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Dependence of polarization offset on driving frequency, film thickness and composition gradient in compositionally graded ferroelectric materials

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Abstract We studied theoretically the effects of frequency and film thickness on the charge offset of the compositionally graded ferroelectric films. The time-dependent space-charge-limited conductivity has been used to investigate the dynamic response of the hysteresis loops as would be measured from a Sawyer-Tower circuit. In addition, the effect of compositional gradient on the charge offset is studied by plotting the charge offset as a function of the Ba concentration in a graded BST structure. A maximum charge offset is predicted at a critical Ba concentration which is consistent with other theoretical predictions based on different mechanisms.

Keywords Polarization offset · Charge offset · Composition gradient · Compositionally graded ferroelectric

1 Introduction

Compositionally graded ferroelectric films have attracted great research interest in recent years for their unusual properties that are not routinely observed for homogeneous ferroelectrics. One of the most notable unconventional behaviors presented by such heterogeneous ferroelectric systems is the large vertical shift in D-E hysteresis loops when they are measured in a Sawyer-Tower circuit driven by an alternating voltage [1–3]. The offsets have been reported to have a strong temperature and electric field dependence. These unconventional features have made graded ferroelectrics attractive for applications in a variety of devices and sensors. On the other hand, it has been demonstrated later that the same anomalous shift behavior is observed in homogeneous (Ba,Sr)TiO_3 thin film by impressing temperature gradients or by imposing non-uniform external stress [4]. However, compositional grading is the most common way to introduce graded ferroelectric properties in ferroelectric materials, leading to the anomalous hysteretic behavior. Although many attempts are made to explain this anomalous vertical offset of hysteresis loops, the origin of the shift as well as its temporal dependence on various parameters is still not fully explored, and is not yet definitively understood.

In this present study, we employ the time-dependent space-charge-limited conduction mechanism [5] to study the effects of driving frequency, thickness and compositional gradient on the vertical offsets in graded ferroelectric thin films placed in a Sawyer-Tower circuit. Our results are quite consistent with other theoretical predictions available in the literature. Our model can be readily extended to study temperature and stress gradient induced polarization offsets.

2 Theory and modeling

The graded ferroelectric film is considered as a stacking of N thin layers of equal thickness $\Delta x = L/N$, where L is the film thickness. The origin $x = 0$ is located at the interface between the ferroelectric film and top electrode. Then the position of any layer inside the film is given by $x = i \cdot \Delta x$, where $1 \leq i \leq N$. The polarization and electric field within this layer are denoted by $P(x, t)$ and $E(x, t)$, respectively, along the x direction. The dynamics of the dipoles is modeled by the Landau-Khalatnikov equation [6]:

$$\gamma \frac{\partial P(x,t)}{\partial t} = -\alpha(x)P(x,t) - \beta(x)P(x,t)^3 + E(x,t) + \kappa(x)\left[P(x+\Delta x,t) + P(x-\Delta x,t) - 2P(x,t)\right] \quad (1)$$

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where γ represents the viscosity that causes the delay in motion of dipole moments. $\alpha(x)$ and $\beta(x)$are the corresponding Landau coefficients of the material at position x. The last term in Eq. (1) comes from energy associated with polarization gradients, where $\kappa(x)$ is the corresponding interaction coefficient between neighboring dipoles.

The time-dependent space-charge-limited conductivity has been demonstrated to be a possible origin that gives rise to the polarization offsets in our previous study of compositionally graded ferroelectric films. It is written as:

$$\sigma(x,t) = \frac{\mu_p - \mu_n}{2}\frac{\partial D(x,t)}{\partial x} + \sqrt{\left[\frac{\mu_p + \mu_n}{2}\frac{\partial D(x,t)}{\partial x}\right]^2 + \sigma_0(x)^2} \quad (2)$$

where $D(x,t) = \varepsilon(x)E(x,t) + P(x,t)$ is the electric displacement at position x, μ_p and $-\mu_n$ ($\mu_p,\ \mu_n > 0$) are respectively p-type and n-type mobilities and $\sigma_0(x)$ is the equilibrium conductivity. The total current $J(t)$ is continuous across the circuit:

$$J(t) = \sigma(x,t)E(x,t) + \frac{\partial D(x,t)}{\partial t} = \frac{V_{ref}(t)}{R_{ref}A_f} + \frac{C_{ref}}{A_f}\frac{dV_{ref}(t)}{dt} \quad (3)$$

where C_{ref}, R_{ref} and A_f are respectively the capacitance of the reference capacitor, input impedance of the oscilloscope placed electrically in parallel with the reference capacitor and cross-sectional area of the ferroelectric film; $V_{ref}(t)$ is the measured voltage of the reference capacitor. The circuit condition is given by:

$$\int_0^L E(x,t)\,dx + V_{ref}(t) = V_o(t) \quad (4)$$

where $V_o(t) = V_{amp}\sin(\omega t)$ is the applied sinusoidal voltage.

The above variables are converted into dimensionless forms by the following relations:

$$P^* = \frac{P}{P_S},\quad t^* = \frac{t}{\tau},\quad x^* = \frac{x}{\Delta x},\quad \alpha^* = \frac{\tau\alpha}{\gamma},$$
$$\beta^* = \frac{\tau P_S^2\beta}{\gamma},\quad E^* = \frac{\tau E}{\gamma P_S},\quad \kappa^* = \frac{\tau\kappa}{\gamma},\quad D^* = \frac{D}{P_S},$$
$$\varepsilon^* = \frac{\gamma\varepsilon}{\tau},\quad j^* = \frac{\tau j}{P_S},\quad V^* = \frac{\tau V}{\gamma\Delta x P_S},\quad C^* = \frac{\gamma\Delta x C_{ref}}{A_f\tau},$$
$$\sigma^* = \gamma\sigma,\quad \mu_p^* = \frac{P_S\gamma\mu_p}{2\Delta x},\quad \mu_n^* = \frac{P_S\gamma\mu_n}{2\Delta x},\quad R^* = \frac{A_f R_{ref}}{\gamma\Delta x} \quad (5)$$

where P_S is the remanent polarization for a bulk sample and τ is a characteristic relaxation time for the system.

With normalized polarization and time parameters, Eqs. (1)–(3) and (4) become

$$\frac{dP^*(x^*,t^*)}{dt^*} = -\alpha^*(x^*)P^*(x^*,t^*) - \beta^*(x^*)P^*(x^*,t^*)^3 + E^*(x^*,t^*) + \kappa^*(x^*)[(P^*(x^*+1,t^*) + P(x^*-1,t^*) - 2P^*(x^*,t^*)] \quad (6)$$

$$\sigma^*(x^*,t^*) = (\mu_p^* - \mu_n^*)\frac{\partial D^*(x^*,t^*)}{\partial x^*} + \sqrt{\left[(\mu_p^* + \mu_n^*)\frac{\partial D^*(x^*,t^*)}{\partial x^*}\right]^2 + \sigma_0^*(x^*)^2} \quad (7)$$

$$J^*(t^*) = \sigma^*(x^*,t^*)E^*(x^*,t^*) + \frac{\partial}{\partial t^*}D^*(x^*,t^*) = \frac{V_{ref}^*(t^*)}{R_{ref}^*} + C^*\frac{dV_{ref}^*(t^*)}{dt^*} \quad (8)$$

$$\sum_{i=0}^{N} E_i(x,t) + V_{ref}^*(t) = V_0^*(t) \quad (9)$$

Also, it is found through calculation that the effects of $\kappa(x)$ on many materials systems are quite limited. Hence we have neglected $\kappa(x)$ in the simulation.

3 Results and discussion

This section is divided into two Sections 3.1 and 3.2. In Section 3.1, we study the dependence of vertical offsets on frequency and thickness in a dimensionless way. By using realistic parameters, we study the effect of spatial variation of compositional gradient on the charge offsets of compositionally graded BT-BST thin film in Section 3.1. The parameters used in our modeling are listed in Tables 1 and 2.

3.1 Effects of frequency and film thickness

In reality, all ferroelectrics possess some finite conductivity, which allows charge transport and accumulation. Since the occurrence of polarization offsets has been interpreted as possibly being originated from asymmetric conductivity in graded ferroelectrics [5], it is desirable to examine the frequency dependence of charge offset. In this calculation, the remanent polarization and permittivity are assumed linearly varying with x in the same direction, and the coercive field and intrinsic conductivity are assumed to be constants as shown in Table 1. The solid line in Fig. 1 denotes the charge offset $Q_{off}^* = C_{ref}^* V_{off}^*$, where V_{off}^* is the shift of the center

Table 1 The dimensionless parameters used in our calculations

Figure	P_r^*	E_c^*	$\varepsilon^*/\varepsilon_0(10^{-2})$	$\sigma_0^*(10^{-4})$	L^*	$\mu_p^*(10^{-3})$	μ_n^*	f^*
1	$0.3 + 0.04x$	0.3	$26 + 0.033x$	1	30	0.01	0.1	Varied
2	$0.3 + 0.04x$	0.3	$26 + 0.033x$	1	Varied	0.01	0.1	0.2

Table 2 Physical properties of $Ba_cSr_{1-c}TiO_3$ used in the calculation

c	α^* (kV · cm/μC)	β^* (kV · cm^4/μC^2)	$\varepsilon/\varepsilon_c^b$
0	39	840	92
0.2	23	743	104
0.4	12	646	140
0.6	4.7	550	374
0.8	−1.4	453	685
1	−6.1	356	491

of the $V_{ref}^*(t)$ versus $E_{ave}^*(t)$ curve and $E_{ave}^*(t)$ is the average electric field in the film, along the vertical axis as a function of applied frequency f^*. As f^* decreases, the charge offset Q_{off}^* increases. This is probably due to the fact that the conductivity effect is enhanced at lower measurement frequency. When the frequency f^* is larger than 0.1, the modeled hysteresis loop is very symmetrical and centered at the origin of the axes, while the simulated hysteresis loop will become significantly distorted if $f^* < 0.005$. This agrees with the analysis reported by Wong et al. [7]. Since the dynamic shifting effect is highly related to the temporal characteristic of the TDSCL conduction, a frequency dependence of the rate of approach to the steady state offset is expected. The dotted line in Fig. 1 represents the relationship between frequency and the time taken to reach steady state. As expected, it requires a longer duration of measurement to reach the steady state with a lower driving frequency. Overall, the results show that the vertical shifting effect will become more significant with decreasing applied voltage frequency and that the time needed to reach steady state is almost linearly dependent on the applied frequency.

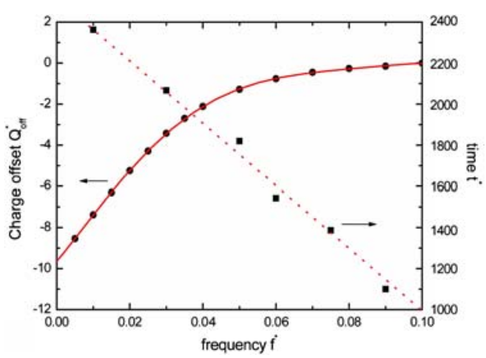

Fig. 1 The frequency dependence of (*a*) charge offset; (*b*) time taken to reach steady state

The effect of thickness of the film on Q_{off}^* is demonstrated in Fig. 2. As the thickness increases, Q_{off}^* will decrease. When $L^* = L/\Delta x$ is sufficiently large (such as $L^* > 100$), there is almost no notable vertical offset of the simulated hysteresis loop. The film thickness dependence of Q_{off}^* is believed to come from the spatial dependence of the TDSCL conduction.

3.2 Charge offset in compositionally graded BST thin film

Compositionally graded barium strontium titanate (BST) thin films have been extensively studied for many years due to their good dielectric performance. To better understand the effect of the compositional gradient on the polarization offset, we plot in Fig. 3 the charge offset as a function of Ba concentration c of $BaTiO_3$-$Ba_cSr_{1-c}TiO_3$ graded thin film. Within the graded BT-BST structure, Ba concentration at the $x = L$ end of the film is denoted by c while the $x = 0$ end has fixed Ba concentration corresponding to pure $BaTiO_3$.

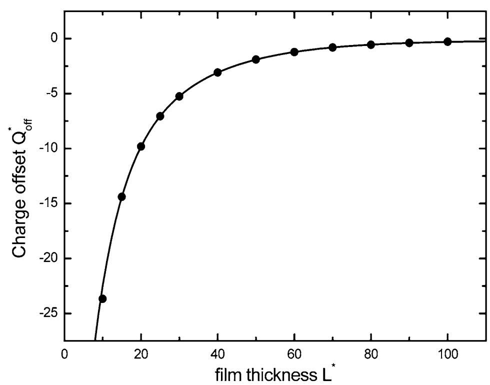

Fig. 2 Thickness dependence of charge offset

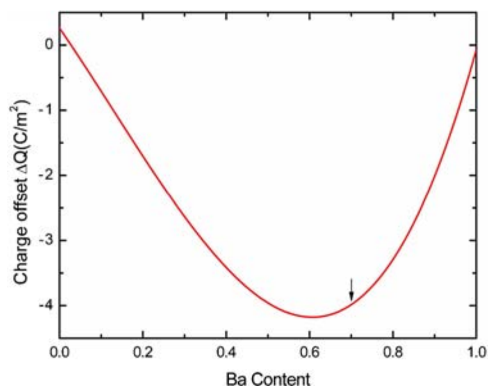

Fig. 3 The calculated charge offset as a function of the Ba concentration in the bottom layer in a down-graded BT-BST structure

The physical properties of $Ba_cSr_{1-c}TiO_3$ used in the calculation are taken from related references and listed in Table 2. The properties for $Ba_cSr_{1-c}TiO_3$with different Ba content are obtained by linear interpolation and a linear relationship between the composition and position is assumed. We have adopted the following values $\sigma_0 = 1 \times 10^{-11}\ \Omega^{-1}\mathrm{m}^{-1}$ and $\mu_n = 1000\,\mu_p = 1 \times 10^{-7}\,\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$ for the intrinsic conductivity and charge carrier mobilities in the BT-BST thin film [8–10]. As insufficient data for the intrinsic electrical conductivity and charge mobilities of compositionally graded BST are provided in the literature, we therefore assume that σ_0, μ_n and μ_p are spatially uniform. It is shown in Fig. 3 that the charge offset is significantly dependent on the compositional gradient. For compositionally homogeneous film (corresponding to $c = 1$), there is no charge offset as expected. The magnitude of charge offset is not a monotonic function of the composition gradient. It initially increases in a continuous fashion with increasing Ba content, reaching a maximum at $c \approx 0.6$, and then decreases. Our results are consistent with theoretical predictions based on different mechanisms available in the literature [4, 11]. Experimentally, a large translation of hysteresis loops along the displacement axis was indeed reported in the literature when $c = 0.7$ [13] which is fairly predictable by our model as shown in Fig. 3 (see the arrow).

4 Conclusion

Summing up, our model adopts Landau-Khalatnikov equation to describe hysteresis loop behaviour and TDSCL conduction mechanism for charge transport in compositionally graded ferroelectrics. The effects of driving frequency and film thickness on the polarization offset of graded ferroelectric thin film, placed in Sawyer-Tower circuit, are specifically discussed and demonstrated to be key factors determining the charge offset. The compositional dependence of charge offset of graded BT-BST thin film is also modeled. It is found that large charge offsets can be obtained by carefully selecting the compositional gradient. Further efforts are worth to theoretically investigate the effects of stress and temperature gradients on the polarization offset in homogeneous ferroelectric structures.

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