

Influence of imperfect surface layers on dielectric and pyroelectric properties of ferroelectric thin film

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Abstract

Using the Ginzburg–Landau–Devonshire theory and taking into account structural difference between imperfect surface layers and bulk ferroelectrics, the dielectric and pyroelectric properties of ferroelectric thin films coated with two metallic electrodes have been studied. The numerical results show that the effects of imperfect surface layers are to increase the effective dielectric susceptibility at room temperature through lowering the phase transition temperature. Both the dielectric susceptibility peak and pyroelectric coefficient peak shift to lower temperatures due to the contribution of the imperfect surface layers. The incompletely screened non-uniform depolarization field makes the susceptibility distribution more uniform.

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1. Introduction

With the advancement of material processing techniques, the quality of ferroelectric (FE) thin films has improved greatly, which intrigued extensive research interest of many scientists and engineers for potential applications of these films [1]. Research on finite-size effects and surface effects on ferroelectric thin film has gained momentum in recent years because these effects have profound influence on the performance of microelectronic and optoelectronic devices that are made of thin layer ferroelectrics. The effects of finite thickness on the phase transition temperature, spontaneous polarization, dielectric susceptibility have been studied experimentally [2–4]. Ising type transverse field model has also been applied to study surface effects in ferroelectric and magnetic thin films by introducing surface pseudospin exchange constant J_s [5,6]. Kretschmer and Binder [7] attributed the size effect in the films to surface degradation,

and introduced the so-called extrapolation length and surface free energy term using the Ginzburg–Landau–Devonshire (GLD) free energy description. The concept has been widely used in many papers dealing with the effect of surface and/or interface in ferroelectric thin films [8–11]. Also from the GLD theory, Lü, Zheng and Cao have studied the influence of imperfect surface on polarization distribution, phase transition temperature and hysteresis loop of ferroelectric thin films using a different formulation [12,13]. They employed a natural boundary condition to solve the differential equation without using the extrapolation length concept, which reflected a more realistic situation since the physical meaning of the extrapolation length is not clear.

The dielectric susceptibility and pyroelectric coefficient are parameters of both theoretical and practical importance, which have been studied theoretically and experimentally by several groups. Using the phenomenological theory, Zhong et al. [14] have calculated the influence of size effects on the dielectric susceptibility of FE thin film based on the extrapolation length concept. The size-driven transition will be accompanied by a dielectric peak. Wesselinowa used a Green's function technique to

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investigate the thickness and temperature dependence of the dielectric susceptibility of FE thin film [15]. Depending on the interaction constants of the surface and the bulk, the dielectric susceptibility can increase or decrease with the decrease of film thickness. Based on a pseudospin–phonon interaction model, the dielectric susceptibility in FE thin films has also been studied by Nie et al. [16] using the double-time Green's function method. The dielectric susceptibility peak shifts up to a higher temperature with increased pseudospin–phonon coupling. From the experimental results, it is known that the Curie temperature in ferroelectric films TGS, KNO_3 increases with decreasing film thickness [2,17,18], whereas the Curie temperature of PbTiO_3 film decreases with decreasing film thickness [19,20]. Size and interface stress effects were also experimentally studied in ferroelectric films [21,22].

In our earlier work we have studied the influence of imperfect surface layers on the polarization properties of ferroelectric thin film. The aim of the present paper is to study the influence of imperfect surface layers on the dielectric and pyroelectric properties of ferroelectric thin films and to discuss possible methods to improve the dielectric susceptibility and pyroelectric coefficient of ferroelectric thin films.

2. The model

The GLD model for bulk ferroelectrics is one of the most successful theoretical models for treating ferroelectricity. Because surfaces are usually less perfect than the interior, they will contribute to the properties difference between thin films and the bulk, hence, it is necessary to generalize the GLD theory for homogeneous ferroelectrics to include surface layers. The difference in crystal structure and/or composition between the imperfect surface layer and the bulk leads to different energy density forms. We introduce a second power polarization term in the GLD free energy and assume its coefficient to be a function of position to reflect the inhomogeneous nature.

The geometrical structure of the thin film for the current study is depicted in Fig. 1. The film is in single domain state resulting from a second-order ferroelectric phase transition at a temperature higher than room temperature. The single polar axis of the film is assumed perpendicular to the film surface, and along the positive direction of the z -axis. We assume that the metal electrodes can completely screen the depolarization effect produced by the surface-bound charges and the film is homogeneous in planes parallel to the surface, i.e. variations occur only along the z direction.

The generalized GLD free energy for a second-order ferroelectric film of unit area is given as follows:

$$G_L = G_0 + \int_{-L}^L dz \left\{ \frac{1}{2} A(T - T_c) P^2 + \frac{1}{2} B\psi(z) P^2 + \frac{1}{4} C P^4 + \frac{1}{2} K \left(\frac{dp}{dz} \right)^2 - \frac{1}{2} E_d P - EP \right\}, \quad (1)$$

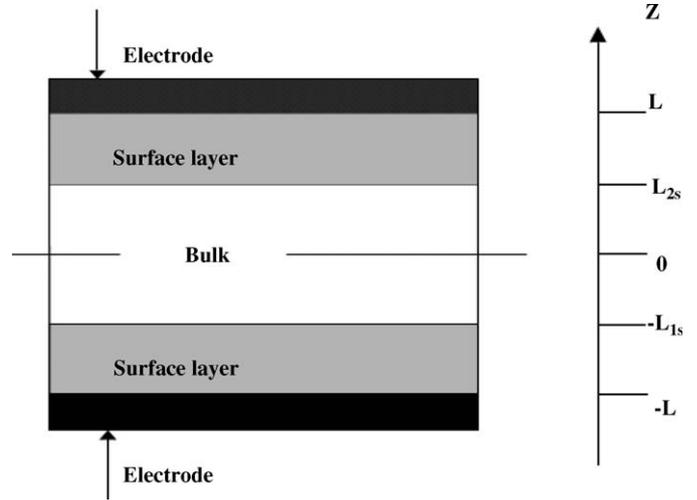


Fig. 1. Geometric structure of the thin film under study.

where G_0 is the free energy of the film in the paraelectric phase. The coefficients A , B , C , and K are independent of temperature T and position z , T_c is the transition temperature of bulk material, E is an applied uniform external electric field along the z direction. The depolarization field produced by nonuniform distributed bound polar charges in the film that is not being screened by the surface electrodes [7] can be written as $E_d = -(P - \bar{P})/\epsilon_0$, where ϵ_0 is the vacuum dielectric susceptibility. The average polarization is given by

$$\bar{P} = \left(\frac{1}{2L} \right) \int_{-L}^L P(z) dz. \quad (2)$$

The depolarization field does not exist if the system is perfect up to the surfaces which are coated with metal electrodes. The depolarization field will also vanish if there are injected charges that totally neutralized the bound charges in the interior [23]. The function $\psi(z)$ in Eq. (1) represents the imperfect surface effect. In order to ensure the continuity of $P(z)$ and its derivative, we require $\psi(-L_{1s}) = \psi(L_{2s}) = 0$ and $(d\psi/dz)_{z=-L_{1s}} = (d\psi/dz)_{z=L_{2s}} = 0$, where $-L_{1s}$ (L_{2s}) is the boundary position of the lower (upper) surface layer in the film (see Fig. 1.)

The Euler's equation for this system is given by

$$K \frac{d^2 p}{dz^2} = A(T - T_c) P + B\psi(z) P + CP^3 - E_d - E, \quad (3a, b)$$

$$\frac{dp}{dz} = 0 \quad \text{when } z = \pm L.$$

The quantity $\bar{P}(E)$ can be measured experimentally from the hysteresis loop and can also be calculated theoretically by using Eq. (2). $\psi(z)$ in Eq. (1) can be obtained by analyzing the compositional variation of the film near the surface region, which will depend on the processing condition instead of intrinsic physical quantities of the film.

3. Numerical results and discussions

It is convenient to rescale the variables into dimensionless forms. We set $t = T/T_c$, $f = P/P_0$ with $P_0 = \sqrt{AT_c/C}$, $e = E/E_0$ with $E_0 = P_0/\epsilon_0$, $\zeta = z/\xi_0$ with $\xi_0 = \sqrt{K/AT_c}$, $\eta = B/B_0$ with $B_0 = AT_c$. Finally, the rescaled Eq. (3a,b) become

$$\begin{aligned} \frac{d^2 f}{d\zeta^2} &= (t-1)f + \eta\psi(\zeta) + f^3 + \sigma(f - \bar{f}) - \sigma e, \\ \frac{df}{d\zeta} &= 0 \quad \text{when } \zeta = \pm l, \end{aligned} \quad (4a, b)$$

where $l = L/\xi_0$, $\bar{f} = \bar{P}/P_0$, and $\sigma = (\epsilon_0 AT_c)^{-1}$. The parameter σ is the ratio of the Curie constant to the Curie temperature of bulk ferroelectrics. In reference to a realistic second-order transition material (Curie constant $\sim 10^3$ K and the Curie temperature $\sim 10^2$ K), we take $\sigma = 6$ as a representative value and the thickness of film is assumed to be $2L = 4\xi_0$ in our numerical calculations.

Since there are no measured data available in the literature on the degree of surface imperfection, we have chosen a simple function as the distribution function $\psi(\zeta)$.

$$\psi(\zeta) = \begin{cases} \frac{(\zeta + l_{1s})^2}{\lambda_1^2}, & -l \leq \zeta \leq -l_{1s}, \\ 0, & -l_{1s} \leq \zeta \leq l_{2s}, \\ \frac{(\zeta - l_{2s})^2}{\lambda_2^2}, & l_{2s} \leq \zeta \leq l. \end{cases} \quad (5)$$

We found that the choice of the functional form does not affect the generality of the results and conclusions so long as the surface degradation effect is reflected by the function.

In Eq. (5) the parameter $\lambda_1(\lambda_2)$ represents the degree of the free energy density variation near the lower(upper) surface. For convenience, we define $\omega_1 = (l - l_{1s})/2l$ and $\omega_2 = (l - l_{2s})/2l$, which represent the relative thickness of the two surface layers in the film, where, $l_{1s} = L_{1s}/\xi_0$, $l_{2s} = L_{2s}/\xi_0$.

The susceptibility profile and the mean susceptibility of the film can be calculated using the formulas below [14]:

$$\chi(z) = \Delta P(z)/\Delta E$$

and

$$\chi_f = \frac{2L}{\int_{-L}^L \{1/[\chi(z) + 1]\} dz} - 1. \quad (6a, b)$$

Rescaling the variables, the above equations become

$$\chi(\zeta) = \frac{\Delta f}{\Delta e}$$

and

$$\chi_f(\zeta) = \frac{2l}{\int_{-l}^l \{1/[\chi(\zeta) + 1]\} d\zeta} - 1. \quad (7a, b)$$

In Fig. 2 the variation of the susceptibility profiles as a function of position z is shown for a film with two symmetric surface layers and the results for different λ

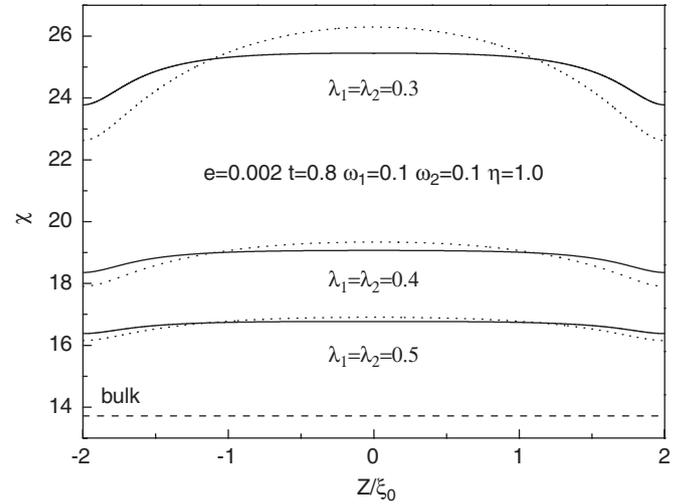


Fig. 2. Dielectric susceptibility distribution along the thickness direction of the film with the same ω values but different λ values at the temperature of $T = 0.8T_c$. The three dotted curves were obtained by neglecting the depolarization field. The dashed line corresponds to bulk material value.

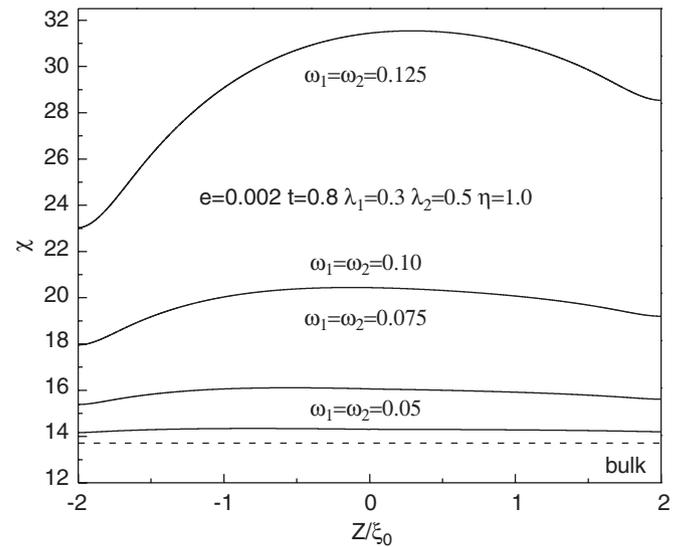


Fig. 3. Dielectric susceptibility distribution for films with two asymmetry surface layers but different relative thickness values at the temperature of $T = 0.8T_c$.

values are also given. The dashed straight line is the dielectric susceptibility value of the bulk material. The dotted line is the result of neglecting the depolarization field.

We can see that the influence of the depolarization field is to flatten the dielectric susceptibility profile. It effectively raises the susceptibility near the surface regions but reduces it in the interior region. The parameters λ_1 and λ_2 have strong influence on the susceptibility distribution. Larger λ_1 and λ_2 values will make the susceptibility distribution more uniform and the value of susceptibility closer to that of the bulk.

In Fig. 3 we plot several curves of susceptibility distribution for films in which two surface layers have the

same thickness but different λ values ($\lambda_1 = 0.3$ and $\lambda_2 = 0.5$). We can see that the distribution of susceptibility is asymmetric and smaller relative thickness of surface layer leads to more uniform distribution of the susceptibility.

In Fig. 4, we have calculated the mean susceptibility as a function of temperature while keeping the parameters of imperfect surface layer constant. For comparison, we also plot the susceptibility versus temperature curve for the bulk material. The imperfect surface layers lowered the phase transition temperature of the film and caused the dielectric susceptibility peak shift to lower temperatures. The influence of the relative thickness of the imperfect surface layers on the dielectric susceptibility is more obvious than that of the parameter λ . Overall, at a fixed temperature, increasing the relative thickness of imperfect surface and lowering the parameters λ can remarkably improve the effective dielectric susceptibility.

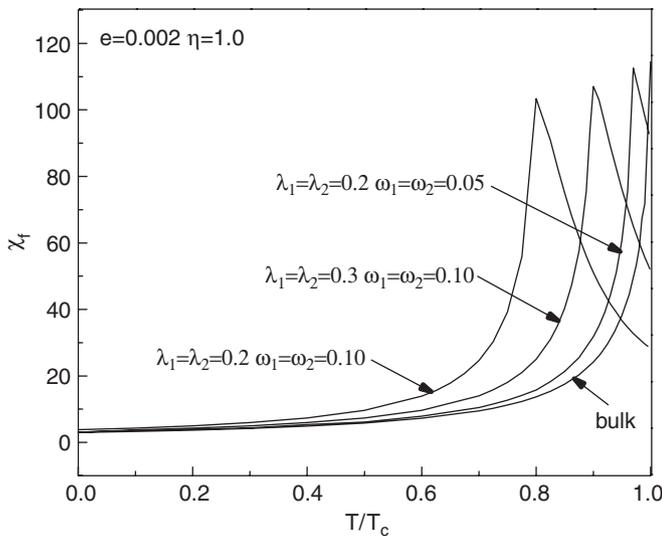


Fig. 4. Mean dielectric susceptibility χ_f as a function of temperature T for a film with two symmetric surfaces.

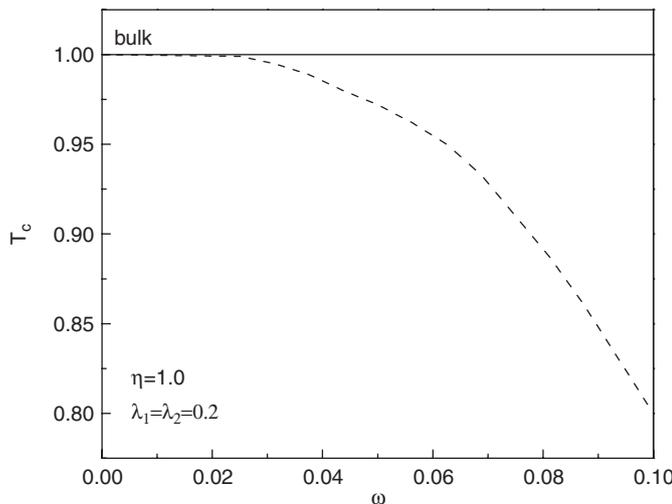


Fig. 5. Transition temperature T as a function of ω with a fixed λ value.

The influence of parameters ω and λ on the transition temperature of the ferroelectric thin film can be seen in Figs. 5 and 6. With the increase of the relative thickness of surface layers, the Curie temperature becomes lower; on the other hand, the increase of parameters λ will increase the Curie temperature.

Due to the nonlinear nature, the susceptibility is a function of field. Using our model, we have calculated the mean susceptibility versus bias electric field for a film with two symmetric surface layers and the results are shown in Fig. 7. One can see that the mean dielectric susceptibility gradually decreases with the increase of bias electric field.

The pyroelectric coefficient reflects the ability to generate charge through temperature variation and its definition

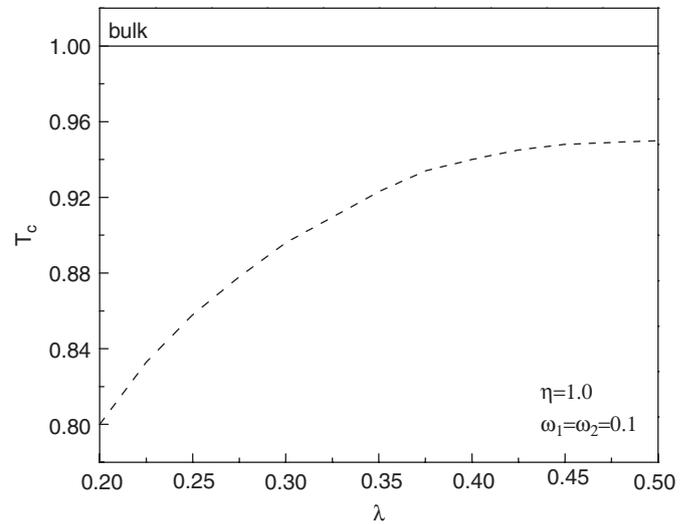


Fig. 6. Transition temperature T as a function of λ with a fixed ω value.

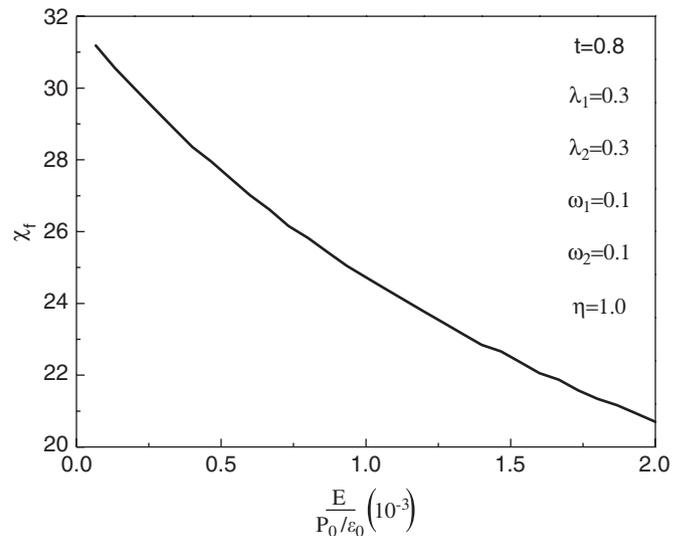


Fig. 7. Average dielectric susceptibility χ_f as a function of bias electric field for a film with two symmetric surface layers at the temperature of $T = 0.8T_c$.

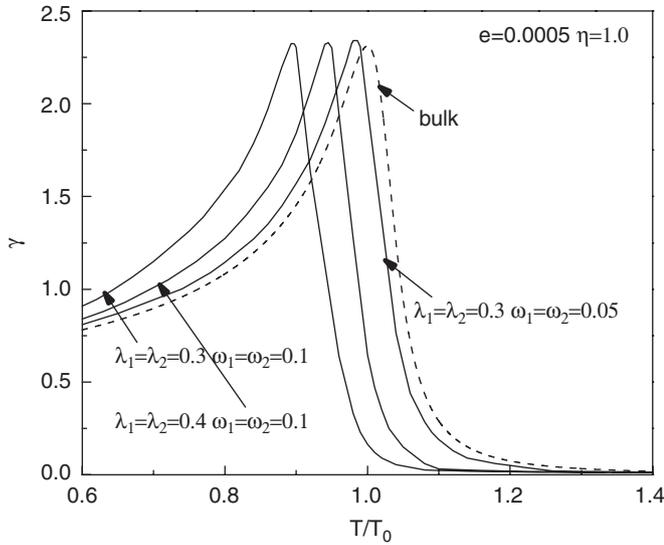


Fig. 8. Pyroelectric coefficient as a function of temperature T for a film with two symmetric surfaces. The relative thickness of surface layers and the degradation parameter λ have been assigned different values and the dashed line is for the bulk.

is given by

$$\rho = \left. \frac{\partial \bar{P}}{\partial T} \right|_T = \frac{P_0}{T_c} \gamma, \quad (8a,b)$$

where $\gamma = (\partial \bar{f} / \partial t)|_t$ is the rescaled pyroelectric coefficient. We have calculated the temperature dependence of the rescaled pyroelectric coefficient for different ω and λ values with symmetric surface layers. The results are shown in Fig. 8. For comparison, we have also plotted the rescaled pyroelectric coefficient versus temperature curve for bulk material (dashed line) on the same figure. One can see that the effect of the surface layers is to shift the pyroelectric coefficient curve toward lower temperature region, effectively making the room temperature pyroelectric coefficient larger. We also found that the influence of the relative thickness of the imperfect surface layers on the effective pyroelectric coefficient is more pronounced than that of the parameter degradation parameter λ .

4. Conclusion

Using a generalized GLD model, the dielectric and pyroelectric properties of a ferroelectric thin film with two imperfect surface layers have been studied. A degradation parameter λ is introduced to describe the degree of polarization variation near the surface region, which could be determined experimentally. However, because of the

lack of experimental data, we have studied numerically a few examples for a second-order ferroelectric system using dimensionless notation. The following conclusions have been obtained: (1) The thickness of imperfect surface layers and the λ parameter both influence the dielectric and pyroelectric properties of the ferroelectric thin film. (2) The phase transition temperature has been decreased due to the presence of the surface layers, which shifts the peaks of the dielectric susceptibility and the pyroelectric coefficient to lower temperatures and effectively increases the amplitude of dielectric susceptibility and the pyroelectric coefficient at room temperature, although such increases are often being suppressed by the substrate constraints. (3) The depolarization field produced by the unscreened bound charges has the effect of making the dielectric susceptibility distribution more uniform. (4) Bias field effectively reduces the mean dielectric susceptibility.

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