Dynamic hysteresis scaling of ferroelectric $Pb_{0.9}Ba_{0.1}(Zr_{0.52}Ti_{0.48})O_3$ thin films



2009 J. Phys.: Condens. Matter 21 485901

(http://iopscience.iop.org/0953-8984/21/48/485901)

J. Phys.: Condens. Matter **21** (2009) 485901 (8pp) doi:10.1088/0953-8984/21/48/485901

# Dynamic hysteresis scaling of ferroelectric $Pb_{0.9}Ba_{0.1}(Zr_{0.52}Ti_{0.48})O_3$ thin films

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Received 6 August 2009, in final form 24 September 2009
Published 30 October 2009
Online at stacks.iop.org/JPhysCM/21/485901

**Abstract**

We measure systematically the intrinsic scaling behavior of dynamic hysteresis for $Pb_{0.9}Ba_{0.1}(Zr_{0.52}Ti_{0.48})O_3$ (PBZT) ferroelectric thin films with Pt electrodes on Si substrates, utilizing the Sawyer–Tower technique. For the as-prepared thin films of similar thickness and microstructure, over the low frequency range, the scaling follows the power law $\langle A\rangle \propto f^{0.28}E_0^{0.91}$ under low $E_0$ and the power law $\langle A\rangle \propto f^{0.35}E_0^{0.78}$ under high $E_0$, where $\langle A\rangle$ is the hysteresis area, and $f$ and $E_0$ are the frequency and amplitude of the external electric field. In the high-$f$ range, the power law for low $E_0$ takes the form of $\langle A\rangle \propto f^{-0.32}E_0^{3.2}$, while that for high $E_0$ takes the form of $\langle A\rangle \propto f^{-0.2}E_0^{2.2}$. It is identified that the dynamic behaviors at low frequency mainly come from the intrinsic domain reversal instead of others like the leakage current, while the depolarization field may influence the frequency exponents at high frequency. We study the temperature scaling of the hysteresis, indicating that the scaling under low $E_0$ is roughly consistent with the $(\Phi^2)^2$ model. Finally, we argue that experimentally obtained power law scaling for $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films prepared under the given conditions may not be reliable due to the polarization fatigue effect.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Considering the potential applicability of high-speed ferroelectric (FE) random access memories (FeRAMs), the problem of dynamic hysteresis has been receiving a great deal of attention in theoretical works [1, 2]. The reversal of ferroelectric domains, i.e. the response of domain reversal to a time-varying external electric field $E$, is the core ingredient of dynamic hysteresis. Because the hysteresis area $\langle A\rangle$, which scales the energy dissipation within one cycle of domain reversal, is the characteristic parameter to scale the dynamic behavior of non-equilibrium first-order phase transitions in ferroelectrics [3], the scaling of the hysteresis area $\langle A\rangle$ against electric field $E$ would be of significance not only for technological applications but also from the fundamental point of interest.

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It has been well established that the dynamic hysteresis of ferroelectric and ferromagnetic systems below their phase transition points can be described by an exponential scaling law $\langle A\rangle \propto f^{\alpha}\cdot E_0^{\beta}$, where $E_0$ and $f$ are the amplitude and frequency of a time-varying applied field, and $\alpha$ and $\beta$ are the scaling exponents dependent on the dimensionality and symmetry of the system under consideration. Up to now, quite a few theoretical models on dynamic hysteresis have been proposed. For example, Rao *et al* studied in detail the three-dimensional $(\Phi^2)^2$ and $(\Phi^2)^3$ models with $O(N)$ symmetry in a large $N$ limit [4, 5], by which the dynamic hysteresis in the low-$f$ and high-$f$ limits can be described respectively by

$$\langle A\rangle \propto f^{1/3}E_0^{2/3} \qquad \text{as } f \Rightarrow 0, \tag{1}$$

$$\langle A\rangle \propto f^{-1}E_0^{2} \qquad \text{as } f \Rightarrow \infty. \tag{2}$$

Although the two models were initially proposed for magnetic systems where spin is the order variable, they

 

**Table 1.** Scaling exponents obtained for different ferroelectric thin films. Note that these thin films are essentially free of the polarization fatigue effect, either due to the oxide electrodes or originating from the materials themselves.

| System | | Low $f$ | | High $f$ | | References |
|---|---|---|---|---|---|---|
| | | $\alpha$ | $\beta$ | $\alpha$ | $\beta$ | |
| $(\Phi^2)^2$ and $(\Phi^2)^3$ models | | 1/3 | 2/3 | −1 | 2 | [4, 5] |
| SBT thin films | | 2/3 | 2/3 | −1/3 | 2 | [13] |
| PZT thin films | | 1/3 | 2/3 | −1/3 | 3 | [17] |
| PZT thin films | | 1/3 | 2/3 | −1/3 | 1 | [30] |
| BNT thin films | | 2/3 | 2/3 | −2/3 | 2 | [16] |
| Soft PZT bulk ceramic | Low $E_0$ | | | −0.33 | 3 | [27] |
| | High $E_0$ | | | −0.25 | 1 | [27] |
| Hard PZT bulk ceramic | Low $E_0$ | | | −0.43 | 3.19 | [29] |
| | High $E_0$ | | | −0.28 | 0.89 | [29] |
| PBZT thin films | Low $E_0$ | 0.28 | 0.91 | −0.32 | 3.2 | This work |
| | High $E_0$ | 0.35 | 0.78 | −0.2 | 2.2 | This work |

are of general significance since the models start from the Landau phenomenological theory and the order parameter (magnetization $M$) is a continuum variable rather than a two-state Ising spin moment (up or down). Therefore, the models can essentially be applied to ferroelectric systems where the Landau phenomenological framework and domain reversal dynamics remain similar in terms of the common nature of all ferroic systems [13–17, 27–29]. In fact, the scaling laws (equations (1) and (2)) have been repeatedly checked by dynamic hysteresis experiments on ferroelectrics rather than ferromagnetics since time-varying $E$ instead of time-varying magnetic field can cover a broad range of frequency but it is tough to cover a broad frequency range for a time-varying magnetic field. Furthermore, it should be mentioned too that such scaling laws are of generality and it is believed that those exponents do not depend on details of the physics underlying the phase transitions of the order parameter in various ferroic systems, as long as the dynamics of domain reversal in those systems remains phenomenologically identical. This is surely the major motivation to repeatedly check the scaling laws in various experimental systems.

However, the experimental data on several well-investigated ferroelectrics coated with various types of electrodes, such as $YBa_2Cu_3O_7$ (YBCO)/$Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT)/YBCO [17, 30], Pt/$Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ (BNT)/Pt [16], Pt/$SrBi_2Ta_2O_9$ (SBT)/Pt [13] and bulk PZT ceramics [27, 29], as summarized in table 1, seem to be quite scattered in terms of the scaling exponents, and moreover no well-accepted reason for the inconsistencies of these data with theoretical predictions has been achieved so far. In addition, the dynamic hysteresis also shows exponential scaling over temperature $T$, which was relatively less concerned in ferroelectric thin films. Therefore, reliable experiments on the dynamic hysteresis scaling of ferroelectric thin films seem to still be an issue worthy of further investigation.

Given the significance of this issue, several problems should be emphasized. First, PZT is one of the most typical ferroelectrics receiving attention, and its dynamic hysteresis is also of significance. However, PZT thin films on Pt-coated Si substrates will show a serious fatigue effect at room temperature which is strongly dependent on the frequency and amplitude of the fatigue testing electric field [6–8], indicating that the hysteresis area after many numbers of polarization switching cycles must include a reduced contribution from the fatigue effect. Unfortunately, currently the dynamic hysteresis was mainly measured using the Sawyer–Tower (ST) technique. During the ST measurement, especially at high frequency ($f \sim$ MHz or higher), the domains were already switched for a large number of times before the hysteresis data collection was completed. Therefore, the as-measured scaling exponents are not reliable. To obtain more reliable results, one needs to eliminate the contribution from the fatigue effect. Although the usage of conductive oxide electrodes, like $YBa_2Cu_3O_7$ (YBCO) [9, 10], can essentially avoid the fatigue effect of PZT thin films, a large leakage current will be caused [9] and, more importantly, the incompatibility with Si-based integrated technologies remains a problem. In an earlier work [11], we demonstrated that $Pb_{0.9}Ba_{0.1}(Zr_{0.52}Ti_{0.48})O_3$ (PBZT) polycrystalline thin films deposited on Pt-coated Si substrates not only exhibit enhanced fatigue endurance over a broad $T$ range, but also maintain ferroelectricity as good as PZT thin films.

Second, if leakage and transient currents, compared with the polarization displacement current in our polycrystalline films, are relatively high, their influence on the dynamic hysteresis loops cannot be neglected. It is known that the leakage current in polycrystalline films was mainly from space-charge-limited conduction in which the trap sites can capture charge carriers [19]. If the field is high enough to provide an energy higher than the difference between the trapping level and conduction band, the trapped charge carriers can be released and become the free charges. This de-trapping process is a function of electric field and temperature [20], making the dynamic hysteresis data suspicious. The transient state is a transition state from a stable state of the circuit to another. The transient current occurs momentarily and fleetingly in response to an abrupt stimulus or change in the equilibrium of a circuit, and will disappear after a long time. So its contribution at high $f$ is usually bigger than that at low $f$. To obtain a reliable intrinsic scaling behavior, leakage and transient currents must be very small.

Third, we are concerned with different scaling behaviors for the minor hysteresis and major hysteresis. The minor and major loops are measured under low and high electric fields, respectively. Therefore, the minor hysteresis is far from saturated but the major one is roughly saturated. It is easily predicted that the dynamics of minor hysteresis is dominated by reversible domain switching while the irreversible switching mainly contributes to the dynamics of major hysteresis. Although theoretically the scaling exponents for the minor hysteresis should be different from those for the major one, no comprehensive experiments on ferroelectric thin films have been performed. For real ferroelectrics, it will be shown in this work that the combined contribution from the minor and major loops is the main reason for the inconsistency between measured scaling exponents and the $(\Phi^2)^2$ and $(\Phi^2)^3$ models.

Finally, the temperature scaling is also essential for our understanding of the dynamic hysteresis of ferroelectric thin

films. The dynamic hysteresis is associated with the first-order phase transitions driven by an external electric field. Therefore, the thermal activation must be one of the intrinsic mechanisms for domain switching. Besides theoretical studies (e.g. $(\Phi^2)^2$ and $(\Phi^2)^3$ models) [4, 5], the data available to ferroelectric thin films seem not to be conclusive. On the one hand, the domain switching is kinetically $T$-dependent and it will become easier at a higher $T$, resulting in a lower coercivity, given fixed $f$ and $E_0$. On the other hand, a higher $T$ corresponds to stronger thermal fluctuations, resulting in a smaller polarization. The dynamic hysteresis is thus strongly $T$-dependent.

In this paper, we deal with the dynamic hysteresis of ferroelectric PBZT thin films for a given thickness and microstructure deposited on Pt-coated Si substrates. We pay attention to the scaling dependence of area $\langle A \rangle$ on $f$, $E_0$ and $T$, respectively. Moreover, in order to verify the influence of polarization fatigue effect on scaling exponents and how it works, we also study the dynamic hysteresis of Pt/PZT/Pt ferroelectric thin films prepared under the given conditions.

## 2. Experimental details

The PBZT thin films with a thickness of ∼300 nm were prepared by the sol–gel process on commercial $Pt/TiO_2/SiO_2/Si$ substrates. For the thin film preparation, lead acetate trihydrate, barium acetate, tetrabutyl titanate and zirconium acetylacetonate were used as the starting materials. The solvent was acetic acid. The concentration of the precursor solution was 0.3 mol $l^{-1}$. The detailed procedure of the preparation was the same as reported earlier [12]. The Pt electrodes of 200 $\mu$m in diameter were sputtered on the films as top electrodes. The crystallinity and structural characterization using x-ray diffraction (XRD) with Cu K$\alpha$ radiation at room temperature was performed.

The dynamic polarization–electric field ($P$–$E$) hysteresis loops were measured using the ST circuit method. The electric field $E(t) = E_0 \sin(2\pi f t)$, where $t$ is time, generated by an ac amplifier (HAS 40141) associated with a function generator (Agilent 33120A, 15 MHz) was applied to the samples under measuring. The $P$–$E$ loops were recorded by an Agilent infiniium oscilloscope (1.5 GHz, 8 Gsa $s^{-1}$). Each loop was obtained after averaging over 4096 domain switching cycles to average out the noise deformations, in particular for the cases of extremely low and high frequency ranges. We calibrated the ST circuit by comparing the data and those obtained by the RT66A standard ferroelectric testing unit, which ensures the reliability of our measurement. In our experiment, the $f$ range covered is $10^{-1}$–$10^5$ Hz with $E_0$ ranging from 0 to 566 kV $cm^{-1}$ ($T$ was fixed at 300 K). For the temperature scaling behavior of PBZT thin films, $T$ was varied in the range of 50–250 K with $E_0$ up to 833 kV $cm^{-1}$ ($f$ was fixed at 1 kHz). The $P$–$E$ loops at low $T$ were measured by inserting the samples into a Janis closed-cycle refrigerator system (Janis Research Company, Inc., USA).

In order to evaluate the impact of leakage current on the hysteresis during the ST measurement, we also collected the leakage current data using a Keithley 2400 at room temperature from 0 to ±833 kV $cm^{-1}$.

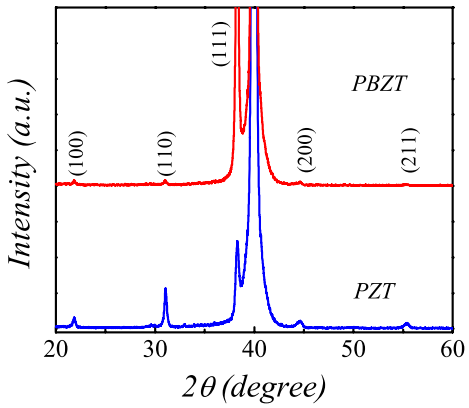


**Figure 1.** X-ray diffraction patterns for PBZT and PZT thin films on Pt-coated Si substrates.

## 3. Results and discussion

Before presenting data on the dynamic hysteresis, we highlight our characterizations of the microstructures of the as-prepared thin films, and details of them were given in earlier reports [11]. Figure 1 only shows the XRD diffraction patterns of the as-prepared PBZT and PZT thin films. It is seen that both the PZT and PBZT thin films on $Pt/TiO_2/SiO_2/Si$ substrates are well developed in polycrystalline nature and no identifiable impurity phase is detected within the apparatus resolution. The two types of thin films show quite similar reflections, while the as-prepared PBZT thin films are slightly (111)-orientation preferred. This issue was carefully discussed in our earlier work [11].

Also we assume no significant artificial effect from the leakage current (including the trapped charges driven by electric field) on the dynamic hysteresis as well as the transient current. The supporting evidence with this assumption will be given later in the discussion.

### *3.1. Hysteresis loop*

We pay attention to the hysteresis evolution with varying $f$, $E_0$ and $T$. As an example of a large package of data, we present in figure 2(a) the measured $P$–$E$ loops at four different $E_0$, given $f = 7$ kHz and $T = 300$ K, and in figure 2(b) the measured loops at four different $f$ given $E_0 = 500$ kV $cm^{-1}$ and $T = 300$ K. Remarkable dynamic effects of the hysteresis in terms of its shape and area evolution as a function of $f$ and $E_0$ are clearly shown. These effects were described in detail in the earlier literature [15] and only a very brief highlight will be given here. Moreover, the hysteresis evolution with $T$ is shown in figure 2(c) which presents the measured loops at four different $T$ given $E_0 = 500$ and 733 kV $cm^{-1}$ at $f = 1$ kHz.

First, given $f$ and $T$, the loop remains unsaturated at low $E_0$, i.e. minor loop. An increasing of $E_0$ enhances the remnant polarization $P_r$ and coercivity $E_c$ on the one hand and, on the other hand, enables saturating the loop, i.e. major loop if $E_0$ is over a threshold $E_{0c}$ which separates the minor loop from the major one. This effect is always true no matter how $f$ or $T$ is. As a consequence, the loop area $\langle A \rangle$ increases monotonically

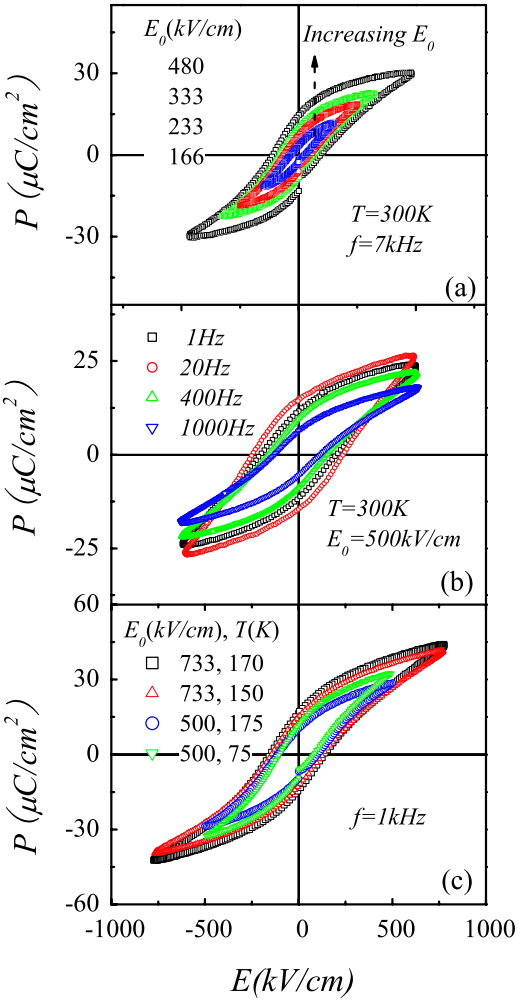


**Figure 2.** Hysteresis loops for PBZT thin films (a) for $T = 300$ K at various $E_0$ and $f = 7$ kHz, (b) for $T = 300$ K at various $f$ and $E_0 = 500$ kV cm$^{-1}$, and (c) for $f = 1$ kHz at different $E_0$ and $T$.

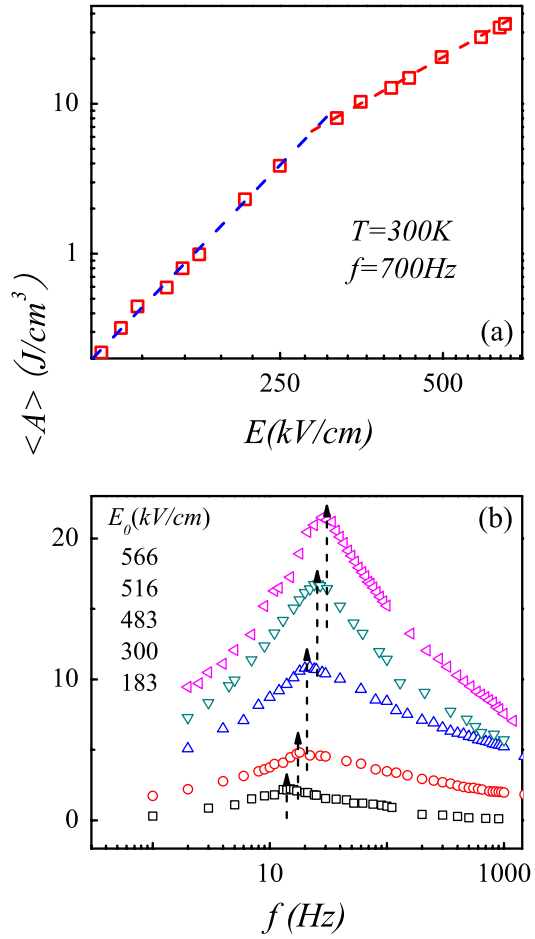


**Figure 3.** Hysteresis area $\langle A \rangle$ as a function of (a) $E_0$ and (b) frequency $f$ at different amplitudes for $T = 300$ K. The direction of the arrow represents the increasing of $E_0$.

with increasing $E_0$. This effect seems quite obvious in physics and no further details will be given here. However, what should be mentioned here is that $\langle A \rangle(E_0)$ has different dependences on $E_0$ for the minor loops and major loops, with one example shown in figure 3(a). It seems that $\langle A \rangle(E_0)$ exhibits linear behavior in the log–log scales and the slope for minor loops is bigger than that for major loops.

The existence of a minor loop is not a novel phenomenon and was reported earlier [17, 18, 27, 29]. The nature of the minor loop usually refers to the multi-domain structure in polycrystalline ferroelectrics where there are various types of domains and a broad distribution of domain orientation and size. In such ferroelectrics, no physically strict definition for a coercive field $E_c$ is possible. The measured coercivity from the hysteresis represents a configuration averaging over the whole package of domains, and one may view it as the nominal coercivity. For those domains of small size embedded in the gaps among the large domains, the coercivity for them to reverse would be statistically lower than those large ones, but these domains may partially recover back to the initial state when the electric field returns back to zero, due to the clamping effect by those large domains. We call these domains as reversible domains. The other domains are then categorized into irreversible domains. However, we notice that a strict classification of these domains may not be possible and also not necessary for the present work.

Qualitatively, real ferroelectrics are offered with two types of polarization components: reversible domain and irreversible domain. Because of the different natures of the two types of domain reversal, it is easily identified that the reversible domain switching is kinetically easier and thus less sensitive to $f$ than the irreversible switching, while the reversible polarization is much more sensitive than the irreversible polarization to $E_0$, thus enabling a more sensitive response of the loop area to $E_0$ and less sensitive response to $f$ for the minor loop case than the major loop case. While the minor loop is contributed by the reversible domain switching plus weak irreversible reversal, the major loops are mainly contributed by the irreversible switching. At $E_0 < E_{0c}$, both reversible switching and more and more irreversible switching events are activated, leading to a more sensitive response of $\langle A \rangle$ to increasing $E_0$ than the case at $E_0 > E_{0c}$, where only irreversible switching works. Detailed characterization will be given below by the scaling exponent analysis.

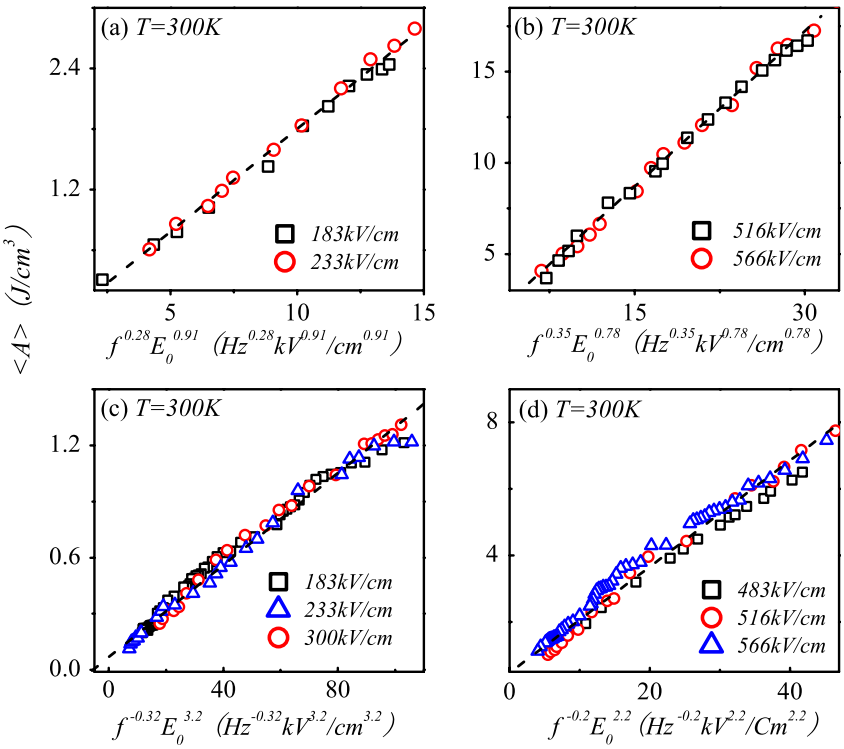


**Figure 4.** Scaling plots of loop area against $E_0$ and $f$ for PBZT thin films for $T = 300$ K (a) at low $f$ and $E_0$ range, (b) at low $f$ but high $E_0$ range, (c) at high $f$ but low $E_0$ range and (d) at high $f$ and $E_0$ range.

Second, given $E_0$ and $T$, the evolution of hysteresis against increasing $f$, as shown in figure 2(b), is more complicated. The major fact is that $P_r$ increases with increasing $f$ in the low-$f$ region and then decreases in the high-$f$ region, while saturated polarization $P_s$ and $E_c$ seem to be always suppressed with increasing $f$, no matter how $E_0$ or $T$ is. The consequence for loop area $\langle A\rangle$ must be a single-peak pattern in terms of $\langle A\rangle(f)$. The coordinate of this peak $(f_{max}, \langle A_{max}\rangle)$ is then dependent on both $E_0$ and $T$. For the $E_0$ dependence of $\langle A\rangle(f)$, as shown in figure 3(b), it is clearly revealed that the single-peaked $\langle A(f)\rangle$ as a whole shifts up and rightward with increasing $E_0$.

The physics underlying the single-peak $\langle A\rangle(f)$ was once carefully analyzed in the framework of domain nucleation-and-growth, driven by $E(t)$ [14, 15]. For the irreversible domain switching, a first-order phase transition driven by external field, its response can be described by a characteristic time $\tau$. It is easily understood that the peaked loop area is essentially the output of the domain switching resonance in response to field $E(t)$ as periodicity $\lambda \sim 1/2\pi f$ becomes comparable to time $\tau$. We are not going to address this issue and readers may refer to the literature [14, 15]. What should be mentioned again here is that the reversible domain switching may have a much shorter characteristic time than the irreversible one, given the same $E_0$, thus being less sensitive to $f$.

Third, we have a look at the effect of $T$ on the hysteresis. Given $f$ and $E_0$, this effect is not simple. Again, this $T$ dependence for the minor loop is different from that for the major loop. One sees that $\langle A\rangle(T)$ is a monotonically increasing function for the minor loop while it is a decreasing function for the major loop. This difference can be qualitatively understood in the same framework as mentioned above. For the minor loops, the reversible domain switching is dominant, which is mainly thermally activated, leading to an increasing $\langle A\rangle$ with increasing $T$. For the major loops, the well-aligned polarization will be reduced with increasing $T$ and coercivity $E_c$ will be reduced too, resulting in smaller $\langle A\rangle$ at higher $T$. We shall come back to the $T$ dependence once more.

### 3.2. Dynamic scaling

For a quantitative description of the dynamic hysteresis of the as-prepared thin films, we investigate the scaling behaviors of $\langle A\rangle$ against $E_0$, $f$ and $T$. First, we look at the results given that $T = 300$ K. To obtain the scaling for PBZT thin films, we fit the measured data in the low-$f$ and high-$f$ ranges, using the power law $\langle A\rangle \propto f^{\alpha}E_0^{\beta}$. It seems that this power law scaling works well for all cases we have fitted. Clarifying the cases of low $E_0$ and high $E_0$, or the minor loops and major loops, the fitting is presented in figures 4(a)–(d) and the data can be described by the following scaling relations within the measured uncertainty:

$$\begin{cases} \langle A\rangle \propto f^{0.28}E_0^{0.91} & \text{low } E_0 \\ \langle A\rangle \propto f^{0.35}E_0^{0.78} & \text{high } E_0 \end{cases} \quad \text{as } f \Rightarrow 0, \qquad (3)$$

$$\begin{cases} \langle A\rangle \propto f^{-0.32}E_0^{3.20} & \text{low } E_0 \\ \langle A\rangle \propto f^{-0.20}E_0^{2.20} & \text{high } E_0 \end{cases} \quad \text{as } f \Rightarrow \infty, \qquad (4)$$

and the relevant exponents are summarized in table 1 for reference.

We first compare equations (3) and (1), i.e. the exponents in the low $f$ range. For the low $E_0$ case, corresponding to the minor loops, the fitted $\alpha = 0.28$ is smaller than theoretically predicted $\alpha = 1/3$, while the fitted $\beta = 0.91$ is larger than the predicted $\beta = 2/3$. On the other hand, for the high $E_0$ case associated with the major loops, the fitted exponents are roughly consistent with (or slightly larger than) theoretically predicted ones. To understand the consistency and difference, one needs to be reminded that, in the low-$f$ range, the low $E_0$ hysteresis is mainly associated with the thermally activated reversible domain switching besides weak irreversible switching. However, the $(\Phi^2)^2$ and $(\Phi^2)^3$ models mainly deal with the dynamic behavior of irreversible domain switching, corresponding to the high $E_0$ case. Therefore, the fitted exponents in the low $f$ and low $E_0$ region would show a large difference from the predicted ones. Obviously, the minor loops must be less sensitive to $f$ but more sensitive to $E_0$ than the major loops, leading to a smaller $\alpha$ than $1/3$ and a larger $\beta$ than $2/3$. This also explains why the fitted exponents are roughly the same as the predicted ones for the high $E_0$ case corresponding to the major loops.

Then we compare the data in the high $f$ range, i.e. equations (2) and (4). For the minor loops corresponding to the low $E_0$ case, the fitted $\alpha = -0.32$ is much smaller in absolute value than the predicted $\alpha = -1$, while the fitted $\beta = 3.2$ is larger than $\beta = 2$, the predicted one. For the major loops occurring in the high $E_0$, the fitted $\beta = 2.2$ is roughly consistent with the theoretical value $\beta = 2$, while the fitted $\alpha = -0.20$ is even smaller in absolute value. No matter in the low $f$ or high $f$ ranges, the larger $\beta$ than the predicted value under the low $E_0$ reflects the fact that in real ferroelectrics both reversible and irreversible domain switching sequences contribute to the hysteresis. However, under the high $E_0$, the irreversible domain switching is dominant, giving rise to an exponent $\beta$ roughly consistent with the model.

What should be mentioned here is that a significant difference between the obtained and predicted $\alpha$ values exists not only in PBZT thin films, but also in other ferroelectric thin films, such as PZT, SBT and BNT. No reasonable explanation of this gap is available. An earlier explanation is that the ionic-type contribution to the hysteresis may not be neglected [17]. Here, one may also need to consider the influence of depolarization field on the hysteresis at high frequency. The domain nucleation and growth are determined by the local value of the electric field (sum of applied external field and depolarization field) [21]. The depolarization field could result from many kinds of incomplete charge compensations, for example from the electrodes, space charges, interface layers, etc [21–26]. Usually in polycrystalline films, the compensation of the depolarization field requires a considerable time. Therefore, at higher frequency, the compensation of the depolarization field is not complete. It is well known that the depolarization field acts as a negative bias against the polarization reversal mechanism, which thus lowers the domain nucleation probability and slows the switching process. As a result, the hysteresis area must show a relatively stronger

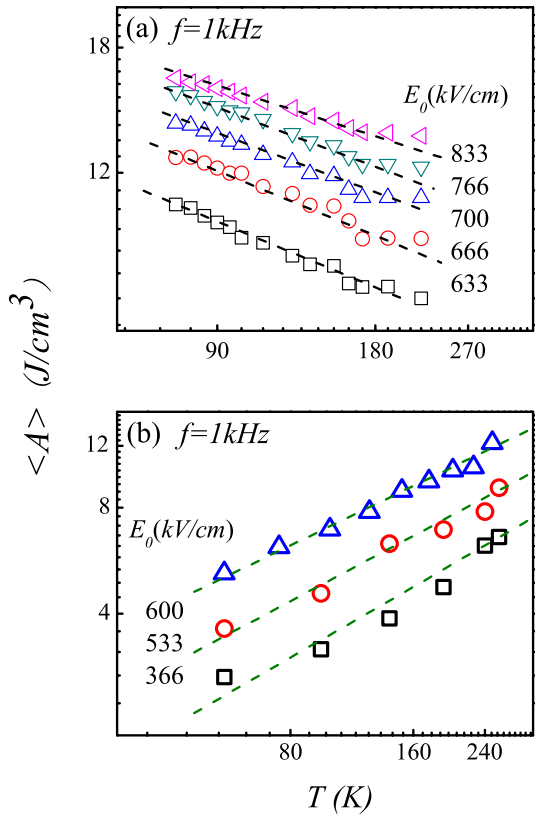


**Figure 5.** Hysteresis area dependence on temperature: (a) for high $E_0$ and (b) for low $E_0$.

dependence on frequency $f$ and a weaker dependence on amplitude $E_0$ [27], which are at least partially responsible for the measured exponent $\beta$ much larger than the predicted one theoretically and a measured exponent $\alpha$ slightly smaller than the predicted one.

The differences among PBZT thin films and soft and hard PZT bulk ceramics are also summarized in table 1. We can see that the scaling exponents ($\alpha$ and $\beta$) of PBZT thin films are similar to that of soft and hard PZT bulk ceramics at low $E_0$, with the difference between them at high $E_0$. In bulk PZT ceramics, it is argued that the different dynamic scaling laws under different fields are caused by the reversal of different domain walls (180° and non-180°) which are activated by the different fields [27, 29]. However, we partially ascribe this difference to the contributions of the reversible and irreversible domain wall switching in this work.

### *3.3. Temperature scaling*

A power law scaling of $\langle A \rangle$ against $T$ was theoretically predicted, and the scaling exponents $\gamma \sim 0.7$ and 1.0 for $(\Phi^2)^2$ and $(\Phi^2)^3$ models were obtained if $E_0$ is not high enough for well-saturated hysteresis [4, 5]. To check this scaling behavior, we perform careful analysis of this scaling behavior, and the typical data at $f = 1$ kHz and different $E_0$ are shown in figures 5(a) and (b). It is found that the scaling behavior is true but the scaling exponent is qualitatively different for the

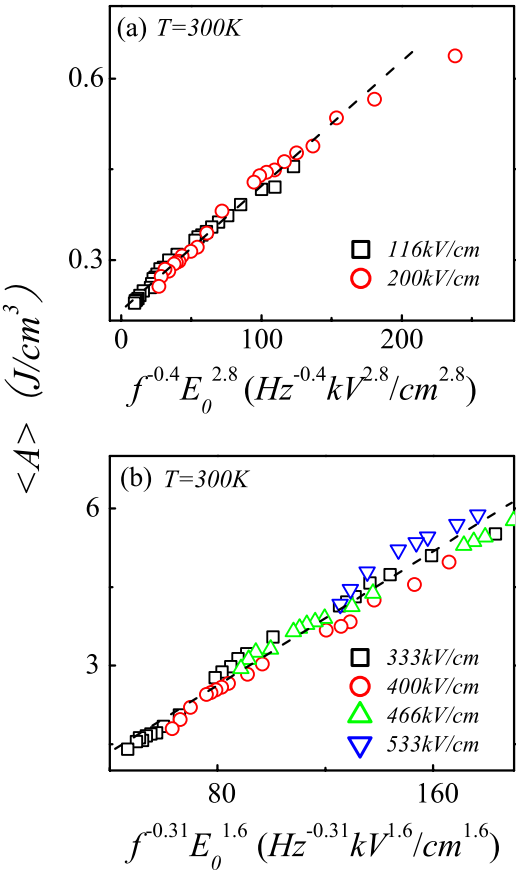


**Figure 6.** Scaling plots of loop area against $E_0$ and $f$ for Pt/PZT/Pt thin films at high frequency with $T = 300$ K (a) for low $E_0$ range and (b) for high $E_0$ range.

low $E_0$ and high $E_0$ cases, as given below:

$$\begin{cases} \langle A\rangle \propto T^{0.68} & \text{low } E_0, \\ \langle A\rangle \propto T^{-0.32} & \text{high } E_0. \end{cases} \tag{5}$$

The fitted exponent at low $E_0$ cases, $\gamma \sim 0.68$, is roughly consistent with the $(\Phi^2)^2$ model predicted value, not that of the $(\Phi^2)^3$ theory. This is due to that in the $(\Phi^2)^3$ theory the system is subjected not only to a time-varying external electric field $E$, but also to a periodically varying temperature which cycles across the first-order phase boundary [5]. It is different from our experiment. Then we see that for the high $E_0$ case the exponent is negative. We would like to mention that a negative $\gamma$ is quite reasonable for the high $E_0$ cases where the loops become saturated but coercivity $E_c$ decreases with increasing $T$.

### *3.4. Hysteresis scaling of PZT thin films: reconsidered*

An essential problem for the dynamic hysteresis is the effect of polarization fatigue. In order to verify this effect, we also study the dynamic hysteresis of PZT thin films deposited on Pt-coated Si substrates. We mainly focus on this effect in the high $f$ range where this effect becomes very significant. In figures 6(a) and (b) we present the measured data at low and high $E_0$, respectively, given $T = 300$ K. They can be fitted by

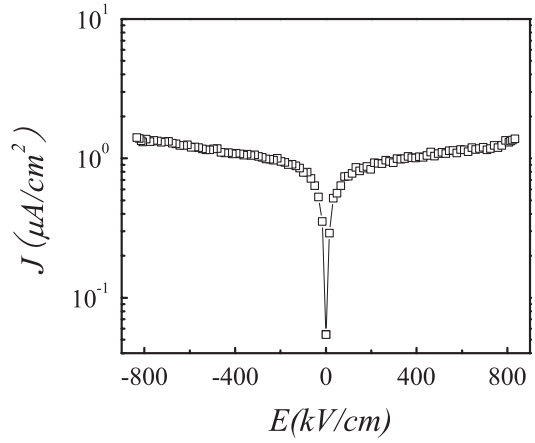


**Figure 7.** Measured $J$–$E$ curve for the PBZT thin films at room temperature.

the following scaling relations:

$$\begin{cases} \langle A\rangle \propto f^{-0.40} E_0^{2.80} & \text{low } E_0, \\ \langle A\rangle \propto f^{-0.31} E_0^{1.60} & \text{high } E_0. \end{cases} \tag{6}$$

In order to verify the fatigue effect, we represent below the scaling relations for the PBZT thin films, obtained under similar conditions:

$$\begin{cases} \langle A\rangle \propto f^{-0.32} E_0^{3.20} & \text{low } E_0 \\ \langle A\rangle \propto f^{-0.20} E_0^{2.20} & \text{high } E_0. \end{cases} \tag{7}$$

An immediate comparison between the fitted exponents for the two types of thin films allows us to argue the significant effect of the polarization fatigue on the dynamic hysteresis in the Pt/PZT/Pt structure. The PBZT thin films have a remarkably larger exponent $\beta$ than that of the PZT thin films, while $\langle A\rangle$ decays much faster for the PZT thin films than the PBZT films, characterized with a larger exponent $\alpha$ in absolute value for the PZT films. In particular, we observe that the fatigue effect is more remarkable in the high $E_0$ cases than the low $E_0$ cases.

An understanding of this effect is direct and no details will be given here. What should be addressed is two other issues. First, it is obvious that the data on the dynamic hysteresis of PZT thin films with Pt electrodes are not reliable. Second, even with remarkable fatigue effect, PZT thin films seem to follow a similar power law scaling behavior, the reason of which remains an issue for further study.

### *3.5. Discussion*

Finally, we come to address the effects of leakage and transient currents on the dynamic scaling behaviors. For the present PBZT thin films, figure 7 illustrates the leakage current density ($J$–$E$ curve) from 0 to $\pm 833$ kV cm$^{-1}$ at room temperature. It is seen that $J$ is $\sim 1.1$ $\mu$A cm$^{-2}$ at the maximum $E_0 = 566$ kV cm$^{-1}$. Given the range of frequency $f$, the lowest $f$ value is 0.5 Hz. The half-periodicity is 1.0 s, and the additional part of the polarization, generated by the leakage

current is $\sim$2.2 $\mu$C cm$^{-2}$, which is much smaller than the probed polarization of $\sim$40 $\mu$C cm$^{-2}$. For $f = 1$ kHz and maximum $E_0 = 833$ kV cm$^{-1}$, its contribution to the polarization is $\sim$1.5 nC cm$^{-2}$ or less. Especially at low $T$ and $E_0$, such a contribution from leakage current must be even smaller. Therefore, we have reason to conclude that the leakage current which is much smaller than the reversal of ferroelectric domains for the present films does not affect the measured hysteresis. Then we discuss the possible influence of transient current. When the equilibrium of a circuit is subjected to an abrupt stimulus or change, the transient current will occur momentarily and fleetingly and disappear after a long time. In our experiments, each $P$–$E$ loop is obtained after averaging over 4096 domain switching cycles and we always apply the voltage on samples during 4096 domain switching cycles. Therefore, the contribution from transient currents experienced 4096 cycles to the $P$–$E$ loop should be very small and the $P$–$E$ loop is a steady state loop. So the measured scaling exponents basically reflect the intrinsic property of the dynamic hysteresis.

What needs to be noticed is that the above discussions are all based on the as-prepared polycrystalline PBZT films with a single composition and thickness, but without discussing the possible influences of sample thickness, microstructure, etc, on the dynamic behavior and scaling relations. Therefore, they may have no universality for other different samples. Up to now, there has been no report and it remains to be an issue for further study.

## 4. Conclusion

In conclusion, we have systematically studied the intrinsic dynamic scaling behavior for PBZT ferroelectric thin films deposited on Pt-coated Si substrates. For the as-prepared thin films of the given thickness and microstructure, the scaling exponents defined for frequency $f$ and amplitude $E_0$ are different from those values predicted theoretically by the $(\Phi^2)^2$ and $(\Phi^2)^3$ models. Such differences at low $E_0$ cases can be partially ascribed to the contributions from reversible domain switching which is usually dominant for the minor loops. At higher frequency, the depolarization field is another important factor influencing the frequency exponents in the ferroelectric thin films. We have also investigated the scaling behavior against $T$. We have verified that the polarization fatigue effect has an essential impact on the dynamic hysteresis.

## Acknowledgments

The authors would like to acknowledge the financial support from the National Natural Science Foundation of China (50832002, 10674061 and 50572038) and the National Key Projects for Basic Researches of China (2009CB623303).

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