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Short communication

Switching-induced charge injection inducing fatigue in lead zirconate titanium thin films

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Abstract

The dependence of the fatigue behavior on driving electric fields and measurement frequencies of $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films with a PbO_x buffer layer were systematically investigated. Its fatigue endurance degraded with increasing driving electric fields at a fixed frequency of 50 kHz and decreasing frequencies at a fixed electric field of ~259 kV/cm. The dielectric constant as a function of switching cycles, which is in agreement with the polarization fatigue, confirms that the local phase decomposition caused by the switching-induced charge injection largely dominates the fatigue behavior in $Pb(Zr_{0.20}Ti_{0.80})O_3$, together with the domain-wall pinning by the point defect agglomeration.

Keywords: $Pb(Zr,Ti)O_3$; Thin Film; Fatigue mechanism

1. Introduction

The polarization value degrades with repeated switching cycles, which is called as the polarization fatigue [1–3]. The polarization fatigue of ferroelectrics seriously limits the practical application in some devices, especially ferroelectric random access memories (FRAM) [1–3]. Some mechanisms or theories have been used to illuminate the origin of the polarization fatigue in ferroelectric materials, such as the domain-wall pinning by the point defect agglomeration and space charge accumulation [4–6], the dead/blocking interfacial layers [7], the nucleation inhibition [8,9], and the local phase decomposition caused by switching-induced charge injection (LPD-SICI) [10,11].

A "LPD-SICI" fatigue model for anti-ferroelectric and ferroelectric materials suggested by Lou et al., emphasizes the extremely high depolarization field generated near the electrode–film interface by the polarization charges at the tip of the needle like domains during switching [10,11]. This model has been recently used to describe the fatigue problem in antiferroelectrics, and has explained why the polarization fatigue in antiferroelectrics is much less severe than that in ferroelectrics under a similar measurement condition [12]. It has been reported that the domain switching is often blocked by the aggregation of oxygen vacancies on domain walls during repetitive switching, leading to a polarization degradation [13].

Lead–zirconate–titanate [$Pb(Zr_{1-x}Ti_x)O_3$, PZT] thin films demonstrate some outstanding properties, such as a low operation voltage and a large remnant polarization, which have been extensively studied because of their potential applications especially for FRAM [14–17]. However, the polarization fatigue of the ferroelectric capacitor results in the failure of devices and seriously limits its applications in the element of the nonvolatile memory [1–3]. Although some models have been used to discuss the fatigue behavior of the PZT capacitor with a Pt electrode, the origin of fatigue behavior is not still well established [8,18]. It is well known that the fatigue endurance of PZT thin films is related to some factors, such as electrode [19,20], interface [21], grain size [22], and measurement frequency [23]. It has been reported by us that $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films with a PbO_x buffer layer demonstrate a very high remanent polarization of ~69.7 μC/cm^2 [17], promising as a candidate material for the high-density FRAM. However, it is of a lack to investigate the fatigue endurance of $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films with a PbO_x buffer layer. In the present work, the fatigue endurance of $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films with a PbO_x buffer layer was

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investigated by varying electric fields and measurement frequencies, and the dielectric behavior as a function of switching cycles was also studied. The experimental result confirms that the LPD-SICI model should be largely involved into the degradation of the fatigue endurance of $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films in this work.

2. Experimental procedure

PbO_x-buffered $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films with a thickness of ~580 nm were fabricated by the radio frequency magnetron sputtering, and the detailed preparation method for this film has been described elsewhere [17]. In this work, Pt is used for the top and bottom electrodes. An impedance analyzer (Solartron Gain Phase Analyzer) was employed to investigate their dielectric properties. Their ferroelectric and fatigue behavior were studied by using a Radiant precise workstation (Radiant Technologies, USA).

3. Results and discussion

Fig. 1(a) shows the fatigue endurance of $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films with a PbO_x buffer layer under different driving electric fields at a fixed frequency of 50 kHz, measured at room temperature. Its fatigue endurance degraded with increasing driving electric fields from ~52 kV/cm to ~310 kV/cm, due to more intensive charge injection and phase decomposition at the domain nucleation sites at the electrode–film interface [10,11]. *P–E* loops after fatigue as a function of driving electric fields were carried out, as plotted in Fig. 1(b). The polarization value decreases and the coercive field increases with increasing driving electric fields. The change of P_r is well in good agreement with the data shown in Fig. 1(a). The increase in E_c value can be attributed to the degradation of the leakage property during fatigue for the materials with a roundish *P–E* loop [8], while the $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin film exhibits well *P–E* loops in this work, as shown in Fig. 1(b). Therefore, the increase in E_c value could be attributed to the presence of the local phase decomposition induced by the switching-induced charge injection. Fig. 1(c) shows that the dielectric constant (ε_r) as a function of measurement frequencies after fatigue under different driving electric fields. The ε_r value steadily degraded with increasing driving electric fields because of the local phase decomposition during fatigue induced by a depolarization field [10,11], where the fatigue induced phase-decomposed interfacial layer is of a pyrochlore like with a very low ε_r value [10]. In a high frequency of 10^3–10^6 Hz, the ε_r value steadily decreases with increasing driving electric fields, indicating the generation of a more local phase decomposition under a higher driving electric field during fatigue [10,11]. Moreover, it was also observed from Fig. 1(d) that the tangent loss (tan δ) becomes much less with increasing driving electric fields, confirming the increase in the number of the free movable charge in $Pb(Zr_{0.20}Ti_{0.80})O_3$. Higher defect concentration

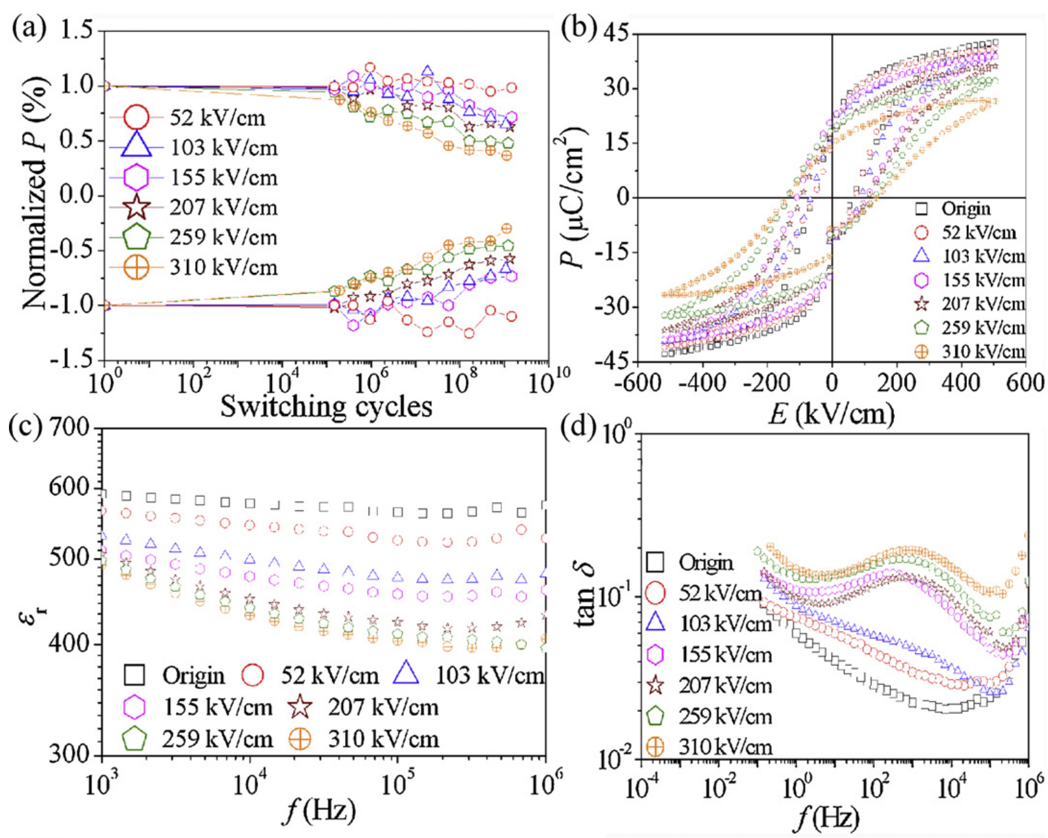

Fig. 1. (a) Fatigue endurance of $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films under different driving electric fields at a fixed frequency of 50 kHz, (b) *P–E*, (c) ε_r, and (d) tan δ as a function of measurement frequencies for different driving electric fields.

results in the increase in the number of defects and pins the domain walls [24], thus leading to the degradation of the fatigue endurance of $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films. Therefore, the local phase decomposition induced by larger depolarization fields could be largely responsible for the driving electric fields-dependent fatigue behavior, while the domain-wall pinning by point defect agglomeration cannot be also rule out.

Fig. 2(a) shows the fatigue endurance for the Au/$Pb(Zr_{0.20}Ti_{0.80})O_3$/Pt capacitor at different fatigue frequencies, measured at room temperature. The polarization value dramatically drops with increasing the switching cycles from $\sim 3.76 \times 10^4$ to $\sim 2.96 \times 10^6$ and then balances at $N \sim 2.96 \times 10^6$ when measured at the fatigue frequency of 100 Hz. However, the polarization value slowly drops with increasing switching cycles for the high measurement frequency of 1 MHz. The drop point in the polarization fatigue shifts to a higher switching cycle with increasing measurement frequencies, and the fatigue endurance is also improved with increasing the measurement frequencies from 100 Hz to 1 MHz. Fig. 2(b) plots the *P–E* loops of $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films under different measurement frequencies. The P_r value decreases dramatically with decreasing the measurement frequencies except for 1 MHz, which is well in agreement with its fatigue endurance in Fig. 2(a). Moreover, the E_c value also increases dramatically after the low measurement frequencies of 100 Hz–100 kHz, while the E_c value almost keeps unchanged for the high measurement frequency of 1 MHz. Fig. 2(c) and (d) shows the dielectric behavior after different measurement frequencies. The ε_r value decreases and the tan δ value increases with decreasing the measurement frequencies. Similar phenomenon was also observed in Fig. 1(c) and (d). The increase in tan δ value indicates the involvement of more defect concentration in $Pb(Zr_{0.20}Ti_{0.80})O_3$ during switching cycles. The deterioration of the normalized *P* with switching cycles as a function of measurement frequencies is shown in Fig. 2(a), and the $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin film possesses a better fatigue endurance as a function of the switching cycles with increasing frequencies. The electromigration of oxygen vacancies is often responsible for the fatigue behavior in ferroelectric perovskite thin films, and the concentration of oxygen vacancies seriously affects their fatigue endurance [4–6]. At a high frequency of 1 MHz, few oxygen vacancies are involved during this fatigue process, as confirmed by *P–E* loops (Fig. 2(a)) and dielectric behavior before and after fatigue test (Fig. 2(c) and (d)). Oxygen vacancies and deep traps in such a state respond slowly to the driving field, and the compensation of polarization charges is performed mainly with free carriers from the top and bottom electrodes [25]. Therefore, the polarization value will not change too much. However, when fatigued at a low measurement frequency, more oxygen vacancies are involved in this case, as confirmed by obviously increasing E_c and tan δ values as well as decreasing P_s value (Fig. 2(b) and (d)). Oxygen vacancies can migrate easily and trapped charges respond steadily to the driving field, and the rearrangement of oxygen vacancies blocks the switching of ferroelectric domains [4–6,24], resulting in the decrease of the polarization value. In

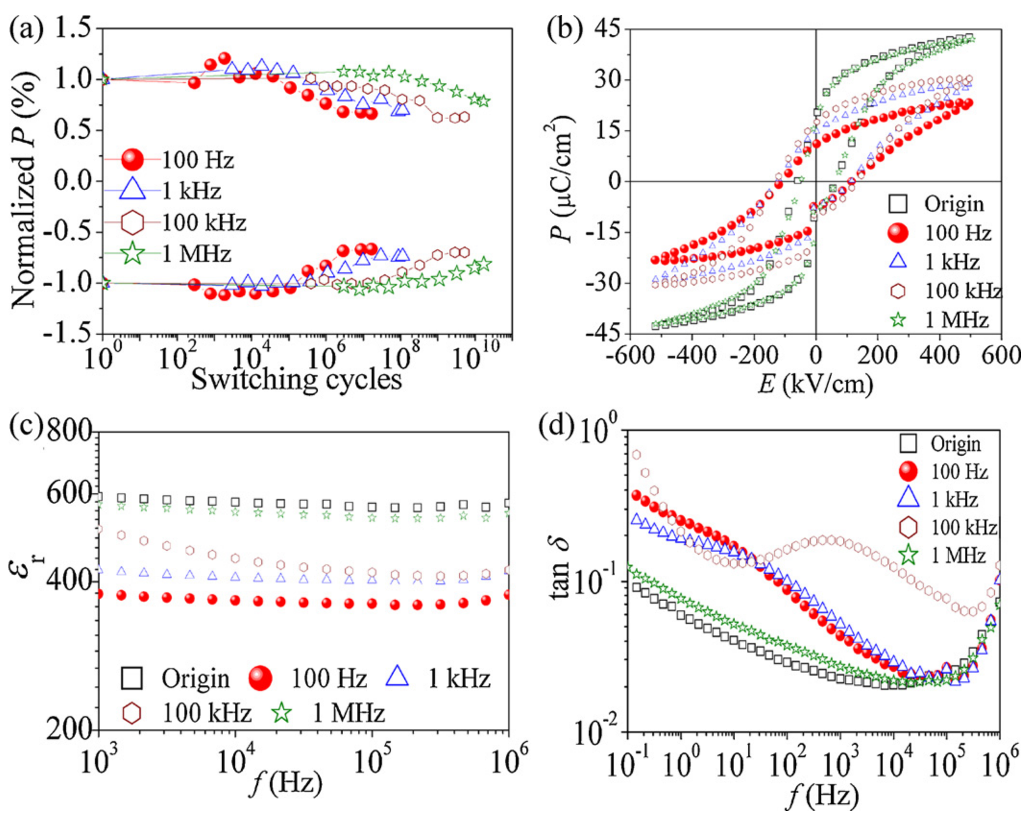

Fig. 2. (a) Fatigue endurance of $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films under different frequencies at a fixed electric field of ~259 kV/cm, (b) *P–E*, (c) ε_r, and (d) tan δ as a function of measurement frequencies for different fatigue frequencies.

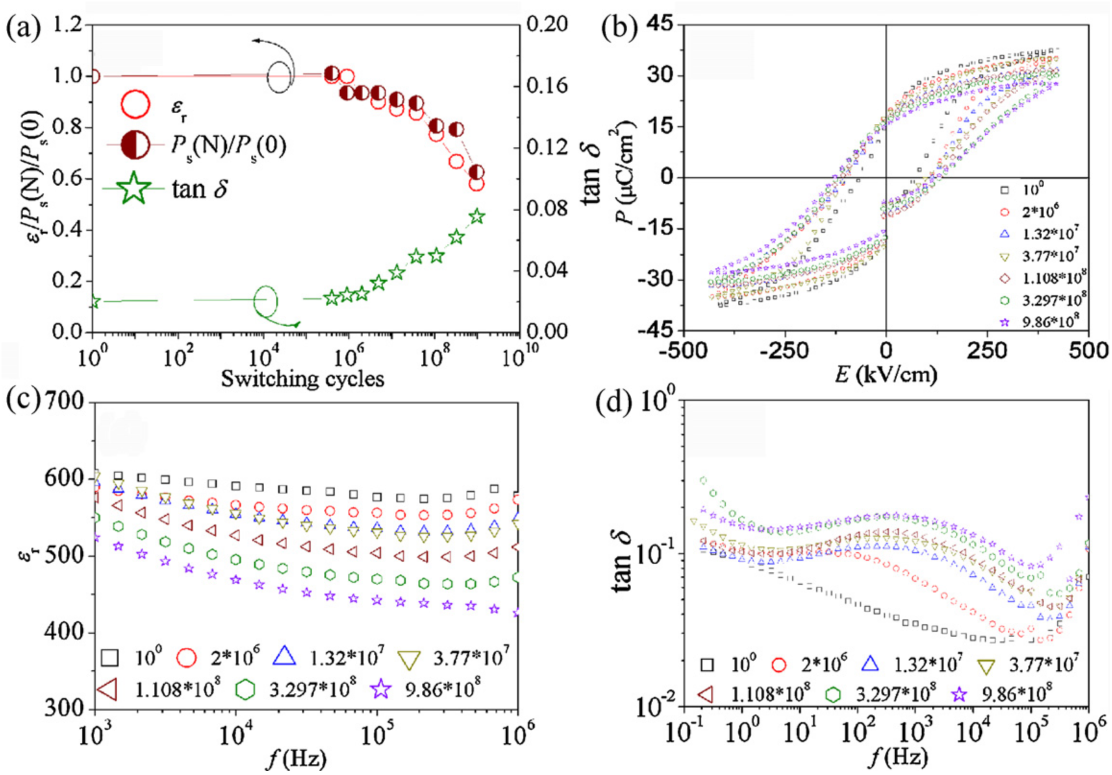

Fig. 3. (a) $P_s(N)/P_s(0)$, ε_r, and tan δ as a function of switching cycles for the $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin film, (b) P–E, (c) ε_r, and (d) tan δ as a function of switching cycles of $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films, when measured at a electric field of ~259 kV/cm and a frequency of 100 kHz.

this work, the fatigue endurance is much better than those of PZT thin films deposited on Pt-coated silicon substrates reported by other authors [26,27]. Enhanced fatigue endurance in this work could be attributed to the improvement of phase purity and the good interface between thin film and Pt bottom electrode [17].

Fig. 3(a) shows the $P_s(N)/P_s(0)$, ε_r, and tan δ values of $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films as a function of switching cycles, when measured at a frequency of 100 kHz and a electric field of ~259 kV/cm. $P_s(N)/P_s(0)$ and ε_r as a function of switching cycles exhibit almost similar behavior, that the $P_s(N)/P_s(0)$ and ε_r values degraded with increasing switching cycles. The decrease in fatigue endurance could be attributed to the severe switching-induced charge injection from the nearer electrode, which is considered as the main cause for the polarization fatigue in ferroelectrics [10,11]. It is of great interest to note that the tan δ values increase with increasing switching cycles, indicating that more free movable defects concentration is involved during switching cycles. Fig. 3(b) shows the P–E loops of $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films at different switching cycles. P_s values decrease up to ~31% of its virgin value after ~9.86×10^8 cycles, and E_c values abnormally increase up to ~86%, due to the increase of the defect concentration of $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films. Fig. 3(c) and (d) shows the dielectric behavior after different switching frequencies. ε_r values degraded and tan δ values increase with increasing switching cycles. Similar phenomenon has been observed for the ferroelectric thin films [28,29]. These results strongly confirm that the switching-induced charge injection largely dominates the fatigue endurance in the $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin film.

4. Conclusions

The fatigue endurance of $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films was investigated by varying frequencies and driving electric fields. The fatigue endurance degraded with increasing driving electric fields at a fixed frequency of 50 kHz, and is improved with increasing measurement frequencies at a fixed electric field of ~259 kV/cm. The dielectric constant as a function of switching cycles is well in agreement with the fatigue endurance, confirming that the switching-induced charge injection plays an important role in the fatigue behavior of lead zirconate titanium thin films.

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