \int_{-L/2}^{L/2} \left\{ \Phi_{ao} + \Phi_{bo} + \frac{\xi_1}{2}(\nabla P_a)^2 + \frac{\xi_2}{2}(\nabla P_b)^2 + \frac{1}{2}\alpha P_a^2 + \frac{1}{4}\beta P_a^4 \right.$$

$$+\frac{1}{6}\gamma P_a^r+\frac{1}{2}Q_1P_a^2\delta\{z\pm a_{n+1}+[\sum_n 2(a_n+b_{n+1})-b_1+a_{n+1}]\}+\frac{1}{2}AP_b^2$$
$$+\frac{1}{4}BP_b^4+\frac{1}{6}CP_b^6+\frac{1}{2}Q_2P_b^2\delta(z\pm b_{n+1}+[\sum_n 2(a_n+b_{n+1})-b_1+b_{n+1}])\Big\}dz \qquad (1)$$

where S is the surface area of the superlattice with plane surfaces at $z=\pm L/2$; Φ_{a0} and Φ_{b0} denote the thermodynamic potential of layer A and layer B in paraelectric phase state. α, β, γ, A, B and C are normalized free energy coefficients, in which elastic coefficients and other relevent coupling parameters are tacitly included. Especially $\alpha=\alpha_0[T-T_1]$ and $A=A_0[T-T_2]$. T_1 and T_2 are phase transition temperatures in the bulk materils of layers A and B respectively. The subscripts of 1 and 2 indices describe two different layers. $T_2>T_1$ is assumed in the present study. ξ_1 and ξ_2 are the gradient terms of order parameters, describing the polarization inhomogeneity. Q_1 and Q_2 are defined as the coherent coupling coefficients, which characterize the coherent coupling at the interface between different regions. Physically the coupling terms can be related to the stored elastic and electrostatic energy caused by coherency coupling. $\delta(z)$ is a delta fuction which describes the coodinates of the interface between two layers.

The integral of Eq.(1) is over all space since the order parameters vary spatially. The local order parameters $P_a(r)$ and $P_b(r)$ are the functions of space coordinates,which is illustrated in Fig.1. The spatial distribution of the polarization can be obtained by solving the Euler-Lagrange equations,

$$\xi_1\frac{d^2P_a}{dr^2}-(\alpha P_a+\beta P_a^3+\gamma P_a^5)=0 \qquad (2a)$$

$$\xi_2\frac{d^2P_b}{dr^2}-(AP_b+BP_b^3+CP_b^5)=0 \qquad (2b)$$

with following coherent boundary conditions at the interfaces,

$$P_a(z)=P_b(z)\big|_{z=[\sum 2(a_n+b_{n+1})-b_1]} \qquad (3a)$$

$$P_a(z)=P_b(z)\big|_{z=[\sum 2(a_n+b_n)-b_1]} \qquad (3b)$$

$$\left[\frac{dP_a}{dz}+\frac{P_a}{d_1}\right]_{z=[\sum 2(a_n+b_n)-b_1]}=0 \qquad (3c)$$

$$\left[\frac{dP_a}{dz}-\frac{P_a}{d_1}\right]_{z=[\sum 2(a_n+b_{n+1})-b_1]}=0 \qquad (3d)$$

$$\left[\frac{dP_b}{dz}+\frac{P_b}{d_2}\right]_{z=[\sum 2(a_n+b_{n+1})-b_1]}=0 \qquad (3e)$$

$$\left[\frac{dP_b}{dz}-\frac{P_b}{d_2}\right]_{z=[\sum 2(a_n+b_n)-b_1]}=0 \qquad (3f)$$

Here $d_1=-d_2$, and $d_1=\xi_1/Q_1$, $d_2=\xi_2/Q_2$, which are the extrapolation lengths, measuring the strength of surface effect[5]. The coherency is defined by the requirement that the local order parameters from one subsystem to another subsystem is continous across all interfaces.

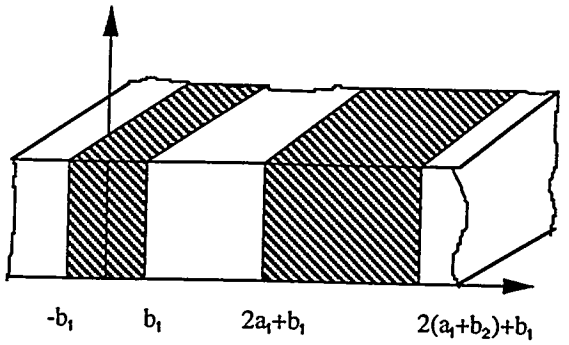

Fig.1. Model superlattice structure described in the text. Here a_n and b_n are the thicknesses of different layers.

III. LOCAL PHASE TRANSITION

The nontrivial solutions of Eqs.(2) can be derived exactly, although, in general, they are quite cumbersome. For breivty, only focusing on the temperature region from $T_2<T<T_1$, the gerneral solutions in the case of $a_n \approx \overline{b_n}$ can be approximately expressed as,

$$P_b=P_{b0}\cos(\kappa_2 r_1) \qquad (4a)$$
$$(r_1=z\pm\sum 2(a_n+b_{n+1})-b_1-b_{n+1})$$
$$P_a=\frac{P_{b0}\cos(\kappa_2 b_{n+1})}{\cosh(\kappa_1 a_{n+1})}\cosh(\kappa_1 r_2) \qquad (4b)$$
$$(r_2=z\pm\sum 2(a_n+b_{n+1})-b_1+a_{n+1})$$

with

$$P_{b0}=\pm\left\{-\frac{B}{2C}\left[1+\sqrt{1-\frac{4A_0C}{B^2}(T-T_{2c})}\right]\right\}^{1/2}$$

(in the case of the first order phase transition) (4c)

$$P_{b0}=\pm\left\{-\frac{B}{2C}\left[1-\sqrt{1-\frac{4A_0C}{B^2}(T-T_{2c})}\right]\right\}^{1/2}$$

(in the case of the second order phase transition) (4d)

$$\kappa_1 = \sqrt{\alpha_0(T - T_1)/\xi_1} = 1/|d_1|\tanh(\kappa_1 a_{n+1}) \quad (4e)$$

$$\kappa_2 = 1/|d_2|\tan(\kappa_2 b_{n+1}) \quad (4f)$$

and

$$T_{2c} = T_2 - (\xi_2\kappa_2^2 / A_0) \quad (4g)$$

where κ_1 and κ_2 are defined as the characteristic lengths, which reflect the correlation radius of the order parameters and describe the breath of polarization fluctuation in two types of layers. For the first order phase transition, from Eq.(4c) the size induced phase transition point can be written as

$$T_2^* = T_2 + (3B^2/16A_0C) - (\xi_2\kappa_2^2/A_0). \quad (4g)$$

Eqs.(4) describe the spatial variations of local order parameters of the superlattice system. Two important features from Eqs(4) are apparent: (i) The phase transition temperature of each layer is intimately related to its physical size and the associated coherent coupling at the interfaces. (ii) The layers with higher Curie points, i.e., the B type of layers; can induce the polarization in the peripheries of the A type of layers, even although the temperature is above the original local Curie temperature of the layers with lower Curie points. In other words, the local polarization $P_a(r)$ ocurring in the A type of layers is caused by the coherent coupling from the B type of layers. As expected, the ferroelectric phase transition can be nucleated in the region, which is intrinsically paraelectric phase. In this case, the polarization occurring in the A type of layers is extrinsic in nature. According to Eqs.(4), the polarization in the B type of layers is plotted as a function of temperature and their physcal size in Fig.2. In addition, the spatail profile of polarization P_a in the A type of layers is also numerically ploted as the functions of both the normalized coordinate and temperature in Figs.3. Quite clearly, at the exact interface, the local Curie point is the transition temperature of B types of layers, and then it decreases quickly as a function of the space coordinaters.

IV. DIFFUSE PHASE TRANSITION

One of important properties for ferroelectrics is their static susceptibility $\chi(T)$ near the Curie range. Next we examine the static dielectric anomalies in our superlattice system. The *average* inverse susceptibility of the superlattice can be expressed as

$$\left\langle \chi^{-1} \right\rangle = \frac{1}{\sum 2(a_{n+1} + b_{n+1})}\left[\frac{\partial^2 \Phi}{\partial P_i^2}\right] \quad (i = a, b) \ . \quad (5)$$

Now we construct a multilayer with 60 alternating layers of $SrTiO_3$/PZT, in which PZT layers are specified as the B type of layers, and they have a designed distribution for their thickness[6]. The thinnest thickness is 6nm, while the thickest film is 14.6nm. The overall temperature dependence of the average dielectric susceptibility and the spontaneous polarization of the multilayer system are numerically plotted in Fig.4. and Fig.5, respectitvely.

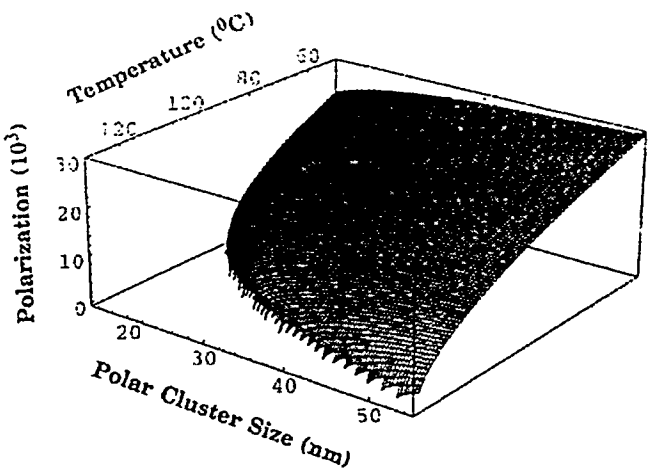

Fig.2. Calculated polarization in the layer B as functions of both temperature and its physical sizes. For the calculation, we take $A_0=10^{-5}$; $B=10^{-12}$; $C=10^{-24}$, $\alpha_0=10^{-4}$; $\beta=10^{-12}$; $\xi_i=10^{-16}$, $T_2=150°C$, $T_1=0°C$ and $a_n=100nm$.

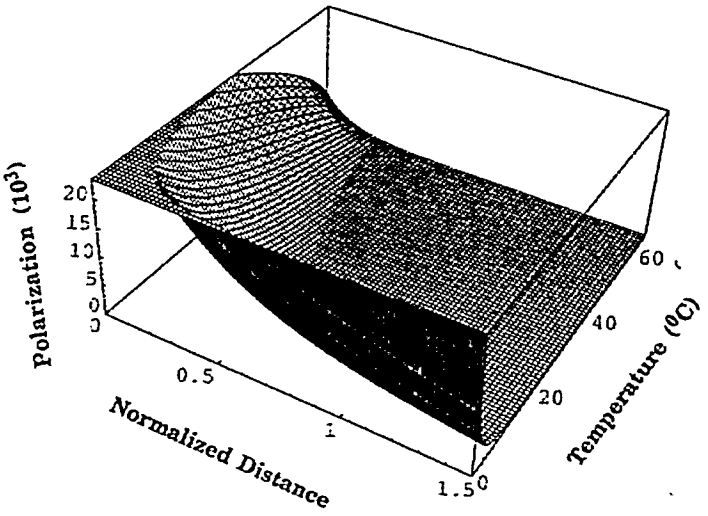

Fig.3. The view of the induced polarization in the A type of layers as functions of both temperature and the normalized distance away from the interfaces. All parameters for the calculation have the cgs unit unless specified.

Fig.4 shows the mean polarization of the superlattice a function of temperature. It can be found that the polarization is gradually weakening and depressing, exhibiting a significant deviation from the normal ferroelectric behavior. Since the thicknesses of PZT layers have a distribution, the local phase transition points in the superlattice will be spreaded into a temperature range, and these local phase transitions are

superposed in some degree so as to keep the entire superlattice system on the verge of structural instability under a broad temperature range.

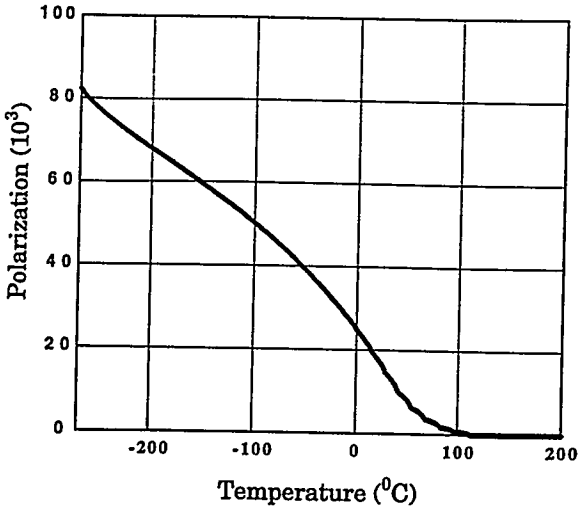

Fig.4. The temperature dependences of the mean polarization of the PZT/STO superlattice with a total thickness of 0.573μm. $a_n=a_{n+1}$=10nm.

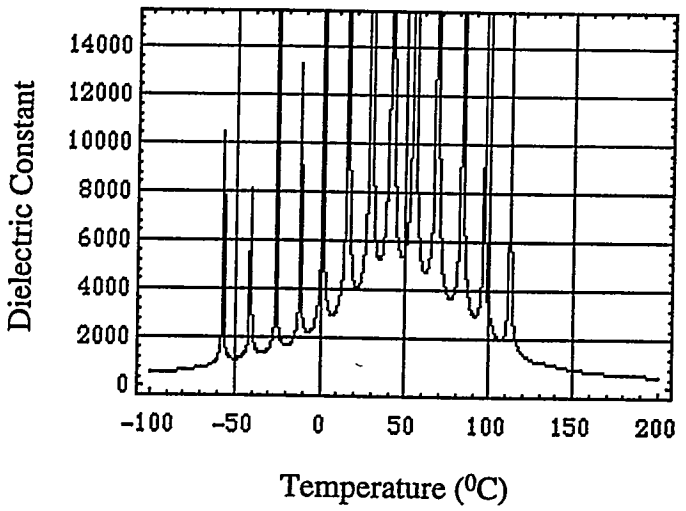

Fig.5. The temperature dependence of the mean susceptibility of the PZT/STO superlattice.

Fig.5. shows the dielectric constant of the superlattices can be well above a value of 4-5,000, and it illustrates a salient feature of dielectric behaviour in ferroelectric superlattice with inmohogenous heterogeneties: a set of localized phase transitions, arising from an intrisic size effect, slightly superpose together and coherently form a giant dielectric response over a very broad temperature range. In other words, there exist a distribution of localized correlation lengths at different temperatures in the superlattice, and a set of localized dielectric singularities in a broad range of temperature together create a giant dielectric (pyroelectric) response. The overall dielectric coeffecients in this case can be exceedingly larger than those suggested by the LST relation[7], or the conversional mean field theoeries. It can been also clealy seen in both Fig.4 and Fig.5 that the local polarization can exist well above the temperature, at which the dielectric constant exihibits its maximun.

V. CONCLUSIONS

A calculation of the dielectric behaviour of ferroelectric supelattices with inhomogeneous heterogeneties has been performed. The coherent coupling between different layers can lead to an exceeding enhancement of dielectric properties in a broad temperature range. The overall dielectric response in the superlattice is controlled by the distrution of thicknesses of the PZT layers, i.e., the heterogeneity, as well as the associated coherent coupling effect.

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