Local Phase Decomposition as a Cause of Polarization Fatigue in Ferroelectric Thin Films

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We show that lead zirconate titanate thin films undergo local phase decomposition during fatigue. The original remanent polarization of the fatigued film is completely restored after furnace annealing in an O_2 atmosphere, following a significant regrowth of a perovskite phase from the pyrochlorelike structure. By comparing our data with other researchers' work on annealing of fatigued ferroelectric samples, we conclude that local phase separation is the *generic* reason for electrical fatigue in ferroelectrics. A fatigue model is proposed in order to interpret our experimental data.

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The microscopic mechanism leading to the suppression of remanent polarization during electrical cycling in Pt-PZT-Pt ferroelectric capacitors, although extensively investigated over the last several decades, remains contentious [1]. There have been numerous different models and mechanisms invoked, including electromigration of oxygen vacancies to form extended defects capable of pinning domains [2,3], formation of a "dead or blocking layer" [4,5], domain locking with electronic charge [6], interface nucleation inhibition mechanisms [7,8], and so forth. Additionally, although many empirical solutions [9] have been proposed and new ferroelectric materials [10,11] have been discovered for ferroelectric memories, none can be considered as the ultimate solution, since they all suffer from other drawbacks, such as lower polarization, higher leakage current, or higher processing temperatures. Therefore, understanding the nature of the fatigue mechanism in PZT films and finding feasible solutions to achieve fatigue-free platinized PZT ferroelectric capacitors for nonvolatile memory applications remains of particular scientific and technological interest.

The $Pb(Zr_{0.3}/Ti_{0.7})O_3$ (370 nm) thin films used in the present work were fabricated by sol-gel methods. Raman studies used a Jobin-Yvon 300 with a 632.8 nm, 20-mW He-Ne laser backscattered from a 2-micron-diameter spot with CCD detector collection. The fatigue measurements were conducted using a Radiant RT6000S ferroelectric test system. Annealing the fatigued samples was performed in a preheated cylinder furnace under O_2 atmosphere at various temperatures for 10 minutes.

(a) Fatigue studies.—Figure 1(a) shows the general fatigue characteristic of our PZT film in this study. P_r dramatically decreases to 27% of its virgin value after 10^{10} cycles, consistent with the sigmoid-shaped curves generally reported in the literature. Optical micrographs of the electrode under systematic fatigue study were recorded before and after each fatigue process. Figures 1(b) and 1(c) show, respectively, the optical micrographs of an electrode in its virgin state and after 10^9 fatigue cycles. Scanning electron microscopy (SEM) clearly indicates that the dark spots in Fig. 1(c) are essentially holes in the Pt electrode down to the degraded up layer of the fatigued PZT film [Fig. 1(d)]. It can be seen that the diameter of the Pt holes is generally less than 1 μm, but is still large enough to allow micro-Raman studies.

The number of the degraded spots (Pt holes) that appear after 10^8 cycles increases as a function of the number of cycles. After 10^{10} fatigue cycles, more than 20 spots were observed via SEM and subsequently shown to be a similar phase by micro-Raman [labeled as "fatigued" in Fig. 2(a)]. It is noted that the spectrum is dramatically different from that of the unelectroded PZT regions [labeled as "normal PZT" in Fig. 2(a)]. Spectra recorded from normal regions show peaks and bands that can be assigned to perovskite-PZT, e.g., peaks at 279 cm^{-1}, 335 cm^{-1}, and 605 cm^{-1}, in good agreement with the literature [12]. However, spectra collected from degraded spots show a broad band from ca. 700 cm^{-1} to 900 cm^{-1}

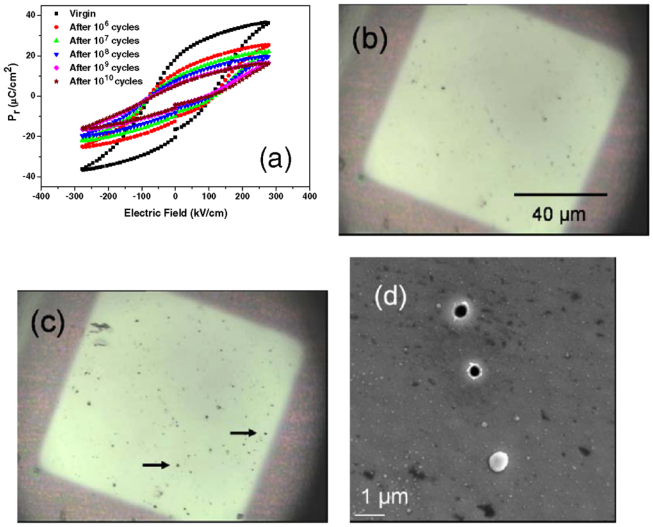

FIG. 1 (color online). (a) Fatigue characteristic of the PZT thin film used in this work. Optical images of virgin electrode (b) and electrode after 10^9-cycle fatigue (c). In (c) two of the dark spots indicated by arrows are due to the automatic removal of the local Pt electrode during fatigue. The SEM micrographs of two degraded spots after fatigue are shown in (d).

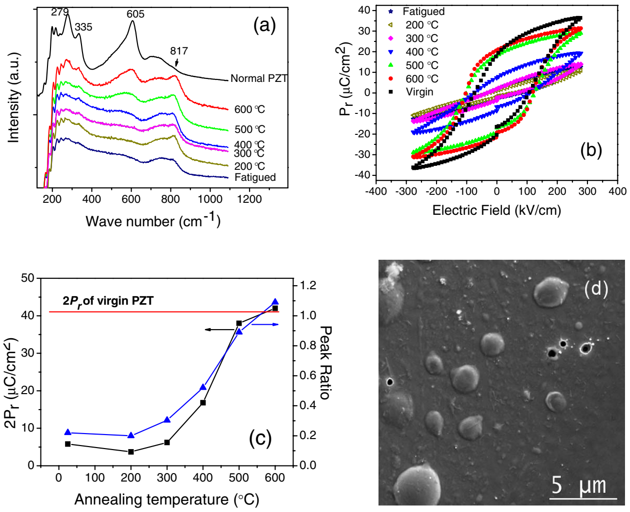

FIG. 2 (color online). Restoration of the perovskite structure from pyrochlorelike phase upon furnace annealing in an oxygen atmosphere (a) and simultaneous restoration of the relative squareness of the hysteresis loop (b). The change of $2P_r$ and the peak ratio of the band at $\sim$600 cm^{-1} and 750 cm^{-1} as a function of annealing temperature are shown in (c), with the virgin $2P_r$ value labeled by a line. (d) shows the micrograph of 10^{10}-cycle fatigued electrode after 600 °C reannealing, displaying numerous bubbles.

with a shoulder centered at 817 cm^{-1}. We tentatively assign the broadband to a pyrochlorelike phase, since this feature is usually observed during annealing of PZT thin films or ceramics powders [13,14]. This broad feature in Raman spectra, recorded from the 500 °C-annealed PZT film, corresponds to regions which show the well-known pyrochlore (222) peak seen at 29.5° in x-ray diffraction 2θ plot [14,15]. The shoulder at 817 cm^{-1} is attributed to well-ordered Ti-O clusters.

(b) Annealing the fatigued PZT film: The present work.—The fatigued PZT film was then annealed in flowing oxygen for 10 min at various temperatures. Micro-Raman studies indicate structural changes of the degraded interfacial spots underneath the Pt holes after systematic annealing [Fig. 2(a)]. Hysteresis loops of the fatigued film upon annealing are shown in Fig. 2(b), indicating the recovery of remanent polarization P_r upon annealing. Figure 2(c) exhibits the change of the $2P_r$ as a function of annealing temperatures, with the virgin value labeled by a line. In order to show the pyrochlore-perovskite transformation [Fig. 2(a)] in a quantitative way, the relative intensity of the peak at $\sim$600 cm^{-1} representing a perovskite structure and the band $\sim$750 cm^{-1} representing a pyrochlorelike phase was also plotted in Fig. 2(c). The absolute intensity of either is evaluated by drawing a baseline between the dip at $\sim$400 cm^{-1} and the tail at $\sim$900 cm^{-1}. The increase of this intensity indicates recovery of a perovskite structure.

Remarkably, the restoration of the hysteresis loop and the perovskite structure at the electrode-film interface (which is the only part of the film visibly observed) both start at 300 °C annealing and show a dramatic change at 400 °C. After annealed at 500 °C, the remanent polarization recovers to the 90% of its original value. P_r recovers completely after 600 °C annealing, although the saturated polarization is still lower than the virgin value. Correspondingly, a significant restoration of the perovskite structure from the degraded phase occurs at 500 °C and 600 °C. The remarkable similarity of the two curves in Fig. 2(c) indicates a *direct* relation between the growth of the perovskite phase (or elimination of the degraded phase) and restoration of electrical properties (e.g., P_r).

It is well known in the literature that Pb/PbO are very volatile. Therefore we suggest that the degraded structure (or Pt holes) is due to the evaporation of oxygen, Pb/PbO, from the interface during the local phase decomposition. Indeed, in a different research area on high-T PZT decomposition, Chen *et al.* [16] and Castellano *et al.* [17] reported that the perovskite structure collapsed into the pyrochlore phase $PbTi_3O_7$ on heating at 800 °C when PbO/oxygen rapidly evaporates. In addition, phase decomposition in PZT has been reported at a temperature as low as 550 °C [18]. Our interpretation seems to be confirmed by Pan *et al.*, who claimed to have seen oxygen leaving a PZT sample during their switching measurements [19], although this experiment could not be repeated by Nuffer *et al.* [20] We note that both of the experiments were unable to detect PbO vapor, which may be the most probable end product during the phase decomposition accompanying electrical fatigue. Additionally, the dark spots only appeared after 10^8 fatigue cycles; however, the dramatic decrease of P_r occurred before 10^8 and was saturated afterwards [Fig. 1(a)]. It is reasonable to argue that there may also be some degraded phases formed locally in the 10^6 and 10^7-cycle fatigued samples. The reason why there is no hint of electrode degradation may be because the pressure of oxygen and Pb/PbO vapor is not high enough to "blow out" the local electrode and form Pt holes. This seems to be confirmed by the observation that numerous gas bubbles form underneath the fatigued Pt surface after reannealing at temperatures higher than 300 °C, indicating degradation of the local interfaces [Fig. 2(d)]. We believe that the bubbles are not experimental artefacts, but rather directly related to electrical fatigue, since the surrounding top electrodes without any electrical treatment on the same film show no bubble formation or degradation after the same thermal treatments up to 600 °C.

There is no way to detect directly the interface structure underneath the Pt electrode without disturbing it. Our experiments provide indirect, but strong, evidence that the fatigue (or recovery) of PZT films is caused by the formation (or elimination) of a degraded region.

Let us conclude this section by correcting the general accepted viewpoint in the literature that fatigued PZT thin films or bulk ceramics can be "cured" by heating the sample just above the Curie temperature. The assumption behind this view is that defects inducing electrical fatigue by pinning domain walls can be removed during the disappearance of the ferroelectric domains when the fatigued sample is heated to their paraelectric phase. Upon cooling, the paraelectric phase transforms to the ferroelectric phase and new domains are formed without pinning. This point has been questioned by some researchers because heating their ceramic samples above the Curie point could not fully rejuvenate the remanent polarization [21–23]. The Curie point of the PZT (Zr:Ti = 30:70) films used in present work has not been measured yet. But bulk materials with the same composition show a Curie temperature at ~440 °C, evaluated from the well-known PZT phase diagram. Thin films normally have a higher Curie point than bulk materials due to the misfit strain between the substrate and the film. Therefore, the Curie point of our films is expected to lie around 500 °C. However, the P_r recovery of our PZT film started at ~300 °C, well below the T_c, and continued on annealing to 600 °C. As we have discussed before, it is more plausible to relate the P_r recovery to the recovery of the perovskite phase from a pyrochlorelike one than to the "Curie point" argument, based on the marked similarity of the two curves in Fig. 2(c). This point will be discussed further in the next section.

(c) Annealing the fatigued ferroelectrics: Work in the literature.—A question arises: is our conclusion generic? By "generic," we do not mean that all the degraded phases induced by fatiguing ferroelectrics are pyrochlorelike, but rather we mean that a decomposition-induced degraded structure at the local interface during electrical cycling is responsible for the decrease of the remanent polarization. Thermal treatment at higher temperatures in oxygen can "cure" fatigue simply by restoring the degraded structure back to perovskite by reoxidation.

The results of independent work by other researchers on annealing the fatigued ferroelectrics have been plotted in Fig. 3, along with our own data. Note that all the data are measured at room temperature after thermal treatment and normalized with respect to the virgin P_r value in order to facilitate the comparison. Remarkably, the recovery of the remanent polarization as a function of annealing temperatures show a *generic* behavior independent of the type of samples [PZT [24,25] or $BaTiO_3$ (BTO) [26]], fabrication methods (sol-gel [25], Remeika flux method [26], or commercially used ceramics fabrication methods [24]), Curie temperatures (~500 °C for the film used in the current work, estimated to be $300 < T_c < 400$ °C in Amanuma's work [25], only 250 °C for the PZT ceramics [24], and only 120 °C for single crystal BTO), and compositions [PZT(30/70) in this work, PZT(40/60, 53/47) in Amanuma's work [25], and a commercialized ternary phase system $Pb(Ni_{1/3}Sb_{2/3})O_3$-$PbTiO_3$-$PbZrO_3$ in Nuffer's work [24]]. Interestingly, the normalized polarizations of all the samples seem to decrease at 200 °C, slightly increase at 300 °C, increase dramatically at 400 °C, and start saturating at 500 °C, apart from the BTO sample due to lack of enough data. Our above argument is further supported by a systemic fatigue-and-annealing study by Pan *et al.* on their commercialized PZT and PLZT ceramics [27]. The P_r recovery curves in that work show the same behavior as Fig. 3. An interesting point about this work is that the rejuvenation is very sensitive to the annealing temperatures and less sensitive to the annealing time, which is exactly the behavior of the crystal growth. Note that Nuffer's study clearly shows that simply heating the samples above the Curie temperature (250 °C for their sample) could not restore the hysteresis loop (P_r even slightly decreases at 250 °C, Fig. 3), which further supports our view made above.

(d) A model for fatigue.—Here we propose a new fatigue model, where fatigue is initiated by charge injection and induced by the local phase decomposition consequently. Figure 4 shows the snapshot of the very early stage of the

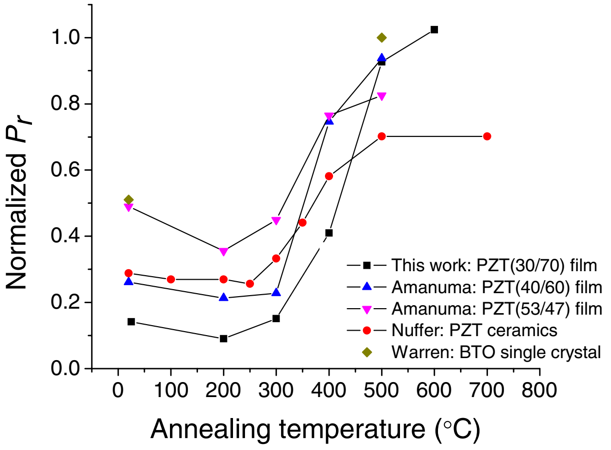

FIG. 3 (color online). Comparison of the present work with other researchers' work on annealing the fatigued ferroelectric samples. Data plotted here are from this work and the work by Amanuma *et al.* (Ref. [25]), Nuffer *et al.* (Ref. [24]), and Warren *et al.* (Ref. [26]).

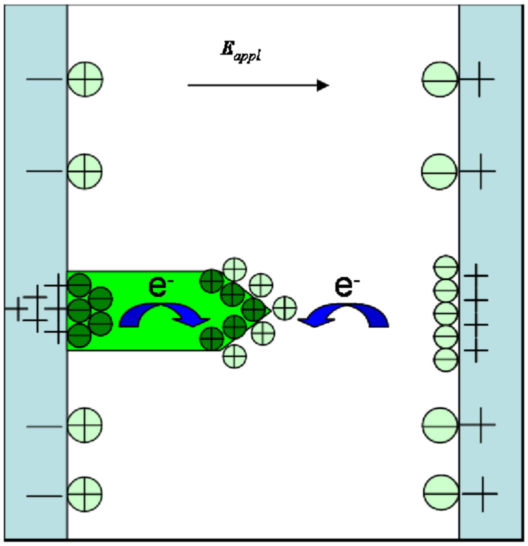

FIG. 4 (color online). The snapshot of the nonequilibrium transient state at the very early switching stage (not to scale).

switching process after applying the first half of the ac field. It can be seen that the bound charges at the tip of the needle domains are completely unscreened, unlike those near the electrodes. We show that the depolarization field of these bound charges on the nearer electrode is negligible, in order of kVcm, when the bound charges propagate to the middle of the total film thickness. However, when it is just about to propagate from the left electrode, i.e., the embryonic nucleus stage, or approaches to the right electrode, this field can be extremely high. In particular, assuming the nucleus has a hemisphere structure, a standard surface integral gives exactly:

$$E_{\mathrm{bc}} = \frac{P_r}{3\varepsilon_i\varepsilon_0} = 1.88\ \mathrm{MV/cm}, \tag{1}$$

where P_r is the remnant polarization (we take $P_r = 20\ \mu\mathrm{C/cm}^2$) and ε_i is the dielectric constant at the interface ($\varepsilon_i \sim 40$). This is an extremely high field which the nuclei have to "suffer" twice for every electrical fatigue cycle. Under such a high field, we believe that there is large current injected from the electrode, which is probably determined by Fowler-Nordheim tunneling via

$$J = C_{\mathrm{FN}} E_{\mathrm{bc}}^2 \exp\left[-\frac{4\sqrt{2m^*}(q\phi_B)^{3/2}}{3q\hbar E_{\mathrm{bc}}}\right], \tag{2}$$

where C_{FN} is the Fowler-Nordheim coefficient which depends on the barrier height ϕ_B and the electron effective mass m^* at the interface. Under such a high tunneling current, local phase decomposition can be expected especially near the nucleation sites (Fig. 4). We believe that local phase separation can induce fatigue in two ways: on one hand, the resultant pyrochlorelike structure forms a parallel-capacitor structure with the bulk film, i.e., the well-known and well-explored "dead layer" sandwich structure; on the other hand, the decrease of the number of the available nucleation sites due to local phase separation also makes switching more difficult.

Let us assume that the probability that decomposition will occur for a nucleation site after one cycle is $1/\lambda$ with $\lambda \gg 1$, the remanent polarization $P_r(N)$ measured experimentally after N cycles is proportional to the number of the survived nuclei for simplicity, and $1/\lambda$ is a monotonically *increasing* function h of the local input power density $E_{\mathrm{bc}}J$ at the nucleation site. For the simplest situation where h is a linear function, considering Eq. (1) and (2) we have [28]:

$$\frac{P_r(N)}{P_r(0)} = D\exp\left\{-AN\frac{C_{\mathrm{FN}}P_r^3}{27\varepsilon_i^3\varepsilon_0^3} \times \exp\left[-\frac{4\sqrt{2m^*}(q\phi_B)^{3/2}\varepsilon_i\varepsilon_0}{q\hbar P_r}\right]\right\} + F, \tag{3}$$

where A is the decomposition probability per unit power density per cycle, $P_r(0)D$ and $P_r(0)F$ are the fatigued and "nonfatigued" remanent polarization, respectively, when N goes to infinity with $D + F = 1$. F is normally much less than D. From Eq. (3), it can be seen that $P_r(N)$ only depends on N, P_r, and ε_i. All the other variables can be simply put into this equation via P_r (T, $E_{\mathrm{appl.}}$, f, crystallographic orientation, etc.), where T is temperature, $E_{\mathrm{appl.}}$ the applied field, and f the frequency. The detailed derivation of our model and its consistency with extensive body of experimental data will be published elsewhere [28]. Although standard electrical fatigue seems to be induced directly by local phase decomposition from the present work, fatigue, in a general sense, can also be induced by optical, thermal, and even reducing processes [6]. We will show in a future paper that a generalized version of our model might also be able to interpret optical and thermal fatigue [28].

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