Pyroelectric properties of finite size ferroelectric thin films with structural transition zones

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1. Introduction

Pyroelectric properties of ferroelectric thin films have been extensively studied both experimentally and theoretically due to their potential applications, such as infrared ray detectors and thermal imaging systems [1]. Experimentally, Stavitski et al. [2] studied substrate-free crystallization of the distorted hexagonal BaTiO$_3$ thin film. They found that the substrate-free crystallized film showed a small but measurable pyroelectric effect, and did not exhibit the phase transition in the 25–423 K temperature range. Akai et al. [3] analyzed the epitaxial Pb(Zr, Ti)O$_3$ (PZT)/Pt film on Si substrate using an epitaxial γ-Al$_2$O$_3$ buffer layer. The result shows that the PZT film presents better ferroelectric and pyroelectric properties than the polycrystalline PZT film. Recently, Guo et al. [4] fabricated the highly (110)-oriented PZT thin film grown on Pt/LaNiO$_3$/SiO$_2$/Si substrate using the sol–gel method and detected excellent pyroelectric properties in the (110)-oriented film. It is indicated that the pyroelectric coefficient can reach up to 7.8 × 10$^{-6}$ C m$^{-2}$ K$^{-1}$ at room temperature, which results from the high values of spontaneous and remnant polarizations.

In the theoretical treatment, Ginzburg–Landau–Devonshire (GLD) theory [5–7] and the transverse Ising model (TIM) [8–14] are the most frequently used approaches to study pyroelectric characteristics of ferroelectric thin films. Using the GLD thermodynamic theory, Sharma et al. [5] discussed the effect of internal stresses on the pyroelectric response in epitaxial Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ (BST 60/40) and Pb$_{0.52}$Zr$_{0.48}$TiO$_3$ (PZT 50/50) thin films. They found that the pyroelectric coefficient steadily increased with the increase of the film thickness for BST 60/40 and PZT 50/50 films on the SrTiO$_3$ substrate. On the microscopic level, using the pseudo-spin theory based on the traditional TIM, the pyroelectric properties and the Curie temperature of a ferroelectric/ferroelectric superlattice with two alternative layers were studied by Tabyaoui et al. [8]. The results demonstrate that there are two pyroelectric peaks for a large-period superlattice, and the pyroelectric peak at low temperature disappears for a small period superlattice. Yao et al. [9] reported the long-range effect on the pyroelectric coefficient and the susceptibility of a ferroelectric bilayer with a ferroelectric interfacial coupling. They observed an obvious thickness direction size effect on the pyroelectric coefficient and the susceptibility under a strong long-range interaction. In addition, the lateral size dependence of the dielectric susceptibility, the pyroelectric coefficient and the Curie temperature was evaluated convincingly by Xin et al. [10] in a monolayer ferroelectric square lattice. The results show that the maximum of the pyroelectric coefficient is found in the edge area of the lattice and its position can be changed by varying the interaction range.
The size effects are important phenomena observed in ferroelectric thin films. Theoretical investigations on the influence of the lateral size on properties of ferroelectric thin films become more meaningful for miniature electronic devices. Based on TIM, the size effects on the spontaneous polarization, the Curie temperature, and the dielectric susceptibility of the ferroelectric thin film have been discussed adequately [15–17], but the investigations of the size effects, especially the lateral size effects, on pyroelectric properties are scanty. Although Xin et al. [10] discussed the influence of the lateral size on the pyroelectric effect of a ferroelectric square lattice, the pyroelectric coefficient as a function of the film thickness cannot be discussed in a monolayer thin film. So far pyroelectric properties of ferroelectric thin films taking into account the lateral and thickness direction size effects have not been studied on the basis of TIM. It is indispensable to study a more realistic model that can take into account not only the lateral size effects but also thickness direction size effects. Furthermore, the traditional TIM method that describes the properties difference of surface layers and the interior of the film is to mainly modify the pseudo-spin interaction \( J_{ij} \) in surface layers from bulk values, i.e., \( J_{ij} \) is assumed to be identical in surface layers and differs from that of the interior of the film (the “single-step” model). However, the structure difference from surface layers to the interior of the thin film is gradual for a realistic ferroelectric thin film. It is not appropriate to employ a “single-step” model to study the properties of ferroelectric thin films. And the influence of the inhomogeneous structural distribution along the lateral direction on properties of thin films may become more remarkable due to the downscaling of film dimensions. Consequently, we put forward a multistep model, i.e., inhomogeneous structural transition is introduced along the lateral and thickness directions. In this paper, distribution functions representing the interactions between pseudo-spins are used to reflect the structural difference from inhomogeneous structural zones to the interior of the film. Such a model reflects a more realistic situation of the film than the previous “single-step” model, and one may find the way to better control the properties of artificially fabricated films.

The motivation of the present work is to introduce the multistep structural change near the lateral edges and surfaces of the film and to use the Fermi-type Green’s function technique to study the influence of film dimensions and lateral structural transition zones on the pyroelectric coefficient of the thin film based on such a modified TIM.

\[ H = - \sum_i \Omega_i S_i^x - \sum_{ij} J_{ij} S_i^x S_j^x, \]  \hspace{1cm} (1)

where \( \Omega_i \) is the transverse field at site \( i \), \( S_i^x \) and \( S_i^z \) are the \( x \) and \( z \) components of a spin-1/2 operator at site \( i \), \( J_{ij} \) is the exchange interaction between sites \( i \) and \( j \), and the sum \( \sum_{ij} \) runs over only the nearest-neighbor pairs. \( J_{ij} = J_{ij}(m, k) \) if sites \( i \) and \( j \) locate in the same square loop (\( m \) is fixed); \( J_{ij} = J_{ij}(m, s_k) \) if two sites are in the \( m \)th and the \( (m+1) \)th square loops, respectively; \( J_{ij} = J_{ij}(m, k) \) if two sites situate in the \( k \)th and the \( (k+1) \)th pseudo-spin layers, respectively.

Because there are no experimentally measured data available to accurately describe the structure imperfection, the exponential function is introduced to characterize the inhomogeneous structural distribution near the edge of a film. For simplicity, it is assumed that the film is symmetric along the \( z \)-direction. So the expressions of exchange interactions \( J_{ij} \) for the upper half- film containing \( L/2 \) \([ or (L+1)/2 \) including the middle layer] layers can be expressed as

\[ J_{ij}(m, k) = J_{ij} e^{-1/(2z_L N \times L \times k)}, \]

\[ 1 \leq m \leq (s - s_1), \quad 1 \leq k \leq L/2 \text{ or } 1 \leq k \leq (L+1)/2 \]  \hspace{1cm} (2a)
where exchange interactions enlarge as film dimensions increase. The number of dipole moments is enhanced as film dimensions
operator the generality of the results and conclusions [18].

The Fourier-transformed Green’s function satisfies the following equation:

\[
\beta_{op}^{(1)}(k) = \frac{1}{2} \left( \Omega - \frac{\partial}{\partial T} \right) \tanh(\omega_i/2k_BT) + \frac{T \beta_{op}^{(1)} - \omega_i^2 \beta_{op}^{(1)} (1 - \tanh(\omega_i/2k_BT))}{4k_BT^2} \tag{15}\]

Employing the simple decoupling method, the higher-order Green’s function in the above equations may be equivalently expressed as

\[
\langle \hat{a}_{op}^{\dagger}(0) \rangle = \langle \hat{S}_L \rangle \langle \hat{a}_{op}^{\dagger}(0) \rangle \tag{10}\]

\[
\langle \hat{a}_{op}^{\dagger}(0) \rangle = \langle \hat{S}_L \rangle \langle \hat{a}_{op}^{\dagger}(0) \rangle \tag{11}\]

Utilizing Eqs. (8)–(11), the Green’s function can be obtained as follows:

\[
\langle \hat{a}_{op}^{\dagger}(0) \rangle = \frac{\omega - \delta_i}{\omega^2 - \omega_i^2}, \tag{12}\]

\[
\langle \hat{a}_{op}^{\dagger}(0) \rangle = -\frac{\Omega_i}{\omega^2 - \omega_i^2}, \tag{13}\]

where

\[
\delta_i = \sum_j J_{ij} \langle \hat{S}_j \rangle, \tag{14a}\]

\[
\omega_i^2 = \Omega_i^2 + \delta_i^2. \tag{14b}\]

Hence, the transcendental equation with respect to the thermal average \(\langle \hat{S}_L \rangle\) and \(\langle \hat{S}_L \rangle\) at site i can be written as

\[
\langle \hat{S}_L \rangle = \frac{\delta_i}{2\omega_i} \tanh(\omega_i/2k_BT), \tag{15}\]

\[
\langle \hat{S}_L \rangle = \left( \frac{\omega_i}{2\omega_i} \right) \tanh(\omega_i/2k_BT). \tag{16}\]

where \(k_B\) is the Boltzmann constant, and \(T\) is the absolute temperature. Evidently, it is the result of the usual mean-field approximation (MFA), which means that the simple decoupling approximation coincides completely with the usual MFA. Adopting the simple decoupling approximation, the result of MFA can also be obtained by the Bose-type Green’s function. However, the treatment is complicated due to the undetermined constant [20].

The polarization \(P_i\) at site i is proportional to \(\langle \hat{S}_L \rangle\), namely

\[
P_i = 2n \mu \langle \hat{S}_L \rangle, \tag{17}\]

where \(n\) is the number of pseudo-spins in a unit volume, and \(\mu\) is the dipole moment of the pseudo-spin.

It is assumed that only \(P_i\) is dependent on the temperature, so the pyroelectric coefficient \(\rho_i\) at site i can be formulated as

\[
\rho_i = \frac{\partial P_i}{\partial T} = -2n \mu \langle \hat{S}_L \rangle. \tag{18}\]

Define \(\lambda_i = \partial \langle \hat{S}_L \rangle / \partial T\), then \(\lambda_i\) satisfies the following equation

\[
\lambda_i = \frac{\gamma_i (T^2 I_{ij} - \omega_i^2 \delta_i)}{4k_BT^2} [1 - \tanh(\omega_i/2k_BT)]. \tag{19}\]

The mean pyroelectric coefficient of the thin film is determined by

\[
\mathbf{P} = \frac{1}{(N^2 \times L)} \sum_{i=1}^{N^2 \times L} \rho_i. \tag{20}\]

For a bulk material with a second-order phase transformation, the transverse field \(\Omega\) and the exchange interaction \(J_{ij}\) are constant. The Curie temperature \(T_C\) can be obtained from the following equation [21].

\[
\tanh(\Omega / 2k_BT) = 2\Omega / \Omega_i. \tag{21}\]

where \(r\) is the coordination number. In our calculations, the corresponding variables are renormalized to dimensionless units by utilizing the bulk material parameters.
3. Results and discussions

In this section, we present results for finite size ferroelectric thin films. The graphs below are based on the numerical treatment of Eqs. (18) and (20). For simplicity, the transverse field at all sites is treated identically in our calculations, and we assign $\Omega_J / J = 0.1$ and $\beta_2 = \beta_1$. We set $t = T / T_b$.

The mean pyroelectric coefficient dependence of the temperature $T / T_b$ with different parameters $J_\infty$ and $z_1$ is shown in Fig. 2. Each curve presents a pyroelectric peak at a certain temperature, which implies that a phase transformation from the ferroelectric phase to the paraelectric phase will take place. This feature has already been found experimentally in the studies of BST [22] and PZT [23] thin films. One can also see from Fig. 2 that the pyroelectric peak shifts to higher temperature with the increase of $J_\infty$ (or $z_1$). This can be explained by that the interactions near the center of the film are strengthened with the increase of $J_\infty$ (or $z_1$), and the stronger interactions near the center of the film push the pyroelectric peak to higher temperature. Consequently, the working temperature range of pyroelectric devices can be improved by strengthening the interactions near the center of the film.

Fig. 3 shows the mean pyroelectric coefficient as a function of the temperature $T / T_b$ with different film dimensions. The corresponding results for the three-layer film with the infinite lateral size and the bulk material have also been given. It can be seen from Fig. 3 that the pyroelectric peak shifts to lower temperature and the peak value decreases with the reduction of the lateral size when the film thickness is fixed (here $L = 2$), which demonstrates that the influence of the lateral size on the pyroelectric effect cannot be ignored and the working temperature range and the sensitivity of pyroelectric devices are both degraded with the downscaling of the lateral size of the film. This feature is in qualitative agreement with the available experimental results of PZT ferroelectric ceramics [24]. For the thin film with $N = 30$ and $L = 2$, the Curie temperature of the film is $T_c \approx 367 K$. The Curie temperature of the finite size thin film is $T_c \approx 237 K$ when $T_b = 659 K$ (the Curie temperature of PZT bulk materials that show attractive pyroelectric properties), which indicates that the smaller lateral size and thinner film puts forward a rigorous requirement for the working environment. Similarly, the pyroelectric peak shifts to lower temperature and the peak value is suppressed with the decrease of the film thickness when the lateral size of the film is fixed (here $N = 40$). Therefore, the effective interactions between pseudo-spins in the film are weakened everywhere with the downscaling of film dimensions including the lateral size and the film thickness, and the weaker interactions between pseudo-spins decrease the Curie temperature and the pyroelectric peak value of the thin film. On the other hand, it can also be seen that the pyroelectric peak positions and the peak values of films with finite sizes in three dimensions are much lower than those of the bulk material and the three-layer film with the infinite lateral size. This can be ascribed to the fact that the weaker interactions between pseudo-spins suppress the peak value and push the pyroelectric peak to lower temperature when the lateral size or the film thickness varies from the infinity to the finite value. In conclusion, the lateral size and the film thickness both determine pyroelectric properties of thin films, and a decrease in the lateral size of the film is disadvantageous for device applications by use of pyroelectric properties.

The lateral size dependence of the mean pyroelectric coefficient of the thin film with different $x_1$ and $J_\infty$ is demonstrated in Fig. 4. Here we set $x_2 = x_1$ in Fig. 4. Each curve exhibits a

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**Fig. 2.** The mean pyroelectric coefficient of the film as a function of the temperature with different $x_1$ and $J_\infty$.

**Fig. 3.** The mean pyroelectric coefficient of the film as a function of the temperature with different $N$ and $L$.

**Fig. 4.** The lateral size dependence of the mean pyroelectric coefficient of the thin film with different $x_1$ and $J_\infty$. 
pyroelectric peak, which means that a lateral size-driven phase transformation from the paraelectric phase to the ferroelectric phase will occur. However, this kind of the feature cannot be easily obtained experimentally in thin films with infinite lateral sizes. As shown in Fig. 4, the pyroelectric peak occurs at the smaller lateral size with the increase of $J_1$ (or $a_1$). This is reasonable because the ferroelectricity of the thin film can preserve at a smaller lateral size for the stronger interactions near the center of the film. Therefore, the lateral sizes of devices can be dwindled by strengthening the interaction intensities near the center of the film, which has potential applications in designing pyroelectric devices.

Fig. 5 shows the dependence of the lateral size on the mean pyroelectric coefficient with different film thicknesses. For comparison, we also give the calculation result of the four-layer film with the infinite lateral size. One can see from Fig. 5 that the pyroelectric peak shifts to the larger lateral size with the decrease of the film thickness. This is indicative of the fact that the interlayer interaction is weakened with the decrease of the film thickness, and the ferroelectricity of the thin film cannot preserve at the smaller lateral size. Therefore, the lateral sizes of pyroelectric devices should be largened for thinner films working at room temperature.

The profile of the pyroelectric coefficient for the second layer ($k = 2$) of the film with different $s_1$ and $b_1$ is shown in Fig. 6. Here we set $b_1 = \beta_1$. Compared Figs. 6(a) with (b), it is indicated that the pyroelectric coefficient is enhanced with the increase of lateral structural transition zones of the film when the parameter $b_1$ is fixed (here $b_1 = 1$). In contrast with Fig. 6(b), Fig. 6(c) shows that the pyroelectric coefficient is suppressed with the increase of $b_1$ when the parameter $s_1$ is definite (here $s_1 = 7$). This can be ascribed to the fact that the strengthening interactions between pseudo-spins suppress the pyroelectric coefficient of the film. Consequently, the mean pyroelectric coefficient of the fixed size film is enhanced by widening lateral structural transition zones and weakening pseudo-spin interactions in these regions, which indicates that lateral structural transition zones of the film could be a crucial factor changing the pyroelectric coefficient of a fixed size film. The enhancement of the pyroelectric coefficient of a fixed size film may be ascribed to the existence of the inhomogeneous structural distribution near the lateral edges. Our results may explain the high pyroelectric coefficient in PZT [25] and BST [26] thin films.

**4. Summary**

In summary, pyroelectric properties of the thin film with finite sizes in three dimensions have been studied by the Fermi-type Green's function based on a modified TIM. The results can be summarized as following. (1) The inhomogeneous structure makes pyroelectric properties of the thin film different from those of bulk materials, and a lateral size-driven phase transformation may be ascribed to the existence of lateral structural
transition zones. The pyroelectric coefficient is improved by widening lateral structure transition zones and weakening the interactions between pseudo-spins in these regions. (2) The lateral size of the film plays an important role in determining the pyroelectric properties of a thinner film. The pyroelectric peak shifts to lower temperature and the peak value is suppressed with the downscaling of the lateral size of the film. (3) The mean pyroelectric coefficient depends sensitively on the interaction intensities near the center of the thin film. The pyroelectric peak shifts to higher temperature and the peak value of the film is enhanced by strengthening the interaction intensities near the center of the film. Our theoretical predictions may be a reference for future experimental work in the study of size effects or fabrications of ferroelectric thin films.

References