Theoretical studies on the pyroelectric properties of two component composite ferroelectric thin film

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Abstract

Using a Ginzburg–Landau–Devonshire type model, the pyroelectric property and hysteresis loop are studied for a composite ferroelectric thin film that contains an insertion of a different type of ferroelectric material in parallel connection with the host ferroelectric film material. If these two types of ferroelectric materials are polarized along the same direction, there are two peaks occur in the pyroelectric coefficient vs temperature curve. If the two ferroelectric materials are polarized in opposite directions, one positive and one negative coefficient peaks occur in the temperature dependence of pyroelectric coefficient curve and the hysteresis loop appears to be a quasi-double loop. The effect of the external electric field on the pyroelectric coefficient is also investigated.

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1. Introduction

Ferroelectric thin films have attracted a lot of interests of scientists in different disciplines since they are very useful in microelectronic device applications [1]. Pyroelectric property is one of the most important properties of ferroelectric thin films, which has been studied for applications in infrared ray (IR) detections. In particular, they have been used as active sensing elements of focal plane arrays in thermal imaging systems [2,3]. With the rapid development of advanced synthesis techniques, the fabrication of ferroelectric multilayers [4] down to nanometer layer thickness is possible [5,6]. Multilayer films have been studied extensively due to their fascinating properties that can differ substantially from that of bulk material or single layer film [7]. They have been found broad application in devices, such as pyroelectric detectors, memory systems and electro-optic modulators [8–10].

In recent years, many experimental works have been done to improve the pyroelectric properties of ferroelectric thin films. High-quality multiplayer ferroelectric thin films based on erbium-doped lead titanate Pb(1−x)1.1Er2Ti1−x/3O3 (PET) where x = 0.05 and Pb1.1(Zr0.58Fe0.25Nb0.2Ti0.02)O3 (PZFNT) have been studied. An unusually high pyroelectric coefficient of approximate 620 µcm−2 K−1 was obtained [11]. Using a specially developed metal-organic deposition (MOD) process, ferroelectric PZT films on Pt/Si substrates were fabricated, high pyroelectric coefficient and improved conversion effects were successfully demonstrated by Buchanan et al. [12]. D. Akai et al. have investigated epitaxial ferroelectric Pb(Zr, Ti)O3 (PZT)/Pt films on Si substrates using an epitaxial γ-Al2O3 buffer layer. The research showed that the PZT films exhibited better ferroelectric and pyroelectric properties than polycrystalline PZT films [13]. The properties of PZT/PT (Pb(Zr0.3Ti0.7)O3/PbTiO3) multilayer thin films with different PZT and PT layer stacking structures have been systematically

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studied by L. Sun et al. The 5PZT/4PT thin film shows higher pyroelectric coefficients [14].

One of the purposes of studying multilayer ferroelectric thin film is to improve the functionality of the film material [15,16]. From the above mentioned results, we can see that the pyroelectric properties of ferroelectric films have been effectively improved through multilayer structure. In practical applications, reliability of devices is the most important factor. For multilayer thin films, molecular diffusion between neighboring layers, particularly in high temperature environment in which ionic mobility increases, will destroy the functions of the multilayer film. Here, we investigate a different film design, i.e., using two types of ferroelectric materials connected in parallel configuration, which is an extension of the two-component film configuration addressed previously in Ref. [7]. The new film configuration demonstrates many new features, particularly in pyroelectric properties. Such composite film design might be an alternative design to the commonly used multilayer films.

The GLD thermodynamic theory for ferroelectrics has been one of the most successful theoretical methods treating ferroelectricity. In the present Letter, we use this method to study the pyroelectric property and the hysteresis loop of the composite film. The two types of ferroelectric materials all have second-order phase transition and having similar material constants except they will have different phase transition temperature.

2. The model

The geometrical parameters of the ferroelectric thin film under investigation are shown depicted in Fig. 1. The ferroelectric thin film contains two kinds of ferroelectric materials arranged in parallel configuration and is coated with metallic electrodes. Ferroelectric (Ferro) II is an insertion in the middle of Ferro I material. As a continuous structure, there is a transition region between Ferro I and Ferro II. The z axis is perpendicular to the film; the x axis is in film plane and perpendicular to the interface between two ferroelectric materials. Assume that η denotes the thickness of the film and the interface between two materials is a plane and the interface between two ferroelectric materials all have second-order phase transition and having similar material constants except they will have different phase transition temperature.

\[
G = G_0 + \eta \int_{-L}^{L} dx \left( \frac{1}{2} A(x) \left( T - T_0(x) \right) \right)^2 + \frac{1}{4} B(x) P^4
\]

where \(E\) is a constant external electric field; \(P\) is the spontaneous polarization and \(G_0\) is the free energy of the system in the paraelectric phase state. We assume that all parameters have the same form of \(x\) dependence, so that

\[
G = G_0 + \eta \int_{-L}^{L} dx \left( \frac{1}{2} A_1 \mu(x) \left( T - T_c \mu(x) \right) \right)^2 + \frac{1}{4} B_1 \mu(x) P^4
\]

where \(A_1, B_1, T_c\) and \(K_1\) are the bulk material parameters of ferroelectric material \(I\), and they are independent of temperature \(T\) and position \(x\); \(T_c\) is the transition temperature of the material of Ferro I.

To find the equilibrium state, we need to solve the Euler’s equation:

\[
\left\{ \begin{array}{l}
\frac{d f}{d \xi} = [t - \mu(\xi)] f + f^3 - \frac{d}{d \xi} [\ln \mu(\xi)] \frac{df}{d \xi} - e \sigma \mu^{-1}(\xi), \\
\frac{d f}{d \xi} |_{\xi = \delta} = 0,
\end{array} \right.
\]

where \(f = P/P_0\), \(P_0 = \sqrt{A_1 T_c/B_1}\), \(\xi = x/\xi_0\), \(\xi_0 = \sqrt{K_1/A_1 T_c}\), \(l = L/\xi_0\), \(\sigma = (\varepsilon_0 A_1 T_c)^{-1}\), \(e = E/(P_0/\varepsilon_0)\), \(T = T/T_c\), and \(\varepsilon_0\) is the vacuum permittivity. The parameter \(\sigma\) is the ratio of the Curie constant over the Curie temperature of Ferro I material. For a practical ferroelectric material with a second-order phase transition, the Curie constant is \(\sim 10^5\) K and the Curie temperature is \(\sim 10^5\) K, therefore, we take \(\sigma = 6\) as a representative value in our calculations.
3. Numerical results and discussions

With continuity consideration, the function $\mu(\zeta)$ is taken as the following form:

$$
\mu(\zeta) = \begin{cases} 
1.0, & -l - \delta_0 - \delta_0 < \zeta < -\delta_0 + \delta_0 \\
1.0 - \gamma (1.0 + \sin(\pi \zeta / 2 \lambda_0)), & -\lambda_0 - \delta_0 < \zeta < -\delta_0 + \delta_0 \\
1.0 - 2\gamma, & -\delta_0 < \zeta < 0 \\
\end{cases}
$$

where $\lambda_0 = \lambda / \xi_0$ is the length of the transition layer in units of $\xi_0$, $\delta_0 = \delta / \xi_0$ is the relative thickness of Ferro II, $T_c(1.0 - 2\gamma)$ is the Curie temperature of material II, and $2\gamma T_c$ is the Curie-temperature difference between the two ferroelectric materials. In the following calculations, $l$ is taken as 8, which means that the length of the ferroelectric film in the $x$-direction is $16\xi_0$.

The pyroelectric coefficient reflects the ability to generate charge through temperature variation, which is defined as:

$$
\alpha = \frac{\partial \bar{P}}{\partial T}/\bar{P} = \frac{\rho_0}{T_c} \alpha',
$$

where $\alpha' = (\partial \bar{f}/\partial t)|_{\bar{f}}$ and $\bar{f} = \bar{P}/P_0$. $\bar{P}(\bar{f})$ is the average polarization of the film. Generally speaking, the spontaneous polarization of the ferroelectrics decreases with the increase of temperature, hence, the pyroelectric coefficient is usually negative. In our calculations, we take the opposite value to make the normalized pyroelectric coefficient $\rho$ to be positive,

$$
\rho = - (\partial \bar{f}/\partial t)|_{\bar{f}}.
$$

The calculations have been carried out for two different configurations as described below.

3.1. Both Ferro I and Ferro II have spontaneous polarization along the $z$-direction

Using Eq. (3) we have calculated the average spontaneous polarization as a function of temperature for different $\delta_0$ and $\gamma$ values and the results are shown in Figs. 2 and 3. In these calculations the relative thickness of the transition layer is $\lambda_0 = 1.0$ and the external electric field takes the value of $e = 0$ and $e = 0.0005$, respectively, in Figs. 2 and 3. Results for single phase (Ferro I) is also calculated as comparison.

It is demonstrated that the mean polarization and the transition temperature of the ferroelectric thin film is lowered due to the inclusion of a second phase slab. Stronger influence comes from Curie temperature difference of the two materials and the volume of the second phase also has influence but not as strong. Specifically, larger $\gamma$ values will make the mean polarization smaller. When parameter $\gamma = 0.1$, i.e. the curie temperature of is $1.0$ for Ferro I and $0.8$ for Ferro II, strong polarization reduction occurs near temperature $= 0.8$ due to the phase transition of Ferro II. For the same reason, there is a strong decrease of polarization near temperature $0.6$ when $\gamma$ is taken as $0.2$. The effect of the parameter $\delta_0$ is to change the spontaneous polarization as well as the transition temperature. Larger $\delta_0$, or wider region of Ferro II, will lead to smaller polarization and lower transition temperature. Comparing the results of Figs. 2 and 3, it can be found that the application of external electric field smoothed the curve because the direction of the external electric field is the same as that of the spontaneous polarization, which makes help the development of polarization.

Figs. 4 and 5 show the temperature dependence of the pyroelectric coefficient. Two cases, i.e., for $e = 0$ (thicker solid line) and $e = 0.0005$ (dashed line), have been calculated. The dotted
Fig. 5. Temperature dependence of the pyroelectric coefficient $\rho$. The polarization directions of the two ferroelectrics are both along the $z$ axis. Parameters used in the calculations are: $\lambda_0 = 1.0$, $\delta_0 = 0.1$ and $\gamma = 0.2$.

Fig. 6. Average spontaneous polarization $\bar{P}$ as a function of temperature $T$. The polarization directions of the two ferroelectrics are opposite and the external electric field is $e = 0$.

Fig. 7. Average spontaneous polarization $\bar{P}$ as a function of temperature $T$. The polarization directions of the two ferroelectrics are opposite and the external electric field is $e = 0.0005$.

Fig. 8. Temperature dependence of the pyroelectric coefficient $\rho$. The polarization directions of the two ferroelectrics are opposite and the electric field is $e = 0.0005$.

Fig. 9. Temperature dependence of the pyroelectric coefficient $\rho$. The polarization directions of the two ferroelectrics are opposite and the electric field is $e = 0.0005$.

3.2. Ferro I and Ferro II have opposite spontaneous polarization direction

First, we have calculated the average spontaneous polarizations as functions of temperature as shown in Figs. 6 and 7. The dashed lines are for the single phase case (with material Ferro I). The values of parameters $\delta_0$ and $\gamma$ are the same in (thinner solid) line is for single phase of Ferro I under an electric field $e = 0.0005$ ($e = 0$). The parameter $\gamma$ is taken as 0.1 and 0.2, respectively, in Figs. 4 and 5. The results in the two figures show that for the ferroelectric thin film studied, two pyroelectric coefficient peaks appear in both $e = 0$ and $e = 0.0005$ cases. The peak height is lower for the two phase situation than for the single phase case. The results clearly show that the effect of the external electric field is to widen peak width at the expense of lowering the peak height. Therefore, if the material properties are gradually changing along the $x$-direction, it is possible to make a more temperature stable pyroelectric material although the maximum value of the pyroelectric coefficient may not be as high. The results in Figs. 4 and 5 are very similar except the peak positions. Hence, we can conclude that the parameter $\gamma$ is a factor determines the peak position of the pyroelectric coefficient.
the cancellation effect of Ferro II. There is a sharp peak near the critical temperature of Ferro II and the peak become sharper when an external field is applied. Such drastic change of polarization will produce strong peak in the pyroelectric coefficient. In Figs. 8 and 9, the pyroelectric coefficient versus temperature are plotted for the cases of \( e = 0 \) and \( e = 0.0005 \). (The direction of the electric field is still along the \( z \) axis.) Two pyroelectric coefficient peaks with opposite directions appear, the lower temperature peak drops sharply and its absolute value is much very larger while the higher temperature peak has relatively small amplitude. The amplitude of the reversed pyroelectric peak is increased by the application of external electric field. Although such sharp change may not be so useful in pyroelectric applications, it might useful as temperature sensitive switch.

Although the reversed polarization region is small, it has very strong influence to the effective properties of the film and the composite film shows some characteristics of antiferroelectrics as shown in the hysteresis loops (Fig. 10). In general, the thicker insertion layer of Ferro II and larger transition temperature difference between Ferro I and Ferro II will reduce the total remanent polarization and the coercive field. The reduction of coercive field is due to the fact that the coercive field of the Ferro II insertion layer is smaller.

4. Summary and conclusions

Using a Ginzburg–Landau–Devonshire model with the addition of transition layer, the pyroelectric properties are studied for a ferroelectric thin film containing a second phase region. The two phases are made of similar material but the inserted section (Ferro II) has lower phase transition temperature. A transition layer is included at the Ferro I and Ferro II interface which guarantees the continuity of the whole film. The following results have been obtained:

1. The difference of the phase transition temperatures and polarization directions of the two materials are two main factors influencing the pyroelectric properties of the films;
2. Interesting pyroelectric characteristics can be achieved when the two ferroelectric materials are poled along opposite directions and a bias-electric field is applied. The abrupt change of the pyroelectric properties could be used to make certain temperature switch.
3. The hysteresis loop of composite film with opposite polarization directions shown typical characteristics of antiferroelectrics.

References