

## ARTICLE

# Symmetric Ferroelectric Switching in Ferroelectric Vinylidene Fluoride and Trifluoroethylene Copolymer Films

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We report the observation of asymmetric switching dual peaks in ferroelectric copolymer films. These dual peaks occurs when the poling electric field is just below the coercive field and can be removed by continuous application of high enough switching voltage. Our experimental observations can be explained by the injection and the redistribution of space charges in ferroelectric films.

**Key words:** Ferroelectric polymer, Ferroelectric switching, Poly(vinylidene fluoride)

## I. INTRODUCTION

Since the discovery of piezoelectricity in 1969 [1], poly(vinylidene fluoride) (PVDF) and its various copolymers, such as its copolymer with trifluoroethylene, P(VDF-TrFE), have been extensively investigated for sensors and transducers [2]. Especially in recent years ferroelectric polymer-based nonvolatile memory devices have attracted much attention due to their high flexibility, low cost, ease of production and integrability with mainstream silicon technology and all-organic electronics [3]. However, there are still some obstacles which restrict the lifetime and reliability of these devices and therefore their wide applications. For example, the thickness dependence of coercive field ( $E_c$ ) in ultrathin ferroelectric films causes lower remanent polarization and more power consumption [4], polarization fatigue causes fast device failure [5], imprint effect causes the shift of operation voltage [6, 7], and low retention causes low lifetime [8]. Some models have been put forward to understand these phenomena both in inorganic and polymeric ferroelectrics, amongst which charge injection model [9, 10] and dead (passive) layer model [11] at metal/ferroelectric interface and even the combination [6, 7] of both models are widely used to explain most of experimental observations in many literatures. Charge injection model emphasizes the influence of trapping of charges at the boundaries between ferroelectric domains on switching dynamics. Passive layer model emphasizes the existence of low-permittivity layer at electrode/ferroelectric interface which reduces the electric field applied to ferroelectric films. Recently, Lou and his colleagues suggest a model of local phase decomposition initiated by switching-induced charge injection (LPD-SICI model), which explains the origin of the pas-

sive layer and also concerns the effect of charge injection [12, 13]. However, though these mechanisms have been successfully used to explain most of experimental observations in ferroelectric inorganics and polymers, how to distinguish and evaluate their contributions is still an open question.

In our previous work on the imprint effect in ferroelectric P(VDF-TrFE) thin films [7], we did not find an obvious dependence of imprint voltage on the shift of switching peaks when the imprint field varied from 60 MV/m to 90 MV/m. However, when we reduced the imprint field just near or below  $E_c$ , asymmetric ferroelectric switching with dual peaks was obtained. In this paper we will report this observation.

## II. EXPERIMENTS

Ferroelectric films were prepared by spin-coating technique from a 7.5% by weight solution of 60/40 P(VDF-TrFE) in butanone. The films had a thickness of  $\sim 1.10 \mu\text{m}$ , which was estimated from the polarization-electric field ( $P$ - $E$ ) hysteresis loops, considering an  $E_c$  of 48 MV/m. The films were annealed at 145 °C for 6 h to increase their crystallinity. Au top and bottom electrodes were vacuum deposited. Measurements of ferroelectric properties were performed by a homemade Sawyer-Tower circuit [7]. Two kinds of measurement waveforms were used in our experiments, which are shown in Fig.1. A positive prepoling pulse with amplitude of 96 V ( $V_p$ ) and width of 1.0 s ( $t_p$ ) was firstly applied to the ferroelectric film and then a negative pulse with various amplitude of  $V_n$  and various width of  $t_n$  was applied. After a waiting time of 1.0 s ( $\Delta t$ ), two cycles of recording voltage with amplitude of 96 V and frequency of 1.0 Hz was applied to obtain ferroelectric positive and negative switching peaks, corresponding to positive and negative voltages, respectively. In waveform A, the first half cycle of the triangular voltage was positive; while in waveform B,

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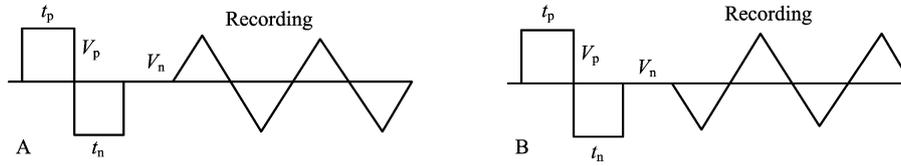


FIG. 1 Two kinds of waveforms used in this experiments. For waveform A, the first half cycle of the triangular voltage was positive, and for waveform B, the first half cycle was negative.

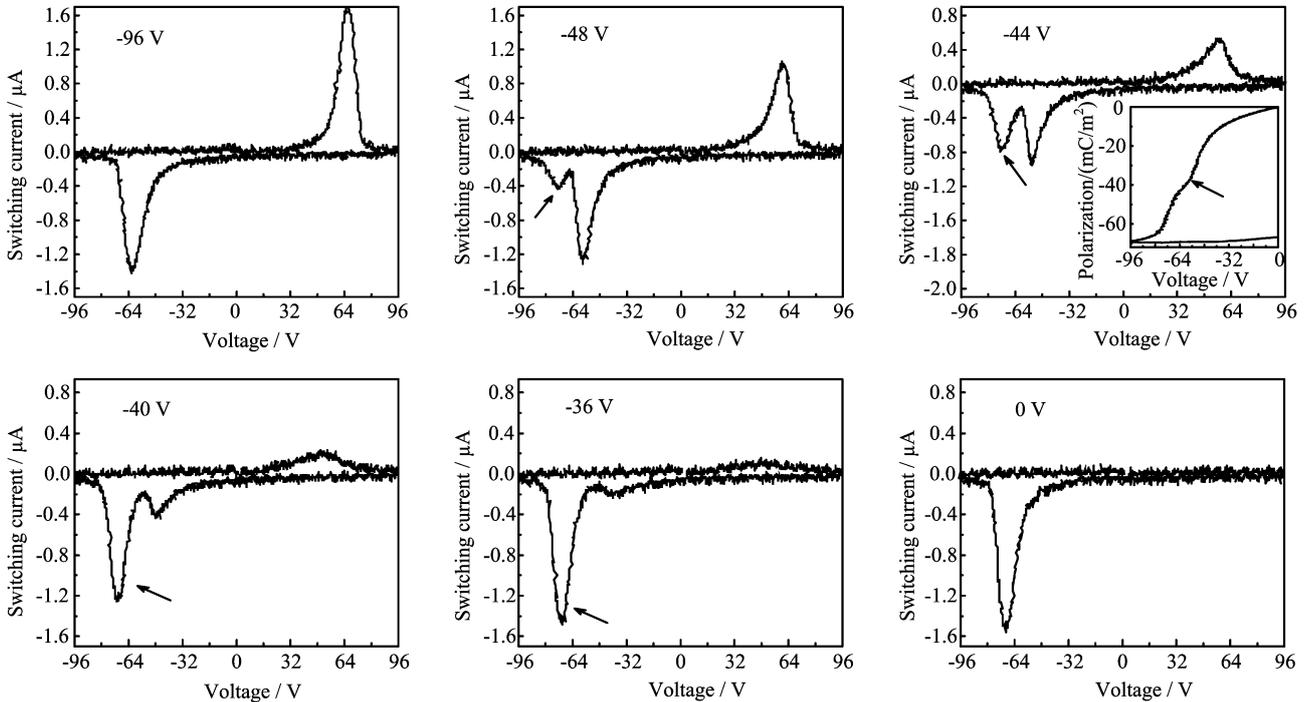


FIG. 2 The dependence of the switching peaks on  $V_n$  ( $t_n=1$  s). The numbers labeled in each images indicated the amplitude of  $V_n$ . The inset showed the integral curve of the negative current response with respect to the time. The arrows indicated the HV peaks. The switching current responses were recorded after waveform A was applied for 10 times.

the first half cycle was negative.

### III. RESULTS

We varied the amplitude of  $V_n$  and recorded both positive and negative switching peaks after the waveform A was applied for 10 times. Figure 2 shows the changes in switching peaks with  $V_n$ , recorded by the first cycle of the applied triangular voltage. From all six curves, we could observe the decrease of the positive switching peaks with the decreased  $V_n$ . The most interesting is the occurrence of switching dual peaks corresponding to the negative recording voltage. When  $V_n$  was much larger (such as  $-96$  V) than the coercive voltage  $V_c$ , the usual symmetric switching peaks could be observed.  $V_c$  of  $53$  V was determined from the  $P$ - $V$  loops, which were not shown here. However, when  $V_n$  was decreased to a value just below  $V_c$ , switching dual peaks occurred when the negative half cycle of the triangular voltage was applied. One peak corresponded to a higher volt-

age and was called HV peak (high-voltage peak), while the other switching peak corresponded to a lower voltage and was called LV peak (low-voltage peak). With the further reduction of  $V_n$ , HV peak grew up accompanied by the decrease of the LV peak. When  $V_n$  was decreased to  $-44$  V, both LV and HV peaks showed nearly the same height. With the further decrease of  $V_n$ , the HV peak became much larger than the LV peak (see  $V_n=-40$  and  $-36$  V). When  $V_n$  was far below  $V_c$ , switching dual peaks disappeared and only one positive switching peak was observed (see  $V_n=0$  V). In our experiment, we observed these switching dual peaks when  $V_n$  varied from  $-50$  V to  $-36$  V, which corresponded to an electric field span of  $\sim 12.7$  MV/m. In fact, with the increase or decrease of both negative peaks, their corresponding voltages also gradually shifted toward the lower voltage. The occurrence of switching dual peaks resulted in an unsmooth  $P$ - $V$  loop with a step-like increase, as shown in the inset in Fig.2.

Further observations indicated that, for the pulse

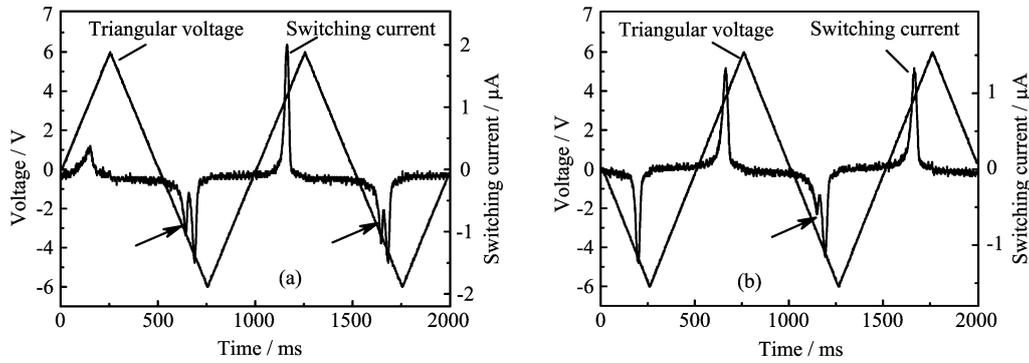


FIG. 3 Switching current responses after the application of (a) waveform A and (b) waveform B with  $V_n$  of  $-44$  V and  $t_n$  of 1 s. Both waveforms were applied for 10 times before measurements. The triangular voltage shown in both figures was attenuated by 16 times. The arrows indicated the switching current.

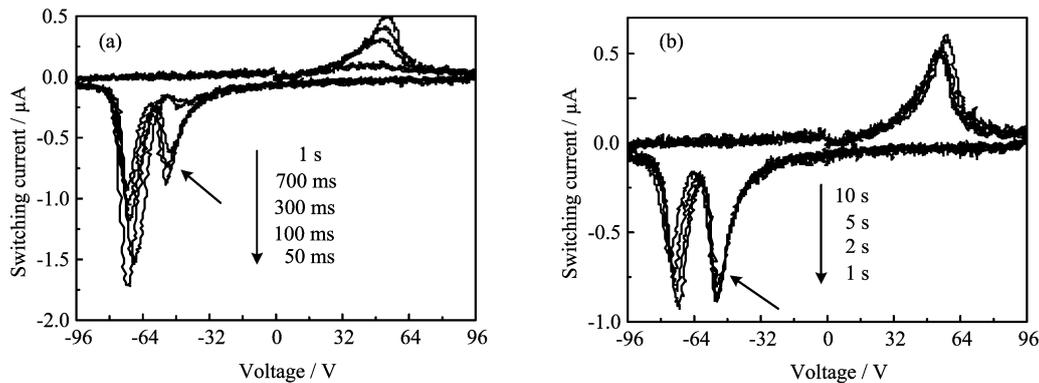


FIG. 4 Influence of the width  $t_n$  of the negative pulse on the switching dual peaks.  $V_n = -44$  V.  $t_n$  varied from 50 ms to 10 s. The arrows indicated the changes in the LV peaks. The switching current responses were recorded after waveform A was applied for 10 cycles.

structure used in our experiments (a positive prepoling pulse followed by a negative pulse with varied amplitude), only after the positive half cycle of the recording voltage was applied, the switching dual peaks could be observed on the succedent negative half cycle. This result is shown in Fig.3. For the application of waveform A (Fig.3(a)), switching dual peaks were observed on both negative half cycles after the positive half cycles were applied. While, for the application of waveform B (Fig.3(b)), no switching dual peaks were observed at the application of the first negative half cycle and, only when the positive part of the recording voltage was applied, the switching dual peaks occurred on the second negative half cycle.

The width  $t_n$  of the negative pulse also influenced the observed switching dual peaks, as can be seen in Fig.4.  $t_n$  varied from 50 ms to 10 s in this observation. Obviously, with the increase of  $t_n$ , the HV peaks gradually decreased in height and slightly shifted toward the higher voltage from  $-67$  V at  $t_n = 50$  ms to  $-76$  V at  $t_n = 10$  s. The LV peaks gradually increased in height when  $t_n$  varied from 50 ms to 1 s, while the further increase of  $t_n$  from 1 s to 10 s showed no obvious influence

on the LV peaks.

These switching dual peaks were metastable and could be removed, at least apparently, by continuous application of alternating triangular voltage, as shown in Fig.5. After 115 cycles, the voltage corresponding to the positive switching peak kept a constant value of 58 V, while the voltage corresponding to HV peaks gradually decreased from  $-74$  V to  $-63$  V and at the same time the voltage corresponding to LV peaks gradually increased from  $-52$  V to  $-63$  V. Both negative switching peaks gradually approached and finally united into one peak after 115 cycles. With the continuous application of the alternating switching voltage, the remanent polarization ( $P_r$ ) also slightly increased, as it is shown in Fig.6.  $2P_r = |P_+| + |P_-|$  increased from  $134.7$  mC/m<sup>2</sup> at 10 cycles to  $136.4$  mC/m<sup>2</sup> at 115 cycles.

#### IV. DISCUSSION

Here we emphasize again the crucial influence of the poling field just below  $E_c$  on the observation of switching dual peaks. In fact, this crucial influence have been observed and proved in inorganic ferroelectrics by many

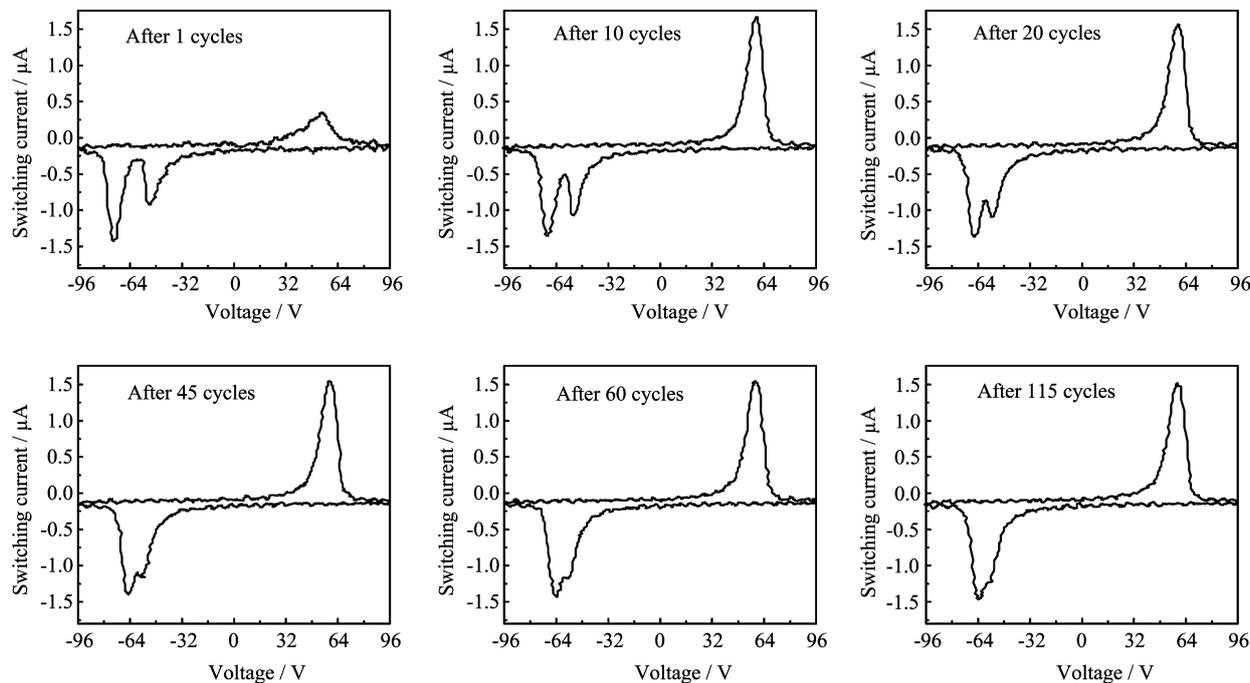


FIG. 5 The removal of switching dual peaks under the continuous application of the triangular voltage with amplitude of 96 V and frequency of 1.0 Hz. The numbers labeled in all images indicated the cycle number of the triangular voltage.

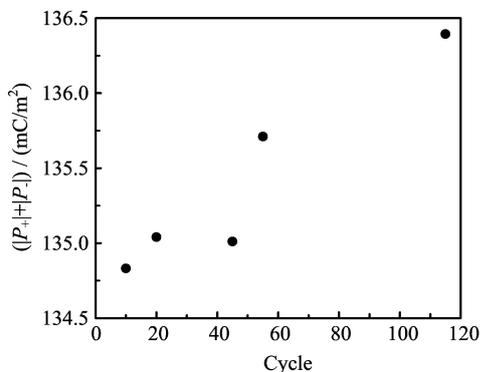


FIG. 6 The change in the remanent polarization after the continuous application of the triangular voltage.  $|P_+|$  was the remanent polarization obtained from the integration of positive switching peak, while  $|P_-|$  was the remanent polarization obtained from the integration of negative switching peak. The data of switching current responses came from those in Fig.5.

authors [9, 14–16]. In the study of the optical and thermal fatigue in  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (PZT) [9, 14], Warren and his colleagues found that the suppression of remanent polarization was maximized by partially switching the ferroelectric film with an opposite voltage slightly below  $V_c$  [14]. Colla and his coworkers found that two-step voltage pulses (first a constant field just below  $E_c$  followed by a high poling field) were more effective to cause electric fatigue than simple square pulses [15]. Our previous work also proved that the two-step voltage pulses

would cause worse fatigue endurance than the simple square pulses in ferroelectric polymers [16]. Switching dual peaks have also been observed in fatigued inorganic [17, 18] and polymeric [19] ferroelectrics and it is believed that the interaction between trapped charges and ferroelectric domains inhibits the reversal of these domains and therefore a much high electric field is required to reactivate these pinned domains [17].

Based on our experimental results and the work from the other literatures, we can give a reasonable deduction that the pinning of ferroelectric domains mainly occurs at the transient state of ferroelectric switching. At this transient state, one of the most important features in the film concerns the existence of a high number of ferroelectric domains and therefore domain walls/boundaries. Furthermore the time for the film lying at this transient state is voltage dependent. This time can be characterized by the switching time  $t_s$ . The decrease of the poling field from 200 MV/m to 33 MV/m will cause the increase of  $t_s$  from  $10^{-6}$  s to  $10^5$  s for P(VDF-TrFE) thin films [20, 21]. According to this deduction, we can use the model shown in Fig.7 to explain our experimental observations. To simplify the model, the injected space charges are shown in A and ignored in B to G, the dimensions of the ferroelectric domains in different polarization states are ignored, and except for specific emphasis the trapping of injected charges during the application of the high triangular voltage is also ignored, due to the much less time for the film lying at the transient state under the application of the high voltage, compared to the time

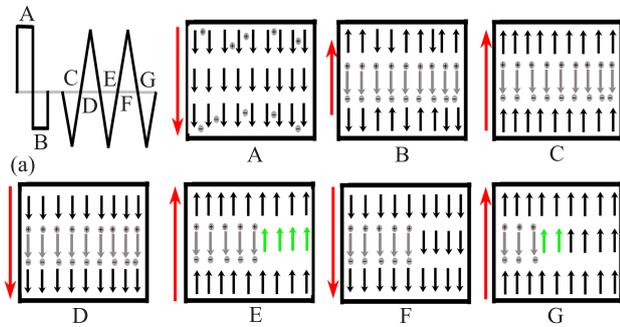


FIG. 7 A schematic diagram to explain the observed asymmetric switching dual peaks. (a) The waveform including A–G seven sections, which corresponded to A–G, respectively. The black arrows indicated the “free” ferroelectric domains; the grey ones indicated the pinned domains and the green ones indicated the de-pinned domains. The red arrows indicated the electric field vector. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.

when the voltage slightly below  $V_c$  is applied.

At section A, a prepoling pulse (96 V) is applied and all ferroelectric domains are oriented downwards. Some space charges are injected into the ferroelectric film, but they seldom interact with the ferroelectric domains at this stage.

At section B, a negative pulse with amplitude slightly below  $V_c$  is applied. Due to the long time for the film lying at the transient state of ferroelectric switching, the space charges injected during section A will be redistributed in the film and trapped at some boundaries of ferroelectric domains. The interaction between the trapped charges and the electrical dipoles makes some domains hard to be reversed and these domains are called pinned domains, indicated by the grey arrows in Fig.7. Thus those domains untrapped by charges are called free domains. In our model, the pinned domains still keep their original orientation downwards. Though the negative pulse is a little below  $V_c$ , the application of such a pulse for long enough time can still cause the reversal of part of the free domains, as is also indicated in Fig.7 section B.

At section C, it can be regarded as the continuation of the section B, though the triangular voltage has much higher amplitude. At this stage, all the free domains are directed upwards. However, due to the inhibition of the trapped charges, the pinned domains are not reversed and still keep their orientation.

At section D, the positive triangular voltage causes all free domains reversed downwards. Due to the same direction, this positive voltage shows no obvious influence on the pinned domains.

At section E, the negative voltage causes all free domains re-directed upwards. However, after the application of section C and section D, there will be a large number of injected charges existing in the ferroelectric

film. At this stage, though the time for the film lying at the transient state is still short, the injected charges have the opportunity to partly counteract the trapped charges, as causes the decrease of the trapped charges and therefore the possibility of re-orientating the pinned domains by a much high voltage. So the combined action of this counteraction effect and the higher voltage may cause the de-pinning of some previous pinned domains. These de-pinned domains are indicated by green arrows. These de-pinned domains also contribute to the switching current responses. However, due to the required high voltage, the voltage corresponding to the switching of the de-pinned domains should be high (the HV peaks). In fact, the observed increase of  $P_r$  in Fig.6 during the continuous application of the triangular voltage also implies the de-pinning of the previous pinned domains, as increases the number of the switchable domains and therefore  $P_r$ . Sections C–E can be used to explain the observation in Fig.3.

Sections F and G repeat the processes of sections D and E. With the continuous application of the recording voltage, more and more trapped charges are compensated and, as a result, seldom pinned domains exist in the film after a large enough number of cycles, as should be the reason that the switching dual peaks can be removed in Fig.5.

The obvious features in Fig.4 are that the HV peak gradually decreases in height and shifts to the higher voltage with increased  $t_n$ , while the LV peak gradually increases in height when  $t_n$  varies from 50 ms to 1 s and the further increase of  $t_n$  from 1 s to 10 s shows no obvious influence on the LV peak. This can also be explained according to our model. The increase of  $t_n$  can cause two results: one is the increased trapped charges and the other is the reversal of ferroelectric domains by the negative pulse below  $V_c$ . The increased trapped charges make it hard for pinned domains to be de-pinned, as results in the decrease and the shift of the HV peaks. The LV peaks are corresponding to the switching of free domains. From the work of Li [21], the switching time for an 800-nm thick P(VDF-TrFE) film is about 1 s at a field of  $\sim 40$  MV/m. So when  $t_n$  is shorter than 1 s, with the increase of  $t_n$ , more domains are switched, which contributes to the increased LV peaks; while when  $t_n$  is longer than 1 s, nearly all switchable domains have been switched and no influence of  $t_n$  on ferroelectric switching can be observed.

## V. CONCLUSION

In this work, we studied the observation of asymmetric switching dual peaks when the opposite poling field was just below the coercive field and these switching dual peaks could be removed by the continuous application of the switching voltage. This asymmetric ferroelectric switching resulted from the injection and the redistribution of space charges in the film.

## VI. ACKNOWLEDGMENTS

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