

Temperature-dependent fatigue behaviors of ferroelectric $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ and $\text{Pb}_{0.75}\text{La}_{0.25}\text{TiO}_3$ thin films

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The polarization switching fatigue of ABO_3 -perovskite ferroelectric thin-film $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PZT) prepared by metalorganic decomposition (MOD) and $\text{Pb}_{0.75}\text{La}_{0.25}\text{TiO}_3$ (PLT) prepared by pulsed laser deposition (PLD), are investigated. The temperature as a degree of freedom is employed to modulate the switching fatigue and unveil the roles of oxygen vacancies associated with polarization switching. It is confirmed that the polarization fatigue is dominated by the long-range diffusion of oxygen vacancies, leading to a superior fatigue resistance at low temperature. More importantly, it is revealed that although PLD-prepared PLT films have a higher density of oxygen vacancies than MOD-prepared PZT films, the evaluated barrier for oxygen diffusion in PLD-prepared PLT films is ~ 1.3 eV, larger than ~ 1.0 eV, the barrier in MOD-prepared PZT films, responsible for a weaker fatigue behavior in PLD-prepared PLT films. © 2005 American Institute of Physics. [DOI: 10.1063/1.1977186]

The problem of polarization switching fatigue (PF) in ferroelectric (FE) thin films represents one of the core issues for FE-random-access memory (FeRAM) applications, and has been receiving special attention in the last decade.^{1,2} The PF effect is related to a gradual degradation of spontaneous polarization upon repeated switching of ferroelectric domains driven by a time-varying external electric field E . Currently, ABO_3 -perovskite FE thin films, such as $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PZT) and $\text{Pb}_{0.75}\text{La}_{0.25}\text{TiO}_3$ (PLT), are no longer the favored candidates for FeRAM applications, due to their serious PF behaviors, however, they are still favored targets for understanding the mechanisms underlying the PF phenomena.³⁻⁵ Here, we limit our attention to the PF problem of PZT and PLT thin films.

In a general sense, the PF mechanisms are always related to charged defects in the thin films, mainly oxygen vacancies. For ABO_3 FE thin films, the fatigue is mainly attributed to long-range migration of defects and their aggregation to form highly defective regions near the film-electrode interfaces where domain switching becomes kinetically difficult.⁶⁻⁸ Besides, it has been proposed⁹ that the switching of 90° domains is important for fatigue, which is not considered. Based on the kinetic features of the PF behaviors, one immediately comes to the conclusion that the PF effect must be significantly temperature dependent.^{8,10} Furthermore, the density of charged defects as a key parameter to control the PF behaviors cannot be emphasized enough. Dawber and Scott proposed a kinetic model (in shorts, DS model),⁴ which relates the long-range diffusion of oxygen vacancies toward the film-electrode interface with the PF sequence. An analytic relationship between polarization P and switching number N [$P(N)$ - N relationship] was developed. The initial condition for application of the DS model is the inhomogeneous density distribution of defects in the films, noting that the regions near the film-electrode interface possesses intrinsically higher density of defects.

However, the effect of existing vacancies on the PF depends on the mobility of those vacancies. Driven under external electric-field E , those initial randomly distributed vacancies in the films may migrate toward the film-electrode interface and finally result in serious fatigue of the films.³⁻⁶ In this letter, we perform an experimental study on the PF behaviors of PZT and PLT thin films at different T , focusing on the oxygen vacancy mobility in the two types of thin films. The PZT thin films were prepared by metal organic decomposition (MOD), which usually offers thin films with relatively low defect density. The PLT thin films were deposited by pulsed laser deposition (PLD) which, however, introduces a high density of vacancies into the thin films, due to the high momentum of ions during deposition.

For convenience, we label the samples with materials and preparation method. For example, PZT-MOD refers to PZT thin films prepared by MOD method. All of the thin films were deposited on commercially available Pt/TiO₂/SiO₂/(100)Si substrates with Pt dots of 0.2 mm diameters as top electrodes. For MOD preparations, the precursors for PZT were synthesized following standard procedures.¹¹ Each film was formed by repeated spinning the precursor at a speed of 3000 rpm for 20 s, heated up to 260 °C for 4 min, followed by a rapid thermal annealing at a temperature $T_a = 700$ °C for 180 s in a flowing oxygen ambient. The processing procedure was already optimized in terms of well-developed crystallinity and ferroelectric hysteresis. For PLD preparations, the stoichiometric targets of PLT were sintered through the standard solid-solution sintering procedure. The PLD experiments were performed by using KrF excimer laser of 248 nm in wavelength, 25 ns in pulse width and 5 Hz in repetition rate, in an ambient of 30 Pa oxygen. A laser fluency of 250 mJ with an energy density of ~ 2.0 J/cm² was employed. The substrate temperature $T_s = 700$ °C was chosen after an optimization in light of the high film quality. All of the as-prepared thin films were checked by x-ray diffraction and scanning electron microscopy (SEM) for the crystallinity. The microstructural characteristics of these films is identical to the well-documented

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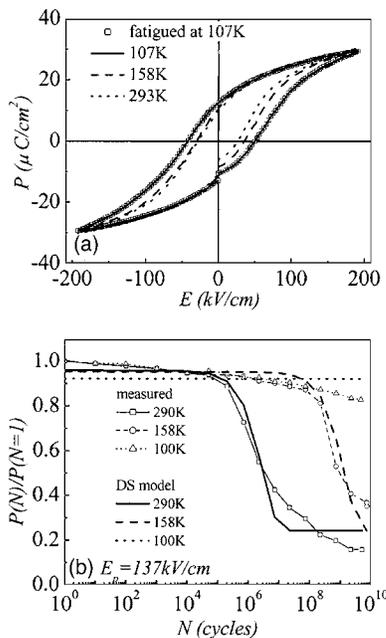


FIG. 1. (a) Ferroelectric hysteresis loops (solid lines) of fresh PZT-MOD films measured at 107 K, 158 K, and 293 K. The squared-dotted loop was measured at $T=107$ K after $N\sim 10^9$. (b) Measured $P(N)$ - N relations (fine lines plus dots) at 290 K, 158 K, and 100 K, respectively, and the fitted curves from the DS model (coarse lines) with parameters shown in Table I. $E_p=137$ kV/cm.

results by other researchers, in a reliable and reproducible sense.^{10,11} The film thickness was measured using a high-precision step profiler and SEM. The PZT-MOD films for test are 365 nm in thickness, and the PLT-PLD thin films are 430 nm in thickness.

The electrical properties, including leakage current, ferroelectric hysteresis, and switching-fatigue behaviors were measured in a temperature-controllable vacuum chamber ~ 20 Pa, in which the samples were housed. Temperature T ranges from 300 to 50 K. For these measurements, a pair of shielded cables was used to connect the Pt electrodes and RT66A standard ferroelectric tester (Radiant Technologies Ltd., NM). The PF testing was performed using a bipolar pulse, with a pulsed width of 8.6 μ s and period of 20 μ s at a frequency of 50 kHz.¹² The nonvolatile component of the switched polarization is $P_{nv}=P^*-P^\wedge$ or $P_{-nv}=(-P^*)-(-P^\wedge)$, where P^* and P^\wedge refer to the pulsed-charge measurement by RT66A tester. We denote P_{nv} by $P(N)$ where N is the number of switching cycles.

In Fig. 1(a), we show several loops of a fresh PZT-MOD film measured at three different T values. Excellent ferroelectric properties with well-defined saturated polarization P_s and remnant polarization P_r are demonstrated over the whole T range. Although both P_r and coercivity E_c increase with decreasing T , the value of P_s remains the same. The equivalent ferroelectric properties for fresh PLT-PLD films are shown in Fig. 2(a). However, at $T\sim 290$ K, the P_r/P_s ratio for PZT-MOD films is ~ 0.47 , much higher than $P_r/P_s\sim 0.25$ for PLT-PLD films, predicting that the PLT-PLD films have quite a high fraction of domains pinned by oxygen vacancies, while in PZT-MOD films there are much less pinned domains. This difference results from a higher density of vacancies in PLT-PLD films than in PZT-MOD films.

The measured $P(N)$ - N relationships for PZT-MOD films at $T=290$ K, 158 K, and 107 K, and for PLT-PLD films at

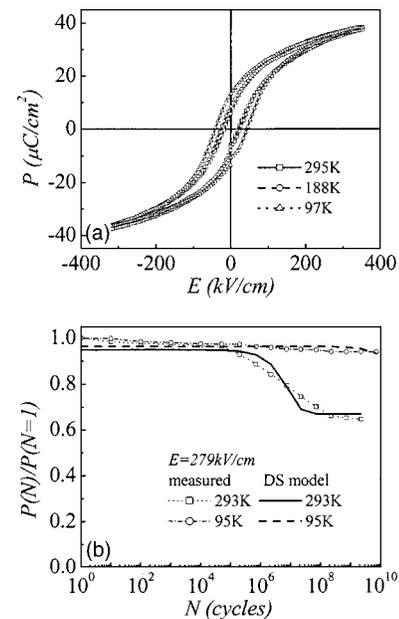


FIG. 2. (a) Ferroelectric hysteresis loops (solid lines) of fresh PLT-PLD films measured at 295 K, 188 K, and 97 K. (b) Measured $P(N)$ - N relations (fine lines plus dots) at 293 K and 95 K, respectively, and the fitted curves from the DS model (coarse lines) with parameters shown in Table I. $E_p=279$ kV/cm.

$T=293$ K and 95 K, are shown in Fig. 1(b) ($E_p=137$ kV/cm, where E_p is the electric field for the PF testing), and Fig. 2(b) ($E_p=279$ kV/cm), respectively. Here, different values of E_p are chosen for PZT-MOD films and PLT-PLD films because of different fields required for saturated hysteresis of the two types of films. It is clearly shown that both types of thin films show serious PF at high- T range, while the PF effect is significantly suppressed as T decreases. The T dependence on PF is very significant. For example, for PZT-MOD films at $T=107$ K, the loop measured at the initial state and that after $N=10^9$ switching cycles ($E_p=192$ kV/cm) are the same [Fig. 1(a)]. A significant difference in the $P(N)$ - N relationship between PZT-MOD films and PLT-PLD films is observed. At $T=290$ K, the fatigue effect [after $N>10^9$] for PLT-PLD films is not as serious as that for PZT-MOD films, assuming that PLT-PLD films have higher vacancy density than PZT-MOD films. It has been generally believed that a higher vacancy density would result in a more serious PF effect, which is not true here. A reason for this strange effect will be discussed below.

The T -dependent PF behaviors are attributed to the long-range migration of oxygen vacancies driven by field E . Here, we employ the DS model to explain the measured results. The intrinsic oxygen vacancies may migrate upward to the regions near the top electrode. The observed PF behaviors can be essentially related to the kinetics of long-range diffusion of these vacancies during the switching cycles. The DS model gives:⁴

$$P(N) = A \exp \left[-6\lambda\mu\epsilon_s^{-1}q\frac{N}{f} \exp \left(\frac{3a}{2} E_A \right) \right] + B, \quad (1)$$

where A and B are two constants scaling the fatigued and nonfatigued fractions of polarization ($A+B\sim 1.0$), f is the frequency (Hz), q is electron charge, ϵ_s is dielectric constant of film; $\lambda=D \exp(\Delta S/k)$, D is the density of vacancies close to the regions where pinning occurs, ΔS is the entropy for

TABLE I. Fitted parameters of Eq. (1) from the measured data.

Materials	T (K)	A	C (cm ⁻³)	ΔE (eV)	B
PZT ($V=5$ V, $E_p=137$ kV/cm)	290	0.713 45	3.7×10^{17}	1.0	0.245 08
	158	0.714	3.3×10^{17}	1.0	0.239 83
	100	0.7166	3.0×10^{17}	1.0	0.208 42
PLT ($V=12$ V, $E_p=250$ kV/cm)	290	0.2845	7.4×10^{20}	1.3	0.679 75
	95	0.284	7.3×10^{20}	1.3	0.681

vacancy movement which is very small comparing to k , Boltzmann constant; μ is the oxygen vacancy mobility; $a = zqb/2kT$, z is the vacancy valence, $b=0.3$ nm is the jump distance for vacancy, and thus $a=3.48 \times 10^{-6}/T$; E_A is the applied electric field which is not simply V/d but $5 \times 10^7 V$ (unit of E_A : V/m) where V is the voltage applied to the film and d is the film thickness.⁴ For PZT and PLT thin films, $\epsilon_s=400\epsilon_0$ is an acceptable value (the values of ϵ_s at room temperature are $\sim 390\epsilon_0$ for PZT and $\sim 360\epsilon_0$ for PLT, measured using RT66A tester), where ϵ_0 is the vacuum dielectric constant.

It should be noted here that parameter D in Eq. (1) is T -dependent, and it depends on the trapping state of oxygen vacancies if filled by electrons. As referred by Dawber and Scott, the trapping is 0.7 eV.⁴ If the density of vacancies at $T=300$ K is denoted by parameter C , one has $D = \frac{1}{C} \exp[\frac{0.7eV}{k}(\frac{1}{T} - \frac{1}{300})]$. Furthermore, the mobility μ for oxygen vacancies is T dependent, i.e., $\mu = \mu_0 \exp(-\frac{\Delta E}{kT})$, where ΔE is the barrier energy and μ_0 is assumed to be not very materials-relevant (for PZT and PLT), noting $\mu \sim 10^{-9}$ cm²/V s at $T=500$ K.¹³

With the above parameters, Eq. (1) can be applied to fit the measured fatigue data with only three parameters, A , C , and B . Table I lists the fitted parameters for PZT-MOD and PLT-PLD thin films. The fitted results are presented in Figs. 1(b) and 2(b) (solid lines), respectively, for PZT-MOD and PLT-PLD films. It is shown that the DS model describes quite well the measured PF behaviors for the two types of thin films at various T . The long-range migration of oxygen vacancies in the films and, consequently, the domain pinning by these vacancies as the dominant origin of PF in ABO₃ FE thin films, is demonstrated.

Looking at the fitted parameters in detail, one sees that the evaluated value of parameter C (vacancy density at 300 K) for PLT-PLD thin films is almost two orders of magnitude higher than that for PZT-MOD films, as argued earlier and confirmed here, which explains a much lower P_r/P_s ratio for PLT-PLD films than PZT-MOD films. More importantly, it is found that $\Delta E \sim 1.3$ eV for PLT-PLD films is higher than $\Delta E \sim 1.0$ eV for PZT-MOD films, indicating a lower mobility for oxygen vacancies in PLT-PLD films than in PZT-MOD films at the same temperature. This presents an intrinsic reason for the fact that at the same T , PLT-PLD films show better fatigue-resistance than PZT-MOD films, in spite of a much higher density of vacancies in PLT-PLD films. Consequently, it becomes obvious that parameter A is smaller for PLT-PLD films and parameter B is smaller for PZT-MOD films, noting that parameter A scales the fraction of polarization destroyed after an extremely large N . In de-

tails, For PZT-MOD films, $A \sim 0.71 \gg B \sim 0.24$, means that in the initial state (fresh sample), most of the domains can be switched and are gradually pinned by the aggregated vacancies through the long-range diffusion. These domains would be finally seriously pinned by the highly aggregated vacancies and become no more switched due to the PF effect. On the contrary, for PLT-PLD films, $A \sim 0.28 \ll B \sim 0.69$, reveals that in the initial state quite a number of domains are already slightly pinned by the high-density oxygen vacancies. These pinned domains may be depinned under a high electric field, but they will be repinned by those hardly migrated vacancies once E decays down to zero. Therefore, the P_r/P_s ratio for the fresh PLT-PLD films is only ~ 0.24 .

The La doping in PLT may be responsible for the higher barrier for vacancy migration in PLT-PLD films than in PZT-MOD films. In fact, it was reported that in perovskite oxides, such as Bi_{4-x}La_xTi₃O₁₂, La ion has a strong interaction with oxygen ion, which enhances the stability of oxygen ion and lowers the mobility of oxygen vacancies.¹⁴ Similar role of La doping in PLT may be argued here (to be confirmed), which reasonably explains the higher energy barrier for vacancy diffusion in PLT thin films.

In summary, we have measured the ferroelectric and switching fatigue behaviors of PZT-MOD and PLT-PLD thin films at different temperatures. It has been revealed that the films show improved fatigue resistance with decreasing temperature. The DS kinetic model for fatigue has been employed to explain the measured fatigue behaviors in the two types of thin films and a good consistency between the model and measured results is shown. A higher mobility barrier of oxygen vacancies in PLT-PLD film than that in PZT-MOD film is found, although the latter has much lower vacancy density than the former, which explains reasonably the weaker fatigue behavior in PLT films rather than PZT films.

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