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High temperature-dependent imprint and switching mechanism of poly(vinylidene fluoride-trifluoroethylene) copolymer ultrathin films with electroactive interlayers

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The imprint and switching behaviors at high temperature have been systematically investigated through the study on the poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) films without and with *in-situ* synthesized poly(3,4-ethylene dioxothiophene)-poly(styrene sulfonic) acid, poly(vinyl phosphonic) acid (PVPA), and copper-phthalocyanine as interlayers. The lower imprint rate and the faster switching speed are observed for the sample with PVPA as interlayer even after 10^7 cycles at 60 °C. Combined with the results for the imprint and switching behaviors at room temperature, the temperature-dependent imprint and switching mechanisms for different electroactive interlayers in this system are proposed. Therefore, the optimum protocol could be designed for FeRAM based on P(VDF-TrFE) film, which would be in favor of the performance and the service life of the related ferroelectric devices even at high temperature. © 2015 AIP Publishing LLC.

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In recent years, poly(vinylidene fluoride)(PVDF) and its copolymers poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) have attracted a great deal of attention in many fields of application due to their good ferroelectricity and some unique features, e.g., low costs, high flexibility, ease of production, thermal and chemical stability, and low-voltage operation.^{1–5} Therefore, P(VDF-TrFE) copolymer is considered as one of the most promising candidates for possible low cost organic memory application based on structures like FeRAM (ferroelectric random access memory).^{6–8} Thus, lots of researches have been devoted into studying the ferroelectric behaviors of P(VDF-TrFE).^{9–14} However, it is observed that the hysteresis behaviors of ferroelectric thin films (<100 nm) exhibit a large decrease of polarization level and an increase of coercive field, causing failure of digital information stored in the devices.^{3,4,15,16} It is well known that one of the important degradation mechanisms in ferroelectrics is imprint, which would limit the lifetime of ferroelectric memory devices.^{5,17,18} Generally, imprint is the displacement of the polarization hysteresis curve along the electric field axis, and it is directly related to charged defects, trapped charges, and the other defect dipole complexes.^{2,4,5,19} In order to improve imprint effect, we are turning our attention to a sandwiched structure with conducting polymer as interlayers between the electrode and ferroelectric polymer. Our previous researches show that the “imprint” performance can be improved dramatically by this structure. These electroactive polymers can be chosen as interlayers, such as poly(3,4-ethylene dioxothiophene)(PEDOT),^{20,21} copper-phthalocyanine(CuPc),²² poly(styrene sulfonic) acid

(PSSH) and poly(vinyl phosphonic) acid (PVPA),²³ polyaniline (PANI),²⁰ and polypyrrole.¹⁵ Since many devices tend to require keeping long-term stability and reliability under various operating conditions, such as 60 °C, more insights are needed to understand the imprint mechanisms for high temperature. However, fewer researches have focused on the imprint behaviors for high-temperature. Thus, it is essential to investigate the imprint mechanisms at high temperature.

In this work, we address the imprint behaviors in ferroelectric P(VDF-TrFE) thin films with different interlayers for high temperature, such as *in-situ* synthesized PEDOT-PSSH, PVPA, and CuPc. In addition, the relationship between the switching time and voltage after imprint time, as well as the switching time as a function of the switching cycles at high temperature are studied. The lower imprint rate and the faster switching speed are observed for the sample with PVPA as interlayer even after 10^7 cycles at 60 °C. While it is observed that the CuPc sample has the largest imprint rate and the longest switching time in three types of interlayer materials. Finally, the possible mechanisms responsible for temperature-dependent imprint and switching are systemically discussed.

Two sets of ferroelectric samples were made: one was the P(VDF-TrFE) capacitor with Ti as bottom and top electrodes (set 1); and the other was the P(VDF-TrFE) film with electroactive material, CuPc, PVPA, and PEDOT-PSSH as interlayers (set 2). For the sample of set 1, the ultrathin films of P(VDF-TrFE) copolymer, with a mole ratio of VDF/TrFE 70/30, were deposited on Ti metallized silicon wafer, and then Ti was evaporated on the top. The film thicknesses of P(VDF-TrFE) and Ti layer are 60 nm and 90 nm, respectively, measured by Alpha-step 500 surface profiler. P(VDF-TrFE) copolymer was provided by Kunshan Hisense

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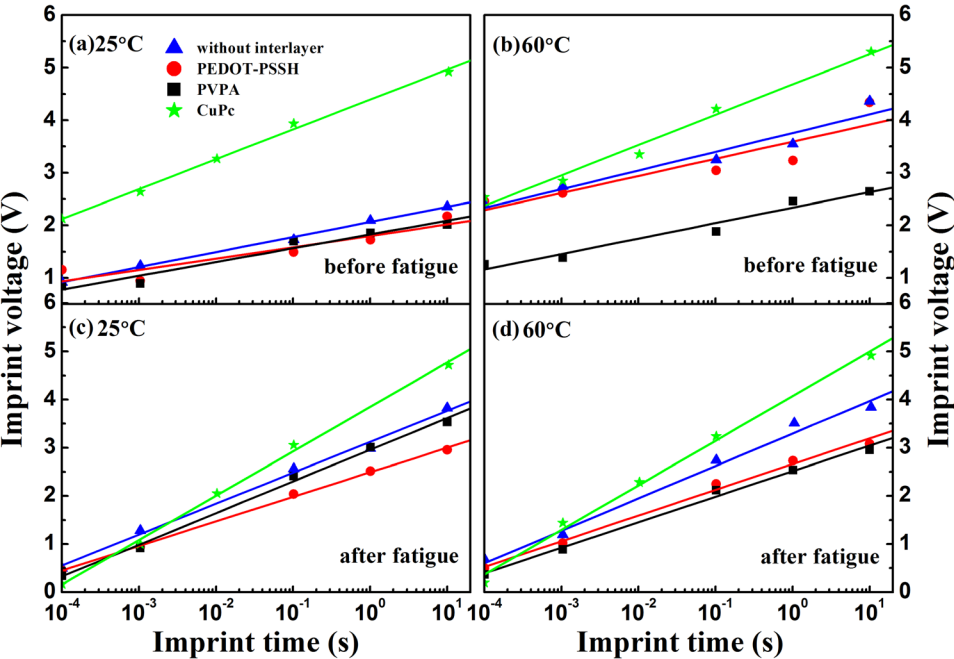


FIG. 1. Imprint voltage as a function of imprint time for P(VDF-TrFE) film with and without electroactive interlayers.

Electronic Co., Ltd. (Suzhou, China). In set 2, the sample with PEDOT-PSSH as interlayers was fabricated by the following procedure: EDOT and PSSH (1:0.3) were freshly mixed and dissolved in de-ionized water with concentration of 0.6%. The mixture of EDOT-PSSH water solution was spin coated onto the Ti metallized n-Si substrate with 50 nm thermally grown SiO₂. The wafer was then heated up to 150 °C for 30 min to remove water and air on the Si surface. After heating for 5 min on a hot plate, 2% H₂O₂ was spin coated on EDOT-PSSH film to polymerize EDOT into PEDOT. After P(VDF-TrFE) was coated, the spin coating and polymerizing process of PEDOT-PSSH were repeated to get interlayer on top of P(VDF-TrFE) film. The Ti electrode was evaporated and the thickness of Ti layer was 90 nm. All the samples were annealed at 130 °C for 1 h. The thicknesses of both bottom and top interlayers were 10 nm, measured by ellipsometer. The capacitors of PVPA and CuPc as interlayers were also fabricated by the same process and standard. PVPA was diluted from 30% to 0.6% with de-ionized (DI) water. For CuPc interlayer, the solid CuPc was dissolved in 0.1 N sodium hydroxide water solution and then was spin coated onto the Ti metallized n-Si substrate. The wafer was then treated with 2.0 N hydrochloride acid and washed with DI water.

The imprint and ferroelectric measurements were obtained on precision pro ferroelectric tester manufactured by Radiant Technologies. Three types of electroactive interlayers, including electron conductive poly(ethylene dioxythiophene)/poly(styrene sulfonate acid) (PEDOT-PSSH), proton conductive PVPA, and highly polarizable material copper-phthalocyanine (CuPc) were used for the comparative study. The samples were initially switched with bipolar positive-negative pulses. The last pulse set the sample to a known polarization state. Once poled, the samples were imprinted with open circuit for times ranging from 10⁻⁴ s to 10 s. The imprint effect and the switching time before and after fatigue behaviors were measured at 25 °C and 60 °C. Here, the imprint voltage is defined as the additional

potential required for the film to exhibit constant polarization switching characteristics. The switching time (τ) is determined from the peak position of the derivative $dP/d \log(t)$, where P is the polarization obtained from the ferroelectric switching experimental date.^{20,24}

The ferroelectric imprint behaviors are studied at 25 °C and 60 °C of Ti-electroded P(VDF-TrFE) films with and without interlayers, respectively, using the logarithmic time dependence of the imprint voltage method. The solid lines with different colors in Fig. 1 are the linear fitting results for the experimental imprint data. The slope of these solid lines represents imprint rate. The results of the imprint rate before and after fatigue at 25 and 60 °C extracted from Fig. 1 are summarized in Table I. Before fatigue, the results obtain from Figs. 1(a) and 1(b), from 25 to 60 °C, the imprint rate of the sample with CuPc as interlayer increases slightly, while the larger increase exists in the samples with PEDOT-PSSH and PVPA as interlayers, from 0.26 to 0.29 V/decade and from 0.22 to 0.33 V/decade, respectively. After fatigue, for the sample with CuPc as interlayer, the imprint rate is as high as 0.93 V/decade at 60 °C, which is close to the value of 25 °C. In addition, one can see that the ratio of the imprint rate at 60 °C and 25 °C is 1.05 and 1.06 for these samples without and with PEDOT-PSSH as interlayer. However, it is found that the imprint rate is down to a low level of 0.53 V/decade at 60 °C for the sample with PVPA as interlayer, and

TABLE I. The imprint rate for the samples with and without electroactive interlayers.

Parameter	Imprint rate (V/decade, before fatigue)		Imprint rate (V/decade, after fatigue)	
	25 °C	60 °C	25 °C	60 °C
Without interlayer	0.29	0.36	0.64	0.67
PEDOT-PSSH	0.22	0.33	0.51	0.54
PVPA	0.26	0.29	0.66	0.53
CuPc	0.57	0.58	0.92	0.93

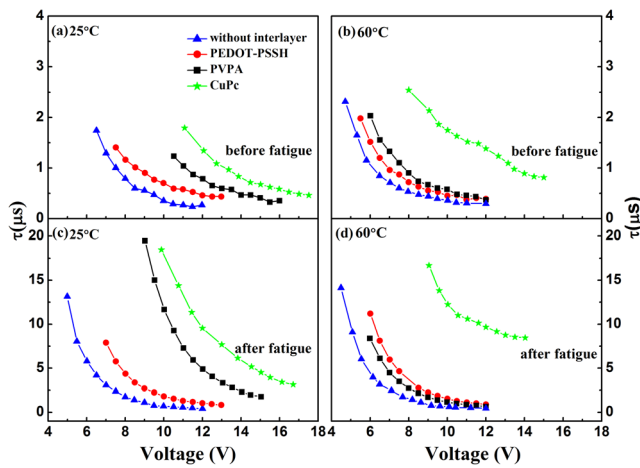


FIG. 2. The voltage dependencies of the switching speed after imprint (10 s) for ferroelectric P(VDF-TrFE) films without and with PEDOT-PSSH, PVPA, and CuPc as interlayers.

the ratio of the imprint rate at 60 °C and 25 °C is 0.80, which shows a better high temperature performance. Whereas, in both before and after fatigue measurements, the imprint rate is more influenced by the change of temperature for the samples without and with PEDOT-PSSH and PVPA as interlayers. This would be associated with the charge injection mechanism of electroactive interlayer so that the imprint effect is improved.^{5,20} Meanwhile, for the high dielectric material CuPc, it shows a good thermal stability and the imprint rate stays constant both at 60 °C and 25 °C.

In order to understand the temperature-dependent imprint mechanism, we turn our attention to the relationship between the voltage and the switching speed after imprint (10 s) at 25 and 60 °C for the P(VDF-TrFE) films without and with PEDOT-PSSH, PVPA, and CuPc as interlayers, as shown in Fig. 2, and the main parameters are listed in Table II. Here, the switching time (τ) is obtained from the PUND (the so-called positive up and negative down) measurements.²² One can see that τ is decreased rapidly with the increase of external voltage at first and then keep constant when external voltage reaches to a certain value at different temperatures. Before fatigue (BF), for the sample with PVPA as interlayer, the switching time (0.79 μ s at 25 °C) is about twice as long as that of the high temperature measurement (0.37 μ s at 60 °C) at a fixed voltage of 12 V. While the switching time of PEDOT-PSSH sample is decreased from 0.46 μ s at 25 °C to 0.39 μ s at 60 °C. However, the opposite trend is displayed for the samples without and with CuPc as interlayer, the ratio of the switching time at 25 °C and 60 °C is 0.9 (without) and 0.96 (CuPc). After 10×10^6 cycles of switching (as shown in Figs. 2(c) and 2(d)), the switching

TABLE II. The switching time of the samples with and without electroactive interlayers.

		Without interlayer	PEDOT-PSSH	PVPA	CuPc
Before fatigue	τ (μ s, 25 °C)	0.27	0.46	0.79	1.34
	τ (μ s, 60 °C)	0.30	0.39	0.37	1.39
After fatigue	τ (μ s, 25 °C)	0.42	1.04	4.90	9.54
	τ (μ s, 60 °C)	0.46	0.91	0.67	9.67

performance would degrade with switching cycles, but the imprint can be improved and the switching process can be activated effectively due to the temperature-dependent effect of electroactive interlayer. The switching time (1.04 μ s and 4.90 μ s for the samples with PEDOT-PSSH and PVPA as interlayers at 25 °C, respectively) is reduced simultaneously (0.91 μ s, 0.67 μ s at 60 °C). It is quite an interesting phenomenon since the switching speed of the PVPA sample is accelerated to the speed of the one before fatigue (0.79 μ s, BF, 25 °C) through the improvement of the imprint properties at a high temperature. When the conductive polymers are introduced as interlayers, the free charge available would partially overcome the degradation during cycles and effectively improve the performance of P(VDF-TrFE) thin film at high temperature. However, the switching time of CuPc sample is much higher than that of any other interlayer materials, which is consistent with the observation in Fig. 1. Hence, understanding the origin of this temperature-dependent observed above is of great significance in potential applications.

As described above, the three types of interlayer contribution to imprint behavior of P(VDF-TrFE) films at high temperature should be clarified. First, since PVPA is a proton conductor, the imprint behavior of the capacitor with PVPA as interlayer is improved dramatically at high-temperature. The temperature-dependent imprint effect in capacitors with proton conducting polymer as interlayer can be described by Arrhenius type temperature dependence

$$\mu \propto \exp\left(-\frac{E}{k_B T}\right),$$

where μ is the proton conductivity, E is the activation energy, k_B is the Boltzmann constant, and T is the absolute temperature. Indeed, on the condition of high temperature, more protons can be dissociated and the motion of protons is faster than the one at 25 °C. Moreover, another interesting characteristic, PVPA as a phosphonic acid, a strong hydrogen bonding network involving both P-OH and P=O as proton donor groups and proton acceptor can contribute to the hopping mechanism of the proton in PVPA. In case of the proton in PVPA dissociates with hopping mechanism, therefore, it shows better ferroelectric properties during the imprint measurement at 60 °C because the proton mobility would be quickened through the increasing thermal activation at high temperature. Second, for the films with PEDOT-PSSH as interlayers, it seems that the imprint effect is improved as the increasing temperature but PEDOT-PSSH can be used to compensate for the ferroelectric dipoles with the way of electron migration and shows a higher imprint rate than PVPA sample at higher temperature. The difference between the imprint properties with proton and electron types interlayer is due to the different types of the high temperature conductivity mechanisms and is discussed in the following. On one hand, the conductivity of PEDOT-PSSH is controlled by the mobility of charge carriers and the number of charge. With increasing temperature, the certain electrons can overcome the gap barrier in the polymer and be available for conduction due to the thermal energy at high temperature, resulting to the conductivity enhancement. On

the other hand, as a big π -conjugated polymer, the electronic band gap of conjugated polymers is normally large, and the conjugated π -electrons are not completely delocalized over the whole PEDOT-PSSH chain, so that the electron mobility is lower than proton. It means that the same temperature imprint process make the higher imprint rate for PEDOT-PSSH sample, where contributions from electroactive interlayer are slightly less than that of PVPA. At last, for the sample with CuPc as interlayers, the effect of a high dielectric permittivity interlayer material is negative for the imprint and switching behavior in (PVDF-TrFE) thin film capacitors, thus it leads to a higher imprint rate and a longer switching time but has less influence on temperature. This behavior can be attributed to the distribution in the energy of the long chain oligomer in CuPc molecules, as more time is required for dipole-dipole motions. It seems that the temperature-induced shift of the imprint rate is limited, and the high temperature conductive mechanism is almost identical with that at room temperature.

It is now well established that the imprint of P(VDF-TrFE) thin films with different types interlayers is associated with the mobility of the charge carriers in the device at high temperature. Since the imprint is closely dependent on the switching dynamics,⁴ it is necessary to understand the switching speed as a function of the switching cycles of P(VDF-TrFE) films with different types interlayers at high temperature, as shown in Fig. 3. All switching time is increased from 20 to 10^7 cycles, because the charges in electroactive interlayers would not benefit the switching speed but likely to improve the fatigue behavior when the polarization switching occurs. Thus, the CuPc capacitor shows the longest switching time at 25 and 60 °C during the whole process for their higher energy of dipole motions. Before 4×10^5 cycles, the switching time, of the samples with the PVPA and PEDOT-PSSH as interlayers, remains constant at

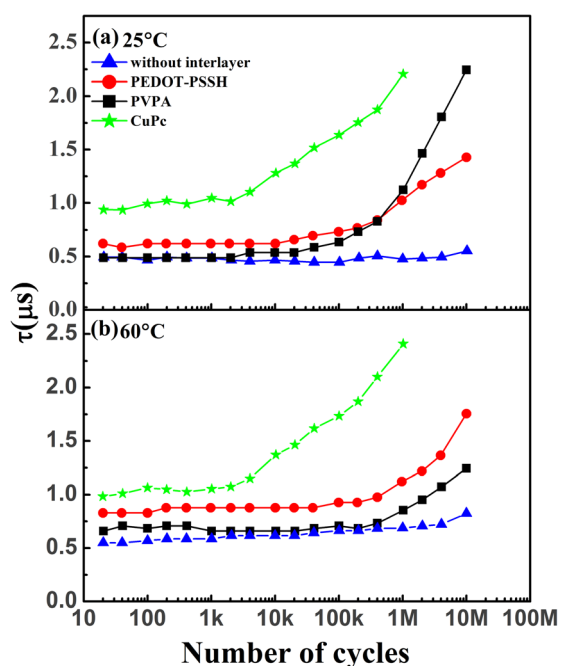


FIG. 3. Switching time as a function of the number of switching cycles of P(VDF-TrFE) films with different kinds of interlayer at 25 °C and 60 °C.

25 °C and 60 °C, respectively. Moreover, one can see that the switching speed of the sample with PVPA as interlayers is obviously quicker than that of PEDOT-PSSH at 60 °C. However, after 4×10^5 cycles of switching, for the PVPA sample at 25 °C, the switching time increases dramatically and is beyond the PEDOT-PSSH, but the opposite phenomenon occurs at 60 °C. The switching speed is decided by the competition between certain switching protocol and the movement energy of charges in electroactive interlayers.⁵ Therefore, under the switching cycles, the switching speed is decreased but the effect of proton conductivity at high temperature makes the actual switching speed increased and plays a positive role. This is the reason of the appearance of the temperature-dependent imprint (Fig. 2).

In summary, the effect of the electroactive interlayers on the imprint and switching behaviors at high temperature has been systematically investigated through the study on P(VDF-TrFE) films without and with PEDOT-PSSH, PVPA and CuPc as interlayers. According to experimental results, we address the key factor in temperature-dependent imprint and switching behaviors for P(VDF-TrFE) copolymer film with electroactive interlayers, namely, electron injection for PEDOT-PSSH, proton hopping for PVPA, and dipole-dipole interaction for CuPc. It is found that the sample with PVPA as interlayer exhibits lower imprint rate and the enhancement of imprint and switching behaviors even after 10^7 cycles at high temperature. Combined with the results of the imprint and switching behaviors at room temperature, the temperature-dependent imprint mechanisms for different electroactive interlayers in this system are proposed. Therefore, the optimum protocol could be designed for FeRAM based on P(VDF-TrFE) film, which would be in favor of the performance and the service life of the related ferroelectric devices even at high temperature.

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