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ON THE THEORETICAL MODELS OF FERROELECTRIC THIN FILMS AND GRADED FERROELCTRICS

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The Tilley-Zeks model, one of the most thoroughly studied thoretical models of thin films, is discussed. To obtain better views on layered ferroelectrics, a new model is proposed and analyzed.

Key words: ferroelectrics, thin films, graded ferroelectrics

1. INTRODUCTION

With the advancement of engineering applications of ferroelectric thin films,[1] more fundamental studies have become important to overcome difficulties, which may be encountered in technical developments. For examples, it seems that the 90° domain walls, formed between a c-domain and an a-domain in ferroelectrics with the tetragonal symmetry, appear commonly in thin films,[2] but it has not yet clarified what influence they will give on the performance or the function of the ferroelectric thin films, and therefore theoretical guiding principles may be needed.[3]

In such situations, theoretical models must play important roles. Such theoretical models should reflect substantial features of the complicated phenomena, be nevertheless simple enough and mathematically tractable at the same time. Regarding ferroelectric thin films there is a model proposed by Tilley and Zeks, hereafter called the Tilley-Zeks model, which has been studied in quite details.[4-16] However, it seems that difficulty may arise when the Tilley-Zeks model is applied to the multi-layered thin films. It is, therefore, desirable at this stage to prepare another model more naturally applicable to such films. We first review the Tilley-Zeks model in the section 2, and then propose a new model for the multi-layered ferroelectrics in section 3. This paper will be concluded with remarks in the final section.

2. The Tilley-Zeks model [4-16]

In this section we consider thin films, which extends from $-L/2$ to $-L/2$, and would undergo the second order phase transition if there is no surface effect (like the bulk case). The Landau free energy then can be written as

$$f=\frac{1}{L}\left\{\int_{-L/2}^{L/2}\left[\frac{\alpha}{2}p^2+\frac{\beta}{4}p^4+\frac{\kappa}{2}\left(\frac{\partial p}{\partial z}\right)^2\right]dz+\frac{\kappa}{2}\left(\frac{p_+^2}{\delta_+}+\frac{p_-^2}{\delta_-}\right)\right\} \quad (1)$$

consisting of the local energy (the α- and β-terms in the integrand), the contribution due to the spatial modulation inside the film (the κ-term) and the contribution from the surfaces governed by the surface polarization and the extrapolation length. In eq.(1), it is assumed that

$$\alpha = a\,(T - T_0) \quad (2)$$

as usual, and β and κ are both positive constants, i.e., $\beta > 0$, $\kappa > 0$, and p_+ and δ_+ denote the polarization and the extrapolation length at $z = L/2$, respectively, and p_- and δ_- at $z = -L/2$, respectively.

Our task is to find the transition temperature α_c and the polarization profile $p(z)$ below the transition temperature. For this purpose let us minimize the free energy, i.e.,

$$\frac{\delta f}{\delta p(z)}=0 \quad (3)$$

then we obtain a differential equation called the Euler-Lagrange equation, and have to solve it under given boundary conditions.

The boundary conditions in the present case are

$$\frac{\partial p_-}{\partial z}=\frac{p_-}{\delta_-} \quad \text{at} \quad z=-L/2 \quad (4\text{-}1)$$

and

$$\frac{\partial p_+}{\partial z}=-\frac{p_+}{\delta_+} \quad \text{at} \quad z=L/2 \quad (4\text{-}2)$$

It should be noted that there are four independent length scales in the present model, that is, the film thickness L, the extrapolation length δ_+, δ_-, and α length scale ξ;

$$\xi = \sqrt{\frac{\kappa}{|\alpha|}} \quad , \qquad (5)$$

which is composed of a material constant κ and temperature α, an external parameter, or three independent length scales when $\delta_+ = \delta_-$, as studied by Tilley and Zeks. The phase transition and the physical properties of the present model are governed by interplay of such length scales.

The extrapolation length here is regarded as a material constant like β and κ, and can be either positive or negative. As a general rule, the surface polarization is larger than that in the bulk for negative extrapolation length, while it is smaller for positive extrapolation length. This suggests that the transition temperature will increase and decrease when the extrapolation length is negative and positive, respectively.

Concrete profiles of the polarization, $p(z)$, are obtained by solving eq.(3), using the free energy functional (1), for given values of δ and L. The average free energy can be obtained by putting $p(z)$ above obtained, into eq.(1) and performing integration.

In the case of positive extrapolation length the polarization in the surface area is smaller than that inside the film, and the transition temperature decreases as film thickness decreases. On the contrary, in the cases of negative extrapolation length, the polarization in the surface area is larger than that of the bulk, and the transition temperature increases as thickness decreases. A very high transition temperature for a very thin film, or an infinitely high transition temperature for an infinitely thin film? It seems to the present author that this is unphysical, and it is obvious that some amendment of the Tilley-Zeks model is needed in the cases of negative extrapolation length.

In this sense, among the results obtained on the basis of the Tilley-Zeks model, we present graphically in Figs. 1and 2 the polarization profiles and the thickness dependence of the average free energy only for the case of positive δ (= $\delta_+ = \delta_-$), respectively, and in Fig. 3 the critical thickness as the function of temperature α and the extrapolation length δ

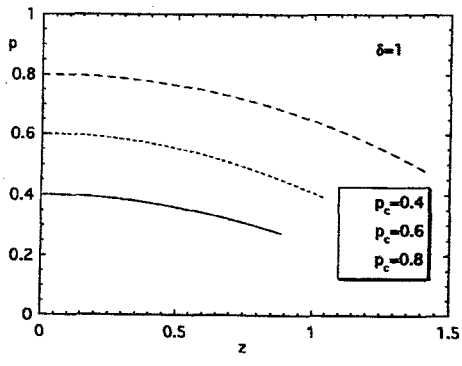

Fig. 1. The polarization profiles for the cases of the positive extrapolation length.

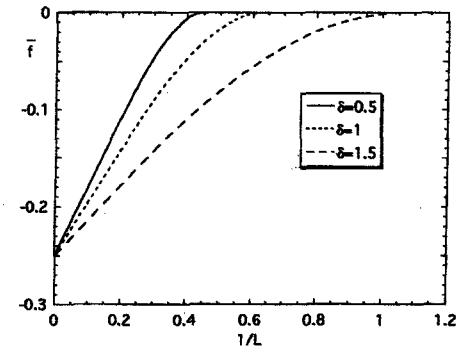

Fig. 2. The thickness dependence of the average free energy density for the cases of positive extrapolation length.

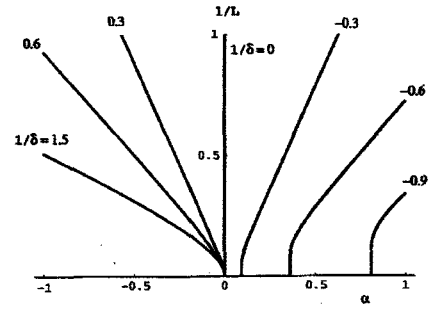

Fig. 3. The critical thickness as a function of temperature and the extrapolation length.

3. Graded Ferroelctrics

Quite often multi-layered ferroelectric thin films and ferroelectric superlattices are produced both for purposes of applications and fundamental studies. To investigate the interface structures some theoretical models may be needed.

Let us consider a case where two ferroelectric thin films are in contact and interact (attractively regarding the polarization) through the interface.[17] It is certainly possible to solve the problem, for example, of the polarization profiles even in this case with the Tilley-Zeks model, because it is mathematically well defined. But, at the same time, it is easily predictable that the polarization profiles near interfaces may show a complicated and physically questionable feature, depending upon combination of the signs of the extrapolation length and the magnitude of the polarization in the bulk of two ferroelectrics (Remember that the extrapolation length are characteristic of each material. It is recommendable for the readers to sketch qualitatively the expected polarization profiles for various combinations of the extrapolation length and the bulk polarization). Upon this presumption, we rather like to propose a

model, in which the extrapolation length is not assumed a priori, but may be derived as the result of energetic considerations.

Here, we consider a double-layered ferroelectrics comprising two distinct layers of different polarization properties, with bilinear interface coupling across the interface. By denoting the polarization as P_1 and P_2 and setting the coordinate x perpendicularly from the interface of the coupled layer, the total energy of the interface structure of the coupled layer in terms of P_1 and P_2 can be written as

$$F = \int f\,dx + f_i \tag{6}$$

with

$$f = (f_1 - f_1') + (f_2 - f_2') \tag{7}$$

where f_1 and f_2 are the free energy densities for the layer 1, extending from $x \to -\infty$ to $x = 0$, and the layer 2, extending from $x = 0$ to $x \to \infty$, respectively, which is expressed as

$$f_j = \frac{1}{2}\alpha_j P_j^2 + \frac{1}{4}\beta_j P_j^4 + \frac{1}{2}\kappa_j \left(\frac{dP_j}{dx}\right)^2, \quad j = 1 \text{ or } 2, \tag{8}$$

where α_j is a temperature-dependent parameter, β_j and κ_j are temperature-independent positive coefficients. The f_j' denotes the energy density of the single domain states of the layer j which is expressed as

$$f_j' = -\frac{\alpha_j^2}{4\beta_j}, \quad j = 1 \text{ or } 2, \tag{9}$$

in ferroelectric states, $\alpha_j < 0$ ($f_j' \neq 0$), while $f_j' = 0$ if $\alpha_j > 0$ (paraelectric state). The energy due to the interfacial coupling between the two ferroelectrics across the interface is given as

$$f_i = \frac{\gamma'}{2}(P_{10} - P_{20})^2, \tag{10}$$

where γ' is the interfacial coupling parameter describing the strength of the interaction, and P_{10} and P_{20} are the "interface polarizations" located at the interface ($x = 0$) between the ferroelectric layers 1 and 2, respectively, which couple across the interface between two ferroelectric layers.

A stable interface structure can be obtained by solving the Euler-Lagrange equations derived from eq. (6) for P_1 and P_2, respectively, as

$$\frac{\delta F}{\delta P_j} = 0, \quad j = 1 \text{ or } 2, \tag{11}$$

with the boundary conditions $P_j = P_{j0}$ at $x = 0$.

Manipulations of eqs. (6) - (11) and the boundary conditions at $x = 0$ will give the total energy in terms of two parameters P_{10} and P_{20}, and by minimizing the total energy with respect to P_{10} and P_{20}, the polarization profile and the energy of the stable state can be found.

We present the results obtained by this model graphically for the polarization profiles in the ferroelectric /paraelectric and the ferroelectric/ferroelectric interfaces in Figs. 4 and 5, respectively.

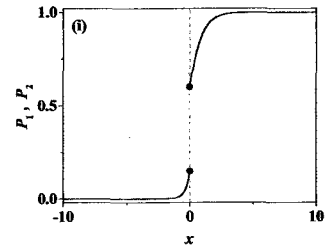

Fig. 4. The polarization profile in the ferroelectric/paraelectric interface.

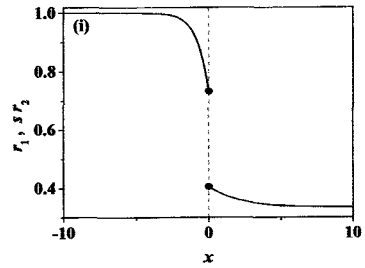

Fig. 5. The polarization profilein the ferroelectric/ferroelectric interface.

It should be noted that the polarization does not changes abruptly across the interface in either case of ferroelectric/paraelectric or ferroelectric/ferroelectric composite, but rather smoothly for the intermediate interfacial coupling, and the polarization is induced even in the paraelectric thin films. Smoothness of the variation of the polarization and the magnitude of the gap in polarizations across the interface depend upon the intrinsic scale length of layered materials and the strength of the coupling. Though we did not take into account the depolarization field (because we assumed in this paper that the polarization component is parallel with the interface), the above findings suggest that the depolarization field will be reduced to some extent in even the case where the polarization is perpendicular to the interface.

From the present model, the physical quantities like the interfacial energy, the extrapolation length can be easily obtained. Especially, it should be noted that the latter is found to be determined energetically, but not as an intrinsic parameter assigned to each material a priori, and to depend upon the intrinsic length scale of each material and the interfacial coupling with the partner material. Readers more interested in this model are referred to Ref.17. The studies of the applied field effects are now under progress.

4. Concluding remarks

In this paper, we first reviewed the Tilley-Zeks model of ferroelectric thin films and, to supplement its disadvantage in applying to the multi-layered films, we proposed a new model, where it is a distinct difference that no extrapolation length is introduced a priori, but it can be derived in terms of the material constants and interfacial coupling with the partner material. Of course both models are mathematically well defined, and solvable. Therefore, it must be judged only by experiments which model is better for reproducing the features experimentally observed of the interface in ferroelectric composites and the multi-layered thin films.

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