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Dynamic hysteresis dispersion scaling of ferroelectric Nd-substituted $Bi_4Ti_3O_{12}$ thin films

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Abstract

The dynamics of ferroelectric hysteresis for Nd-substituted $Bi_4Ti_3O_{12}$ thin films as a function of frequency and amplitude of time-varying external electric field is measured utilizing a Sawyer–Tower (ST) circuit. The frequency ranges from 1 to 10^6 Hz and the amplitude range is 101–400 kV cm^{-1}. Given a fixed field amplitude E_0, the hysteresis area A first grows and then decays with increasing frequency f. We study the characteristics of the dynamic order parameter Q against field amplitude E_0. The frequency dependence of the hysteresis area over the low-frequency range can be expressed as $A \propto E_0^{2/3} f^{1/3}$. However, over the high-frequency range, the frequency dependence takes the form $A \propto E_0^2 f^{-2/3}$. We demonstrate that the hysteresis dispersion approaches its scaling state when the field amplitude E_0 is higher than 170 kV cm^{-1}, and a unique effective characteristic time τ_1 exists for the domain reversal that is inversely proportional to the field amplitude.

1. Introduction

$PbZr_{1-x}Ti_xO_3$ (PZT) and $SrBi_2Ta_2O_9$ (SBT) are two conventional ferroelectric materials for non-volatile random access memory (NvRAM) applications [1]. However, they still have some disadvantages from the point of view of practical applications. PZT thin films with Pt electrodes show poor fatigue resistance upon polarization switching, while SBT thin films possess a low remnant polarization value (P_r). Recently, trivalent rare-earth cations, such as La-, Sm- and Nd-doped Bi-layered oxides $Bi_4Ti_3O_{12}$ (BTO) are emerging as promising candidates for NvRAM because of their relatively large P_r value and excellent fatigue resistance [2]. By systematically studying La-, Sm-, Nd- and Gd-substituted BTO films, Chon *et al* [3] reported that thin films of Nd-substituted BTO, $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ (BNT), have large P_r and fatigue-free characteristics.

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A lot of work on BNT thin films with different Nd compositions has been reported [4]. In this paper, we would like to focus on the frequency response and check the scaling hypothesis of the hysteresis dispersion for BNT thin films under a time-varying external field E. The hysteresis area A represents the energy dissipation within one period of domain reversal so that it presents us with much information on the dynamics of domain reversal driven by a time-varying electric field, which is helpful for us to predict the performance of ferroelectric thin films as used in NvRAM devices. Meanwhile, the dynamic hysteresis, i.e. the hysteresis area A as a function of amplitude E_0 and frequency f of the applied field E, can also help us to understand the dynamics of domain reversal, in particular the characteristic times of domain nucleation and domain boundary motion as concurrent processes during the domain reversal [5].

The theoretically well-established dependence relations of hysteresis area A on E_0 and f were derived from a three-dimensional $(\Phi^2)^2$ or $(\Phi^2)^3$ model with O(N) symmetry in the large N limit [6, 7]. Over the low-f range and high-f range, respectively, these models predict a power-law dependence:

$$A(f, E_0) \propto \begin{cases} f^{1/3} E_0^{2/3} & \text{as } f \Rightarrow 0 \\ f^{-1} E_0^2 & \text{as } f \Rightarrow \infty. \end{cases} \tag{1}$$

This prediction was originally proposed for ferromagnetic systems and subsequently extended to ferroelectrics [7]. The first aim of this paper is to check the applicability of equation (1) for ferroelectric BNT thin films.

However, we understand that the domain reversal in ferroelectrics can be explained by the concept of nucleation and growth mechanism. A scaling hypothesis was recently proposed to understand the dynamics of domain reversal in ferroic systems [8]. For a time-varying electric field $E(t)$ at time t, say $E(t) = E_0 \sin(2\pi f t)$, the nucleation velocity of new domains and domain boundary motion rate can be characterized by two characteristic times, t_n and t_g, respectively. For ferroelectric thin films under $E(t)$, the domain nucleation and domain boundary motion cannot be two sequences well separated in time; they must overlap with each other. In order to characterize the kinetics of domain reversal where the two sequences proceed concurrently, it is physically reasonable to define a third time $t_\mathrm{e} \sim (t_\mathrm{n} t_\mathrm{g})^{1/2}$, which may be called the effective time of the domain reversal [9]. If such a characteristic time t_e exists uniquely, the hysteresis area A as a function of f at different values of E_0 would be scalable by a one-parameter scaling function [10]. That is the so-called scaling hypothesis of hysteresis dispersion. Whether the hysteresis dispersion for BNT thin films supports this one-parameter scaling hypothesis would be the second issue of the present study, noting that this hypothesis has been confirmed with PZT and SBT thin films [10, 11].

2. Experimental details

The BNT thin films used in this study were prepared onto oxidized Si substrates coated with a bottom electrode consisting of a thin TiO_2 adhesion layer plus a sputter-deposited Pt layer by pulsed laser deposition (PLD). The BNT thin films were deposited at 750 °C for 25 min using a KrF excimer laser of wavelength 248 nm and pulsewidth 30 ns. The films used for the subsequent measurement are ∼500 nm thick. In our experiments, the average pulse energy was about 200 mJ/shot (an energy density of ∼1.2 J cm^{-2}), the deposition frequency was 5 Hz and the pressure of flowing oxygen during deposition was 30 Pa. After the deposition, the films were *in situ* annealed in the chamber at 750 °C in a 0.5 atm oxygen atmosphere for 10 min. Pt top electrodes of 200 μm in diameter were sputter-deposited at room temperature with a shadow mask. Finally, a 10 min post-annealing at 750 °C was conducted to improve the adhesion of the top electrode with the film surface and relax the stress in the films. This sample

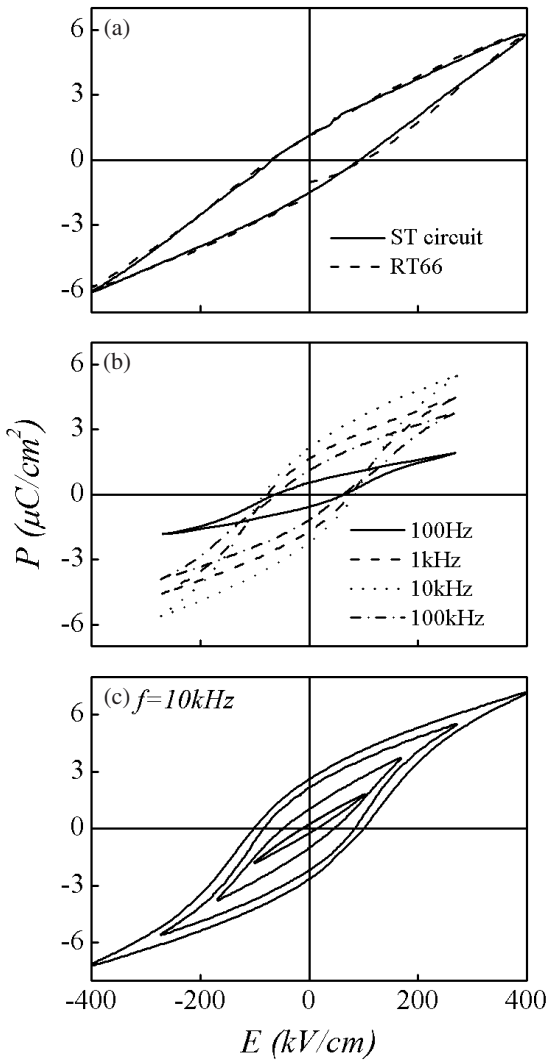

Figure 1. Measured hysteresis loops (a) by the ST method and an RT66 testing unit, (b) by the ST method at $E_0 \sim 280$ kV cm^{-1} and four different frequencies and (c) by the ST method at $f = 10$ kHz and four different amplitudes.

preparation procedure represents the standard one for ferroelectric thin films for NvRAM applications [2, 3].

The dynamic hysteresis was measured using the Sawyer–Tower (ST) method [12]. In order to ensure the reliability of the data by the ST method, we compare the data obtained with the ST method and the data measured by the standard RT66A ferroelectric testing unit (Radiant Technologies Inc., NM, USA). In figure 1(a), where two hysteresis loops measured by a RT66A unit at a hysteresis time of 112 ms and by our ST circuit at $f = 10$ Hz (period 100 ms) respectively are shown, the two loops are very consistent with each other, although the hysteresis is not well saturated, demonstrating the reliability of the presented ST data.

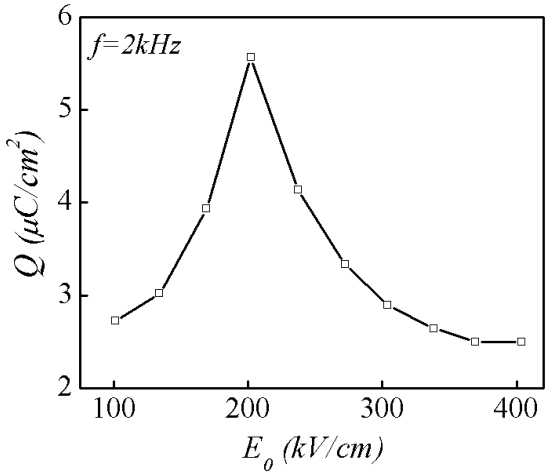

Figure 2. Dynamic order parameter Q as a function of amplitude E_0 at $f = 2$ kHz.

3. Results and discussion

Figures 1(b) and (c) present the as-measured hysteresis for various f at $E_0 \sim 280$ kV cm^{-1} and various E_0 at $f = 10$ kHz, respectively. As expected, the dependence of the hysteresis shape and area on f is very remarkable. In figure 1(b), one notes a remarkable evolution of hysteresis pattern upon varying f. At a low f, such as $f = 100$ Hz and 1 kHz, respectively, the loop area is relatively small with a low coercive field E_c and a small remnant polarization P_r, while these parameters increase with increasing f up to $f = 10$ kHz. However, with further increasing f, such as $f = 100$ kHz, the loop area again becomes small as does the remnant polarization and coercive field. The loop looks more saturated at $f = 1$ kHz than at $f = 100$ Hz, while toward $f = 100$ kHz the hysteresis finally evolves into a pattern far from saturation. Figure 1(c), shows that given a fixed f (say $f = 10$ kHz), the loop area A increases with amplitude E_0 over the whole f range (as do P_r and E_c), a well-understood effect.

The hysteresis evolution mentioned above can also be characterized by a dynamic order parameter Q defined as the time-averaged polarization over a complete period of the oscillating field ($Q = \frac{\omega}{2\pi} \oint p \, dt$) [8]. This parameter should be zero if the hysteresis is symmetric with respect to zero point, i.e. a perfect domain reversal driven by field E. In figure 2, Q is plotted against E_0 at a fixed frequency $f = 2$ kHz. Initially, when a low E_0 is applied to an unpoled sample, it leads to a partial dynamic alignment of the domains. This alignment is further improved with increasing E_0, but not all domains can be effectively reversed under such a low anti-parallel field. This results in an enhanced Q value until the maximum value reached at $E_0 \sim 202$ kV cm^{-1}. This field is much higher than E_c for BNT thin films. Afterwards, the value of Q decays rapidly with increasing E_0, indicating a perfect domain reversal.

To look at the frequency dependence of the hysteresis area over the low-f and high-f ranges, respectively, we plot the data of A against $E_0^m f^n$ where m and n are arbitrary numbers, assuming that equation (1) is applicable. Within the measurement uncertainty, the low-f data fit relation $A \propto f^{1/3} E_0^{2/3}$ quite well. For clarity, only the lower parts of the data are given in figure 3(a). An analysis on the high-f data reveals that A decays slowly with f but the dependence on E_0 is in agreement with the predicted scaling. In figure 3(b), it is clearly shown that the data over the high-f range can be scaled as $A \propto f^{-2/3} E_0^2$. This indicates that the decay of A with f over the high-frequency range is much slower than the predicted linear

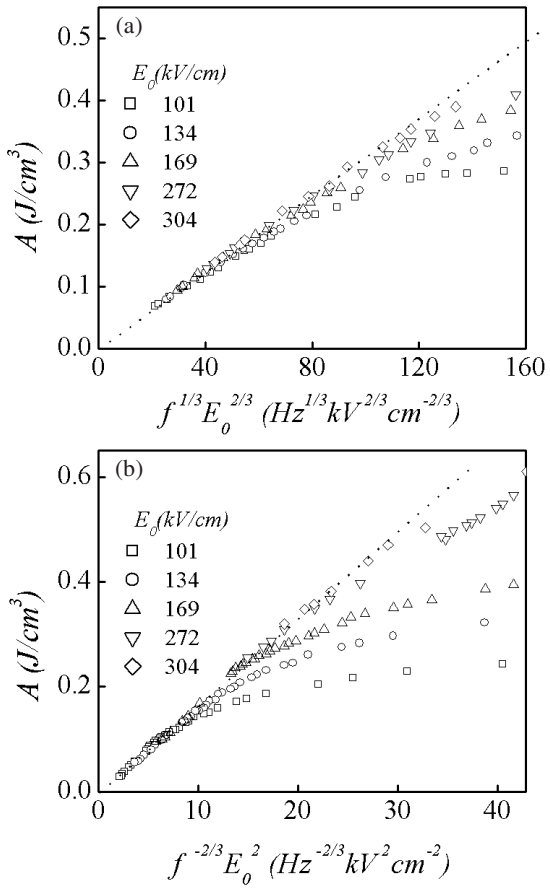

Figure 3. Frequency response of hysteresis area A plotted against (a) $f^{1/3}E_0^{2/3}$ over the low-frequency range and (b) $f^{-2/3}E_0^2$ over the high-frequency range.

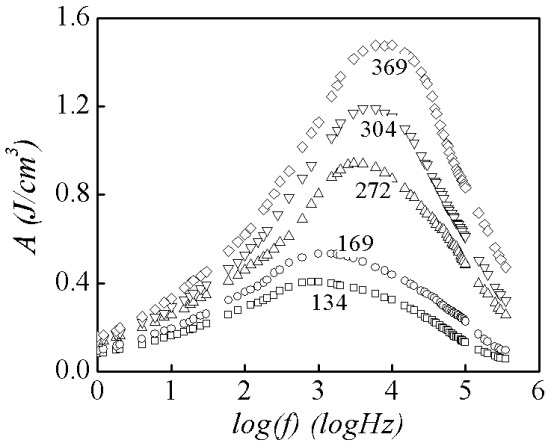

Figure 4. Hysteresis area A as a function of frequency f at five different amplitudes.

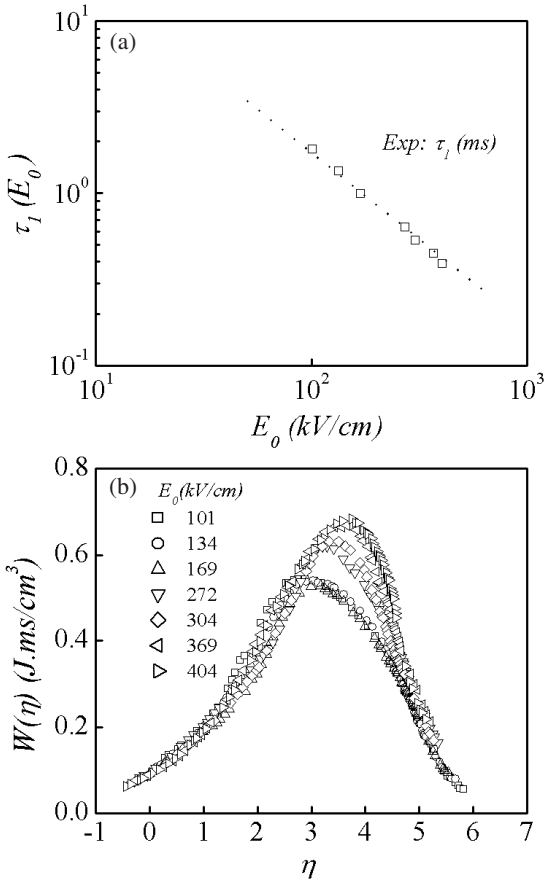

Figure 5. (a) Characteristic time τ_1 as a function of amplitude E_0, and (b) scaling function $W(\eta)$ as a function of scaling variable η.

rate as shown in equation (1). We then argue that the dynamic hysteresis in a BNT thin film capacitor does not follow the $(\Phi^2)^2$ or the $(\Phi^2)^3$ model.

The as-evaluated frequency dispersions of hysteresis area, $A(f)$, under various E_0 are presented in figure 4. It is clearly indicated that for all cases $A(f)$ exhibits a single-peaked pattern with both the peak position and the peak value increasing when E_0 increases. Furthermore, all $A(f)$ curves remain similar to one another in shape, which is quite similar to the structure function in quenched binary alloys [10], predicting the possibility of one-parameter scalability. To proceed with the scaling analysis, the simplest way is to evaluate an arbitrary nth momentum $S_n = \int_0^\infty f^n A(f)\,\mathrm{d}f$. We redefine the dispersion using $\log(f)$ as a variable and have the following scaling parameter [10]:

$$\begin{aligned}
&\gamma = \log(f)\\
&S_n(E_0) = \int_{-\infty}^{\infty} \gamma^n A(\gamma, E_0)\,\mathrm{d}\gamma, \qquad n = 1, 2, \ldots\\
&\gamma_n(E_0) = S_n(E_0)/S_0(E_0)\\
&n_2(E_0) = \gamma_2(E_0)/\gamma_1^2(E_0)\\
&\tau_1^{-1} = 10^{\gamma_1}
\end{aligned} \tag{2}$$

where γ is the modified frequency, γ_n is the nth characteristic frequency and τ_1 is the effective characteristic time. τ_1 as a function of E_0 is plotted in figure 5(a). It seems that a good linear relation between the as-defined τ_1 and E_0 exists apart from the cases where E_0 is lower than 170 kV cm^{-1}. On the one hand, this linear relation is consistent with the scaling hypothesis [9, 10], which indicates possible applicability of the scaling hypothesis. On the other hand, the dispersions under a low E_0 should not satisfy the scaling hypothesis because of the deviation of τ_1 from the linear relation $\tau_1 \propto E_0^{-1}$. In order to further investigate the scalability of the hysteresis dispersion, we assume that one-parameter scalability exists and construct the following scaling function:

$$\begin{aligned} W(\eta) &= \tau_1^{-d} A(\gamma, E_0) \\ \eta &= \log(f\tau_1) \end{aligned} \tag{3}$$

where η is the scaled frequency; the dimension d should meet $d \equiv 1$.

We replot all the dispersion curves $A(f)$ after the above scaling transform, as shown in figure 5(b). Clearly, except for the two curves at $E_0 = 101$ and 134 kV cm^{-1}, all other $A(f)$ curves roughly fall onto the same curve within the measurement uncertainties. This indicates that the hysteresis dispersions for BNT thin films under sufficiently high field amplitude E_0 support the dynamic scaling hypothesis. However, compared with the excellent scaling behaviours demonstrated for PZT and SBT thin films [9, 12], the scaling behaviours revealed here for BNT thin films still require further checking, noting that the dispersion data around the peak range show significant scattering.

4. Conclusion

In summary, we have studied the frequency response and scaling on hysteresis dispersion in ferroelectric $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ thin films. Power-law frequency dependences $A \propto E_0^{2/3} f^{1/3}$ over the low-frequency range and $A \propto f^{-2/3} E_0^2$ over the high-frequency range are proposed to characterize the dynamic hysteresis. However, we have revealed that the hysteresis dispersions for BNT thin films under sufficiently high field amplitude E_0 exhibit a scaling behaviour. The effective characteristic time for the domain reversal is inversely proportional to the field amplitude.

Acknowledgments

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