Effects of interfacial pseudo-spin coupling fluctuations on the
dielectric properties of ferroelectric superlattices

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Abstract

Using effective-field theory with correlations, we investigate the effects of interfacial pseudo-spin coupling fluctuations on the susceptibility and polarization of ferroelectric superlattices within the framework of transverse Ising model. It is found that the interfacial coupling fluctuations increase the susceptibility in the low temperature region. For a strong interfacial coupling, the phase transition temperature decreases with the strength of fluctuations of the interfacial coupling. The dependence of the susceptibility on the superlattice period of \textit{BaTiO}_\textsubscript{3}/\textit{SrTiO}_\textsubscript{3} are plotted for different interfacial coupling fluctuations strength. At room temperature, when the interfacial coupling fluctuation increases, the peak position of the susceptibility will shift to a large superlattice period.

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I. INTRODUCTION

Recently developments in the fabrication of thin films have been applied to the ferroelectric thin films. Due to their good ferroelectric, dielectric, piezoelectric and pyroelectric properties, ferroelectric heterostructures have attracted much attention and have many potential applications, for instance, to nonvolatile dynamic random access memories (FDRAM), thin film capacitors, detectors, sensors, optical instruments. New ferroelectric materials with excellent dielectric properties at small sizes have also been considered to make electric device such as the small size capacitors. Thus, a high dielectric constant film with thickness less than 0.1µm is a target for ferroelectric research.

Giant permittivity associated with the motion of domain walls was reported in epitaxial heterostructures having alternating layers of ferroelectric and nonferroelectric oxides [1]. Experiments have also been carried out on the dielectric enhancement and Maxwell-Wagner effects in ferroelectric superlattice structure [2]. The lattice mismatch and interfacial strain in ferroelectric multilayer are thought to be the main causes for the dielectric enhancement [2,3]. Theoretically, it is found that the dielectric property of the ferroelectric superlattice is very sensitive to the interfacial coupling and the thickness of the component [4]. The effects of stress on ferroelectric thin films have been studied within the framework of Landau theory [5,6] with the conclusion that higher tensile stress enhances, while the higher compressive stress reduces the mean susceptibility. By taking the four-spin interaction into account, a ferroelectric-ferroelectric phase transition was found for large periods at low temperature [7]. In Refs. [8,9], the effects of long-range interactions and a non-ferroelectric layer on the dielectric properties of ferroelectric multilayer were studied. Defects zones and the mismatch at the interface between successive ferroelectric layers were observed in Ref. [3]. It is anticipated that a ferroelectric multilayer with a high concentration of interfaces (where the bonding and the structure will in general depart from that of the interior of the layers or the bulk) will have some new properties. A complex and inhomogeneous interface may be important, or even dominant, in the superlattice structure when the individual constituent layer is only a few unit cells. So far, the effect of the interfacial structure on the dielectric property of a ferroelectric superlattice has not been thoroughly investigated. Analogous to the structure fluctuation or the bond randomness in the amorphous ferromagnets [10], the disordered structure of the ferroelectric interface must give rise to the randomness in the
interaction of the dipolar moments.

In this paper, we introduce interfacial pseudo-spin coupling fluctuations in the transverse Ising model (TIM) to investigate the effects of interfacial structure inhomogeneity on the dielectric properties of ferroelectric superlattices. The coupling fluctuations may also exist in the interior layers of the superlattice. However, compared with the magnitude of the coupling fluctuation within the interface, the fluctuations in the interior layers are weaker. We focus our attention on the effects of the interfacial pseudo-spin coupling fluctuation. The dielectric property and phase transition temperature of ferroelectric Ising superlattices have been investigated in the context of the mean-field theory [11] and effective-field theory [12], and it is found that the dielectric constant has a maximum for a small superlattice period at room temperature. It is well known that mean-field theory should not be applied to investigate fluctuation effects near the phase transition point. Here we adopt effective-field theory (based on the Ising spin identities and the differential operator technique) which is superior to mean-field theory. It is found that in the low temperature region the larger interfacial coupling fluctuations, the higher the susceptibility of the superlattice. Remarkably, interfacial coupling fluctuations lower the phase transition temperatures when the interfacial coupling is stronger than the pseudo-spin coupling in the interior layers. Finally, parameters that imitate $BaTiO_3/SrTiO_3$ superlattice are applied to our model. We find that large interfacial coupling fluctuations will increase the dielectric constant of $BaTiO_3/SrTiO_3$ structure at room temperature, decrease the dielectric constant at high temperature, and further more change the critical thickness of the superlattice at which there exists a maximum value of the dielectric constant. We postulate that an interfacial disorder such as the interfacial coupling fluctuation is one of the reasons for dielectric enhancement in the ferroelectric multilayer.
We consider a ferroelectric superlattice composed of two different components (A and B) with an interface (I). $L_a$, $L_b$, and $L_{in}$ are the thicknesses respectively of A, B, and the interface in a unit cell of the superlattice. Each layer is defined on the x-y plane and with pseudo-spin sites on a square lattice (see Fig. 1). As in Refs. [11, 12], we consider only one interfacial layer ($L_{in} = 1$). The coupling constants between pseudo spins in the interfacial layer and in the interior layer can be different from that between spins within the interior layers. The system is described by the Ising Hamiltonian with a transverse field,

$$H = - \sum_{<ij>} J_{ij} S_i^z S_j^z - \sum_{<mn>} \bar{J}_{in} S_m^z S_n^z - \sum_i \Omega_i S_i^x - 2\mu E \sum_i S_i^z,$$

(1)

where $\Omega_i$ is the transverse field. $S_i^z$, $S_i^x$ are components of spin-1/2 operator at site $i$, $J_{ij}$ is the coupling constant between the nearest neighbor pseudo spins within the component A or B, $\bar{J}_{in}$ is the nearest neighbor coupling constant in the interfacial layer and that between the interface and the interior layers of component A or B. $\bar{J}_{in}$ is assumed to be randomly distributed according to the independent probability distribution function $\rho(\bar{J}_{in})$. $\mu$ is the effective dipole moment, and $E$ is the applied electric field. The parameters $J_{ij}$ and $\Omega_i$ are taken as:

$$J_{ij} = \begin{cases} J_a & \text{for } i, j \in \text{component A} \\ J_b & \text{for } i, j \in \text{component B} \end{cases}$$

(2)

$$\Omega_i = \begin{cases} \Omega_a & \text{for } i \in \text{component A} \\ \Omega_{in} & \text{for } i \in \text{the interface I} \\ \Omega_b & \text{for } i \in \text{component B} \end{cases}$$

(3)

For the ferroelectric material with the first-order phase transition, a four-spin interaction term must be included in the Hamiltonian (1). Here, we will focus our attention on the effects of the coupling fluctuation in the interface, and the four-spin interaction term is not considered for simplicity. The average values of pseudo spins in each layer of the superlattice can be derived from the effective-field theory with correlations. For instance,
for $L_a = L_b = 3$, we have

$$R_1 = << S_1^z >>, = << [cosh(\frac{1}{2} \nabla J_m) + 2 < S_8 > sinh(\frac{1}{2} \nabla J_m)].$$

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_1 > sinh(\frac{1}{2} \nabla J_a)]^4.$$  

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_2 > sinh(\frac{1}{2} \nabla J_a)] >_r . f(x, \Omega_a)|_{x=0},$$

$$R_2 = < S_2^z >= [cosh(\frac{1}{2} \nabla J_a) + 2 < S_1 > sinh(\frac{1}{2} \nabla J_a)].$$

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_2 > sinh(\frac{1}{2} \nabla J_a)]^4.$$  

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_3 > sinh(\frac{1}{2} \nabla J_a)], f(x, \Omega_a)|_{x=0},$$

$$R_3 = << S_3^z >>, = << [cosh(\frac{1}{2} \nabla J_a) + 2 < S_2 > sinh(\frac{1}{2} \nabla J_a)].$$

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_3 > sinh(\frac{1}{2} \nabla J_a)]^4.$$  

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_4 > sinh(\frac{1}{2} \nabla J_a)] >_r . f(x, \Omega_a)|_{x=0},$$

$$R_4 = << S_4^z >>, = << [cosh(\frac{1}{2} \nabla J_a) + 2 < S_3 > sinh(\frac{1}{2} \nabla J_a)].$$

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_4 > sinh(\frac{1}{2} \nabla J_a)]^4.$$  

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_5 > sinh(\frac{1}{2} \nabla J_a)] >_r . f(x, \Omega_a)|_{x=0},$$

$$R_5 = << S_5^z >>, = << [cosh(\frac{1}{2} \nabla J_a) + 2 < S_4 > sinh(\frac{1}{2} \nabla J_a)].$$

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_5 > sinh(\frac{1}{2} \nabla J_a)]^4.$$  

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_6 > sinh(\frac{1}{2} \nabla J_a)] >_r . f(x, \Omega_a)|_{x=0},$$

$$R_6 = < S_6^z >= [cosh(\frac{1}{2} \nabla J_a) + 2 < S_5 > sinh(\frac{1}{2} \nabla J_a)].$$

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_6 > sinh(\frac{1}{2} \nabla J_a)]^4.$$  

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_7 > sinh(\frac{1}{2} \nabla J_a)], f(x, \Omega_a)|_{x=0},$$

$$R_7 = << S_7^z >>, = << [cosh(\frac{1}{2} \nabla J_a) + 2 < S_6 > sinh(\frac{1}{2} \nabla J_a)].$$

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_7 > sinh(\frac{1}{2} \nabla J_a)]^4.$$  

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_8 > sinh(\frac{1}{2} \nabla J_a)] >_r . f(x, \Omega_a)|_{x=0},$$

$$R_8 = << S_8^z >>, = << [cosh(\frac{1}{2} \nabla J_a) + 2 < S_7 > sinh(\frac{1}{2} \nabla J_a)].$$

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_8 > sinh(\frac{1}{2} \nabla J_a)]^4.$$  

$$[cosh(\frac{1}{2} \nabla J_a) + 2 < S_9 > sinh(\frac{1}{2} \nabla J_a)] >_r . f(x, \Omega_a)|_{x=0},$$

where function $f(x)$ is defined by

$$f(x, \Omega_i) = \frac{x}{2\sqrt{x^2 + \Omega_i^2}} tanh(\frac{1}{2} \sqrt{x^2 + \Omega_i^2}).$$  

(5)

To proceed further, we have to approximate the thermal multiple correlations on the right side of Eq. (4). We shall use the Zernike decoupling approximation,

$$< S_i^x S_j^y ... S_k^z S_l^z > \approx < S_i^x > < S_j^y > ... < S_k^z > < S_l^z > .$$  

(6)
In order to describe the coupling fluctuations in a simple way, we assume that the distribution of $J_{in}$ is taken to be

$$\rho(\bar{J}_{in}) = \frac{1}{2} \left[ \delta(\bar{J}_{in} - J_{in} - \Delta J_{in}) + \delta(\bar{J}_{in} - J_{in} + \Delta J_{in}) \right],$$

and the parameter $\delta_{in}$ (which is introduced to describe the magnitude of the coupling fluctuation in the interface) is defined as

$$\delta_{in} = \frac{\Delta J_{in}}{J_{in}}.$$  \hspace{1cm} (8)

The symbol $< ... >_r$ in Eq. (4) denotes the average over random bonds. These random bond averages are given by

$$< \cosh(\nabla \bar{J}_{in}) >_r = \cosh(\nabla J_{in} \delta_{in}) \cosh(\nabla J_{in}),$$

$$< \sinh(\nabla \bar{J}_{in}) >_r = \cosh(\nabla J_{in} \delta_{in}) \sinh(\nabla J_{in}).$$

The equations for $R_i$ in (4), where $i$ runs over all layers in one period of the superlattice, form a set of nonlinear simultaneous equations from which each $R_i$ can be calculated numerically. The average polarization of the superlattice can then be obtained as

$$P_{av} = \sum_{i=1}^{L} 2\mu R_i / L,$$

with $L = L_a + L_b + L_{in}$. When the applied electric field $E$ is varied, the average susceptibility of the superlattice is obtained numerically from

$$\chi = \frac{\partial P}{\partial E} \big|_{E=0}.$$  \hspace{1cm} (11)

By changing the value of $\delta_{in}$, we can investigate the effects of the interfacial coupling fluctuations on the susceptibility and the polarization of the ferroelectric superlattice. The numerical results and discussions are given in Sec. III.
III. RESULTS AND DISCUSSIONS

Effects of interfacial coupling and the thickness on the ferroelectric multilayer have been studied in detail \[4, 14\]. Here, we focus our attention on the effects of the fluctuations of the interfacial pseudo-spin coupling. We first fix the thickness of the superlattice to investigate the above effects. In Fig. 2 and Fig. 3, we take \( L_a = L_b = 5 \), \( J_a = 2J_b \), and \( \Omega_a = \Omega_b = 0.5J_b \), where \( J_b \) is taken as the unit of energy. Fig. 2 and Fig. 3 are plotted for weak and strong interfacial pseudo-spin couplings respectively. As shown in Fig. 2 \((J_{in} = \sqrt{J_aJ_b})\), for a weak interfacial pseudo-spin coupling, the fluctuations of the interfacial coupling result in an increment of the susceptibility of the ferroelectric superlattice only in the low temperature region. The phase transition temperature is almost constant as the interfacial coupling fluctuation is increased. This is reasonable, because the phase transition temperature is mainly determined by the component \( A \) which has a stronger pseudo-spin coupling than in \( B \) and in the interface. The average polarization of the superlattice has a slight decrease as the interfacial coupling fluctuation is increased (See Fig. 2(b)). The effects of the interfacial coupling fluctuations are more pronounced for a strong interfacial coupling \((J_{in} = 3\sqrt{J_aJ_b})\). In Fig. 3(a), the susceptibility of the superlattice will increase greatly with increasing \( \delta_{in} \) below the transition temperature, and the peak positions of the susceptibility shift to lower temperatures. The dependence of the superlattice polarization on the temperature for selected values of \( \delta_{in} \) are plotted in Fig. 3(b). We can thus see that the interfacial coupling fluctuations play an important role in the dielectric properties and phase transition temperatures of ferroelectric superlattices for strong interfacial pseudo-spin couplings.

In Fig. 4, we fix the interfacial coupling fluctuation to investigate the effects of the superlattice period on the dielectric properties. With the increase of the period of the superlattice, it is found that the peak value of the susceptibility decreases and the peak position shifts to higher temperatures. And a ferroelectric-ferrroelectric phase transition occurs for a large period of the superlattice at low temperature, which is also observed by use of the mean-field theory in Ref. 7.

In order to study the interfacial coupling fluctuation effects of real physical systems, we consider a \( BaTiO_3/SrTiO_3 \) superlattice with the parameters in Fig. 1 chosen as \[11, 12\] \( J_a = 264K \), \( \Omega_a = 0.01K \), \( J_b = 24K \), \( \Omega_b = 87K \), \( J_{in} = \sqrt{J_aJ_b} \), and \( \Omega_{in} = \sqrt{\Omega_a\Omega_b} \). We also
assume that the interfacial coupling fluctuations are described by Eq. (7). The susceptibility curves are plotted in Fig. 5. When $\delta_{in} = 0$, there exists a peak value of the susceptibility around $L_a = L_b = 4$ at room temperature, and our result at $\delta_{in} = 0$ recovers that of Ref. [12]. For large fluctuations of the interfacial coupling ($\delta_{in} = 6.0$), the peak position of the susceptibility occurs at a large value of the period at room temperature. However, as shown in Fig. 5(b), the susceptibility at higher temperatures will decrease with the increase of $\delta_{in}$.

In summary, the susceptibility (and its peak value) of the superlattice will increase with greater interfacial coupling fluctuations in the low temperature region. When the interfacial coupling is strong, the effects of the interfacial fluctuations on the susceptibility and polarization are more pronounced than for weak interfacial couplings. The peak position of the susceptibility shifts towards a large period for large interfacial coupling fluctuations at room temperature. We conclude that interfacial coupling fluctuations is one of the reasons for dielectric enhancement in the ferroelectric multilayer structure.

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FIG. 1: Schematic illustration of the model of a ferroelectric superlattice. The interfacial layer is marked by hollow symbols.
FIG. 2: The dependence of the susceptibility(a) and the mean polarization(b) of the ferroelectric superlattice on the temperature for a given weak interfacial coupling $J_{in}$ and different interfacial coupling fluctuations $\delta_{in}$.
FIG. 3: The dependence of the susceptibility (a) and the mean polarization (b) of the ferroelectric superlattice on the temperature for a given strong interfacial coupling and different interfacial coupling fluctuations $\delta_{in}$. 

$$J_{in} = \sqrt{3J_a J_b}$$

- $\delta_{in} = 0.0$
- $\delta_{in} = 0.5$
- $\delta_{in} = 0.9$
FIG. 4: Plot of the susceptibility versus temperature of the ferroelectric superlattice with different superlattice periods.
FIG. 5: The period dependence of susceptibility for some selected interfacial coupling fluctuations 
(a) at room temperature, (b) at 500 K.