Polarization fatigue in poly(vinylidene fluoride (78%)-trifluoroethylene (22%)) ferroelectric thin films: a pulse train study*

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This paper investigates the influences of polarization fatigue on remanent polarization and switching time by pulse train measurements in ferroelectric poly(vinylidene fluoride (78%) and trifluoroethylene (22%)) thin films. Fatigue was carried out by a series of bipolar switching pulses with constant pulse width (on-time) and various interval times between pulses (off-time). The experimental observations indicated that the off-time period showed no obvious influence on fatigue rate and the switching time increased with the increase of fatigue cycles. The origination of these phenomena was discussed according to the charge injection model.

Keywords: ferroelectric polymer, polarization fatigue, switching time, charge transfer

PACC: 7780F, 7360R

1. Introduction

In recent years, ferroelectric polymers have drawn much attention due to their potential application in nonvolatile memory devices.[1] The copolymer of vinylidene fluoride and trifluoroethylene [P(VDF-TrFE)] is the best-known ferroelectric polymer and a particularly attractive material in memory applications for its large spontaneous polarization, excellent polarization stability, short switching time and easy processing.[1−3] Nonvolatile memory elements based on ferroelectric polymers such as organic field-effect transistors have been realized in many laboratories.[4−7]

Electrical fatigue (pictured by the decrease of on/off ratio and memory window with increased on/off cycles) is a crucial characteristic which determines the lifetime and stability in ferroelectric memory devices.[8] The study of fatigue in devices includes two parts: one is the electrical fatigue in each component, especially the fatigue characteristic in ferroelectrics,[8] and the other is the electrical fatigue of the total system.[9] Due to the multi-component structure of the memory devices and their correlation (such as the interface between two components), the total system should exhibit more complicated fatigue characteristics, which would be the integration of each component. In the study of electric fatigue in ferroelectric films themselves, remanent polarization (P_r) and switching time (t_s) are two important parameters. The value of P_r is relative to the memory window and on/off ratio, and the switching time of polarization reversal determines the programming time of memory devices. In ferroelectrics, ferroelectric fatigue (polarization loss of ferroelectric films due to electrical stress) is a serious factor which has restricted the applications of ferroelectrics in nonvolatile memory devices because it would not only degrade the polarization level but also affect the switching time and therefore the programming time. Fatigue in inorganic ferroelectrics has been comprehensively studied and well understood.[8] However, fatigue in ferroelectric polymers has not attracted much attention until recent years. Electrical fatigue in P(VDF-TrFE) films was first reported by Guy *et al.*[10] The influences of processing conditions,[11] electrode materials,[12,13] voltage profile,[14] operation temperature,[15] and film crystallinity[16] on electric fatigue were successively studied. In our previous work, remanent polarization in fatigued P(VDF-TrFE) films could be partly recov-

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ered after a long-time rest (such as 65 days).[17] In this paper, we report the influence of a short time interval (off-time) on electrical fatigue in ferroelectric P(VDF-TrFE) films.

2. Experimental details

Copolymer films were spin-coated on Al-deposited glass slides from a 5.0% by weight solution of P(VDF-TrFE) (78/22 molar ratio, from MSI Sensor, PA) in butanone. The films had a thickness of 800 nm and were annealed at 142 °C for 6 h to increase their crystallinity. Then top Au electrodes were deposited in vacuum.

Measurements of ferroelectric properties were performed by a homemade Sawyer–Tower circuit, which was shown in Fig. 1(a). A function generator was used to produce a definite signal, which was applied to the ferroelectric film via a signal amplifier to induce ferroelectric switching and thereafter electric fatigue in the film. The current response of the ferroelectric film was recorded by an oscilloscope from the sampling resistance.

Ferroelectric fatigue was carried out by applying a series of bipolar fatigue pulses [Fig. 1(b)] with amplitude of 140 MV/m, high enough to cause ferroelectric switching. To determine the influence of off-time ($t_{\rm off}$), the width of all the pulses was set to a constant value: 5 ms, while $t_{\rm off}$ varied from 0 ms to 245 ms. The period for one fatigue cycle was $2t_{\rm on} + 2t_{\rm off}$.

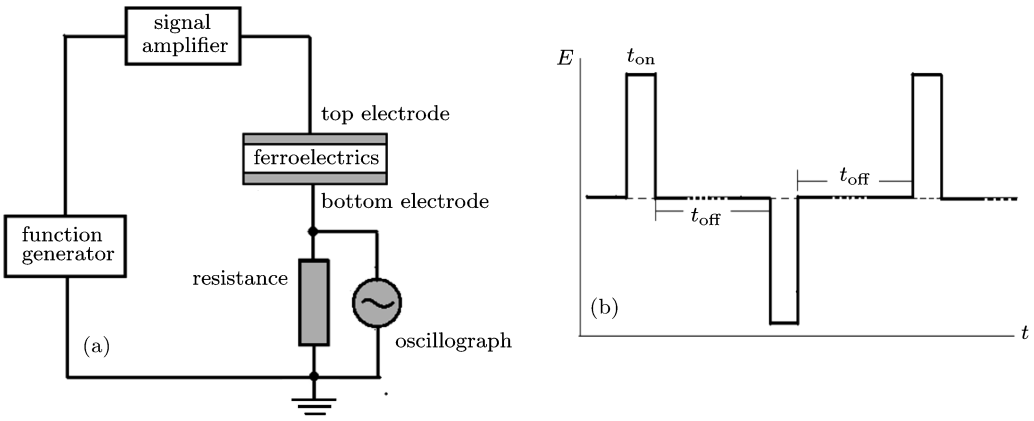


Fig. 1. Sawyer–Tower circuit (a) and pulse train used to fatigue samples (b).

Polarization–electric field (P–E) hysteresis loop was measured by applying a bipolar triangular voltage with frequency of 1.0 Hz and amplitude of 140 MV/m. The hysteresis loop was obtained by integrating the current response during ferroelectric switching process. To determine the fatigue stage, the fatigue process was interrupted at pre-calculated intervals to monitor the hysteresis loop.

After hysteresis loop measurement, switching time was immediately measured. At first, a pulse of 140 MV/m was applied for 1.0 s to pre-polarize the electric dipoles toward one direction. Then, after a short circuit treatment of 1.0 s, the film was re-polarized by a pulse of +140 MV/m and the dipoles were oriented toward the opposite direction. The resulting current response was recorded. By integrating the current response, the electric displacement D was determined, which could be approximately expressed as

$$D(t) = \varepsilon E + 2P_{\rm r}[1 - {\rm e}^{-(t/t_{\rm s})^{\gamma}}] + \sigma E t, \qquad (1)$$

where ε is the permittivity of the ferroelectric polymer, $P_{\rm r}$ is the remanent polarization, $t_{\rm s}$ is the switching time, γ is a parameter related to the shape of the switching curve and σ is the DC conductivity. $t_{\rm s}$ can be determined from the time of the maximum ${\rm d}D/{\rm d}\log t$.[18]

3. Results

Figure 2 showed the effect of repeated polarization switching on the polarization–electric field hysteresis loop (P–E loop). The virgin sample showed a

loop with rectangular shape and had the highest remanent polarization (P_r), which was 0.1 C/m^2. However, with the increased number of polarization switching, P_r gradually reduced. For example, it decreased to 0.085, 0.076 and 0.060 C/m^2 after 1.1×10^4, 6.0×10^4 and 2.2×10^5 cycles, respectively.

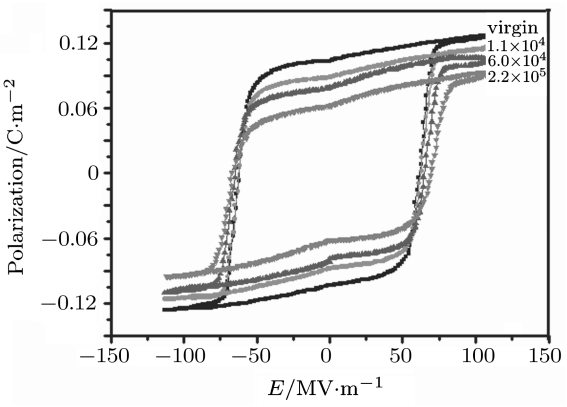


Fig. 2. Hysteresis loops at the beginning and after 1.1×10^4, 6.0×10^4 and 2.2×10^5 fatigue cycles.

We applied a series of fatigue pulses with different t_{off} to study the influence of off-time on electric fatigue. Normalized P_r was plotted in Fig. 3 as a function of logarithm of the number of switching cycles. Remanent polarization showed the same attenuation rate with increased fatigue cycles though t_{off} varied from 0 ms to 245 ms. The results indicate that the short off-time showed no obvious influence on fatigue rate, at least in our experimental condition.

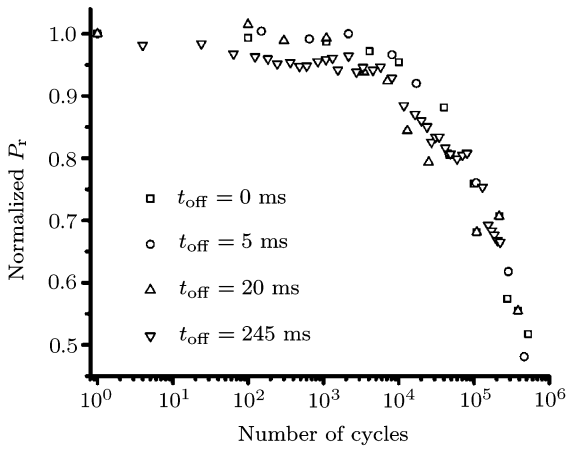


Fig. 3. Normalized P_r as a function of logarithm of the number of cycles. Fatigue was carried out by a switching voltage with a field of 140 MV/m. The off-time (t_{off}) for four samples varied from 0 to 245 ms.

To study the influence of repeated polarization switching on t_s, a series of fatigue pulses with different t_{off} were applied on samples. By integrating the current response, the resulting D was shown in Fig. 4(a) as a function of log t. With increased time, all curves gradually increased to saturation values, which implied the completion of the dipole reversal. The maximum D value obtained from the virgin sample was smaller than those from fatigued samples. This could be due to the increased current leakage in fatigued samples, as could be confirmed by the measurement of current–voltage (I–V) characteristic before and after fatigue process. A typical I–V measurement was shown in Fig. 5. Before each I–V measurement, the film was pre-polarized by a positive pulse of 140 MV/m to align the electrical dipoles, and then I–V characteristic was recorded by a positive ramp varying from 0 to 85 V. It was obvious that with the increase of fatigue cycles the I–V curves shifted upward, as indicated the worse insulating property in fatigued films.

As mentioned above, t_s could be determined from the time of the maximum $\mathrm{d}D/\mathrm{d}\log t$,[18] as was shown in Fig. 4(b). The results indicate that repeated switching caused a marked increase of t_s. For example, t_s of the virgin sample was 3.06 ms, and then it increased to 4.92 ms, 5.38 ms and 5.9 ms after 2.3×10^4, 6.0×10^4 and 2.5×10^5 fatigue cycles, respectively

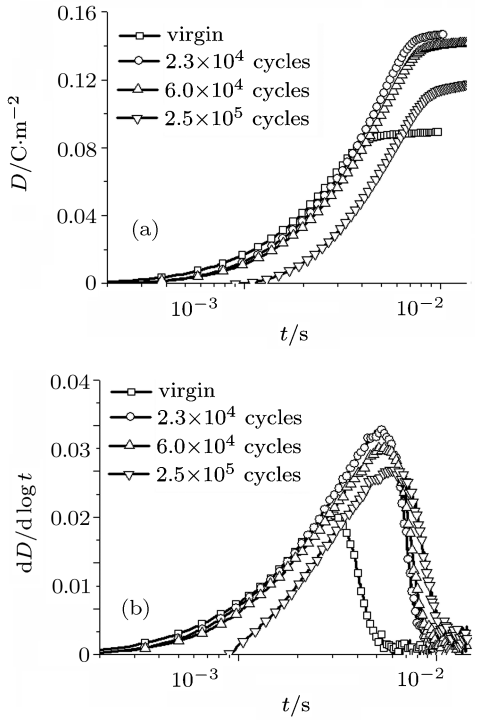


Fig. 4. Switching characteristics of a sample fatigued by a voltage with t_{off} of 245 ms.

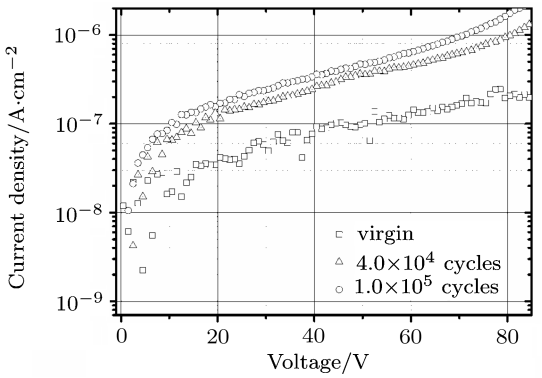


Fig. 5. Current–voltage characteristics of a P(VDF-TrFE) film before and after electrical fatigue. The legend indicated the fatigue cycles.

Changes of switching time Δt_s with the increased fatigue cycles were shown in Fig. 6, where the off-time ranged from 0 ms to 245 ms. The quantity Δt_s was defined as $\Delta t_s = t_s - t_{s0}$, where t_{s0} denotes the switching time of the virgin sample and t_s is the switching time after certain fatigue cycles. It clearly showed that Δt_s increases with increasing fatigue cycles. For example, in the case of $t_{off} = 5$ ms, Δt_s increases from 1.17 ms at 1.7×10^4 cycles to 2.33 ms at 1.1×10^5 cycles. Furthermore, the change in Δt_s with fatigue cycles was non-linear. At the early fatigue stage with fatigue cycles less than 3×10^3 cycles, no obvious changes could be observed in Δt_s. With further increased fatigue cycles from 3.0×10^3 to 1.0×10^5 cycles, Δt_s dramatically increased. All of the three curves showed nearly the same increasing rate. After 1.0×10^5 fatigue cycles, Δt_s seemed to get saturated and no obvious changes were observed.

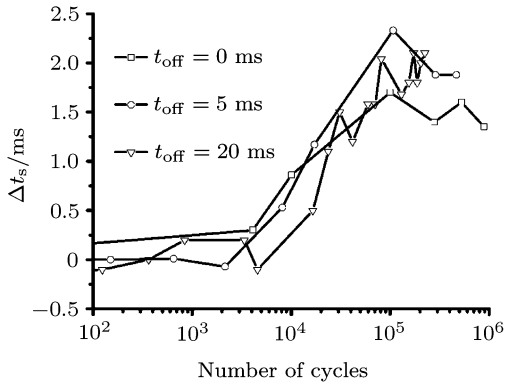


Fig. 6. Changes of t_s as a function of logarithm of the number of fatigue cycles. Fatigue was carried out by fatigue pulses with a field of 140 MV/m and t_{off} of 0, 20 and 245 ms, respectively.

4. Discussions

Our experimental observations indicate that the off-time from 0 to 245 ms shows no obvious influence on polarization fatigue and switching time increases with increased fatigue cycles in 78/22 P(VDF-TrFE) thin films. Due to the time limit, in our present study we do not extend the off-time to a larger value, such as several seconds or even several minutes, though our previous work has proved that remanent polarization in fatigued ferroelectric polymer films can be partly or even fully recovered after a long-time rest (tens of days).[17] In this paper, we only discuss the influence of short time interval on electrical fatigue.

Polarization fatigue in inorganic ferroelectric has been well studied and several mechanisms have been proposed,[8] in which the injection and the trap of space charges are thought to be the most possible reason to cause fatigue.[19] In the study of the influence of space charges on dipole orientation and consequently ferroelectricity in polymers, Sussner *et al.* found that, if using blocking electrodes, piezoelectricity would dramatically decrease.[20] Eisenmenger *et al.* found the time dependence of the polarization distribution across the film thickness in PVDF and P(VDF-TrFE), and proposed that the injection and migration of space charges determined the polarization distribution.[21] All these experimental results indicate the influence of trapped charges on ferroelectricity in polymers. Furthermore, in the study of electrical fatigue in ferroelectric polymers, the influences of voltage profile,[14] electrode materials,[12,13] and film crystallinity[16] were determined. The microscopic butterfly loop observed from fatigued P(VDF-TrFE) films also showed a slim shape, which was much similar to that from P(VDF-TrFE) films irradiated by high energy electron beam.[22] In our recent work,[23] we found the crucial influence of the transient state of ferroelectric switching on electric fatigue in ferroelectric polymers and the worse fatigue endurance caused by two-step voltage pulses (first a low-voltage pulse with amplitude slightly below coercive voltage V_c followed by a high-voltage pulse with amplitude much higher than V_c). This observation was consistent with the LPD-SICI model,[8] which also concerned the effect of charge injection. All these experimental observations imply the crucial role of trapped charges on polarization fatigue in polymers. It is believed that polarization fatigue in polymers mainly originates from the injection of space charges through electrodes into ferroelectrics and these charges can be trapped at the boundaries of crystallites[24] and by the defects[16] in ferroelectrics.

To understand electric fatigue observed in our

pulse train experiments, the fatigue process can be divided into two parts to consider what happens at each part: one is when the fatigue pulses are applied (on-time period) and the other is the off-time period.

At the on-time period, electric dipoles are repeatedly reversed by the positive and negative pulses. Space charges can be injected through electrodes into ferroelectrics. These injected charges can be trapped at the boundaries of crystallites and by the defects in ferroelectrics. Due to the high fatigue electric field, these charges can penetrate deeply into ferroelectrics and interact with the inner electric dipoles. The interaction between dipoles and trapped charges can greatly increase the barrier height of dipole rotation and consequently inhibit the dipole reversal.[25] Besides, this interaction also makes it difficult for these trapped charges to escape from ferroelectrics.[25]

At the off-time period, though the applied electric field has been removed, there are still some space charges injected into ferroelectrics due to imprint effect.[26] The term imprint summarizes time-dependent effects of ferroelectric polarization, especially when the applied field is removed. Experimentally, the imprint effect is observed as a shift of ferroelectric switching peaks toward higher voltage with increased off-time.[27] Imprint effect is explained by the interface screening model in ferroelectric polymers, which assumes the existence of a very thin non-ferroelectric layer at the surface of ferroelectric materials and charge injection from the electrodes into the non-ferroelectric layer.[26] Due to the lack of high driving electric field, space charges can only be trapped at the non-ferroelectric layers near the surfaces and cannot penetrate deeply into ferroelectrics. Besides, the amount of trapped charges due to imprint effect is far less than the amount during the application of the field. Furthermore, these trapped charges in the non-ferroelectric layers are much easier to escape from the trap sites, especially when an opposite field is applied. As a result, compared with the contribution from the charge injection driven by the applied field, the contribution from imprint effect to electric fatigue can be negligible. Also we want to emphasize that the trapped charges, driven by the applied field, can hardly escape from their trap sites during the off-time period. In our previous work, we observed the partial recovery of remanent polarization in fatigued samples only after a longtime rest of 65 days.[17] In our present observations, the off-time is shorter than 1.0 s, so it is reasonable that the escape of trapped charges should be neglected.

Our previous work have proved that fatigue is much sensitive to bipolar rectangular voltage[14] and consequently we regard that the amount of trapped charges is determined by the total time of exposure to the field. In all the pulse train experiments, the fatigue pulses have the same amplitude of 140 MV/m and width of 5 ms and the contribution from the off-time period can be negligible, so the degradation of remanent polarization with increased fatigue cycles should show the same rate regardless of the off-time varying from 0 ms to 245 ms.

The trapped charges cause not only the degradation of polarization, but also the increase of switching time. In the fatigue progress, more and more charges are injected and trapped in the ferroelectric film. The interaction between trapped charges and electric dipoles increases the barrier height during dipole reorientation and hence results in the increase of switching time.

5. Conclusion

In summary, we investigated the changes in remanent polarization and switching time in 78/22 P(VDF-TrFE) thin films during fatigue progress via pulse train measurements. We observed that the short off-time period showed no obvious influence on the fatigue rate and the switching time increased with the increase of fatigue cycles. The origination of these observations was discussed according to the charge-injection model.

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