Influence of Poly(methyl metacrylate) Addition on Resistive Switching Performance of P3HT/P(VDF-TrFE) Blend Films

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Organic semiconducting/ferroelectric blend films attracted much attention due to their electrical bistability and rectification properties and thereof the potential in resistive memory devices. Blend films were usually deposited from solution, during which phase separation occurred, resulting in discrete semiconducting phase whose electrical property was modulated by surrounding ferroelectric phase. However, phase separation resulted in rough surface and thus large leakage current. To further improve electrical properties of such blend films, poly(methyl metacrylate) (PMMA) was introduced as additive into P3HT/P(VDF-TrFE) semiconducting/ferroelectric blend films in this work. It indicated that small amount of PMMA addition could effectively enhance the electrical stability to both large electrical stress and electrical fatigue and further improve retention performance. Overmuch PMMA addition tended to result in the loss of resistive switching property. A model on the configuration of three components was also put forward to well understand our experimental observations.

Key words: Resistive switching, Ferroelectric/semiconducting blend film, Spin coating, Phase separation

I. INTRODUCTION

Resistive random-access memory (RRAM), often referred to as a memristor [1], has attracted much attention due to its advantages of high storage density, nonvolatility, and ease of production. RRAM memory is expected to be constructed by cross-bar array, which usually results in cross-talk problem. The common solution is to integrate resistive elements with transistors or diodes [2], which surely complicates the production of RRAM. Resistive characteristic of organic semiconducting/ferroelectric composites was first reported in 2008 [3] in P3HT/P(VDF-TrFE) binary blend films, in which spinodal decomposition induced phase separation, resulting in discrete poly(3-hexylthiophene) (P3HT) phase surrounded by the continuous ferroelectric phase of P(VDF-TrFE), the copolymer of vinylidene fluoride and trifluoroethylene. The resistive property of semiconducting phase was controlled by the polarization state of ferroelectric phase. Thus resistive switching characteristic was realized in such semiconducting/ferroelectric blend films. Semiconducting/ferroelectric blend films well solved the cross-talk problem. Soon several kinds of semiconducting/ferroelectric resistive films were developed based on various semiconducting materials, such as PFO (poly(9,9-dioctylfluorenyl-2,7-diyl)) [4], F8BT (poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thia-diazol-4,8-diyl)]) [5], and PCBM ([6,6]-phenyl-C61-butyric acid methyl ester) [6].

However, phase separation also resulted in an extremely rough surface. As a consequence, the high roughness induced large leakage current and thus led to low fabrication yield of such resistive devices. Since organic semiconductors and ferroelectric polymers obeyed upper critical solution temperature behavior. This implied that it could be possible to get both phases miscible by increasing the process temperature. Based on this understanding, it was expected to get smoother surface roughness. Li et al. deposited P(VDF-TrFE) and PFO phase separated films by wire-bar coating technique at 50 °C and got obviously improved film roughness [4]. In our previous work, we developed temperature-controlled spin coating to deposit P3HT and P(VDF-TrFE) blend films at relatively high environmental temperature and also got well improved fabrication yield of such resistive devices [7].

To further improve electrical characteristics of such blend films, we tried to introduce another component as additive into P3HT/P(VDF-TrFE) to form three-component blend films. Amorphous poly(methyl metacrylate) (PMMA) was one of promising candidates. Structures and morphologies of PMMA/P(VDF-TrFE) blend films showed significant modification compared to those of P(VDF-TrFE) alone. PMMA addition effectively enhanced the electrical stability and further improved retention performance. Overmuch PMMA addition tended to lose the resistive switching property. A model on the configuration of three components was also put forward to well understand our experimental observations.

Key words: Resistive switching, Ferroelectric/semiconducting blend film, Spin coating, Phase separation

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TrFE) blends are greatly dependent on PMMA content. PMMA and P(VDF-TrFE) are miscible with PMMA volume content less than 15% [8–11]. When PMMA content is between 15% and 30%, the formation of blends with relatively smooth film morphology is still possible, however phase separation in both amorphous and crystalline regions becomes more probable [10]. Phase separation occurs when PMMA content is larger than 30%, resulting in a rough surface topology [10, 11]. Due to the miscibility of P(VDF-TrFE) and PMMA, small amount of PMMA addition into P(VDF-TrFE) could effectively improve interfacial adhesion, retention and electrical fatigue of ferroelectric polymer films [8, 12, 13]. Furthermore, work on PMMA/P3HT blend films indicated that vertical phase separation occurred and thus resulted in layer separated structure with PMMA layer lying underneath P3HT layer [14–16]. The occurrence of such vertical phase separation was expected to improve the electrical breakdown property of the P3HT phase. Therefore, here PMMA was introduced into P3HT/P(VDF-TrFE) to form three-component blend films, of which the structural and electrical characteristics were measured to determine the influence of PMMA addition.

II. EXPERIMENTS

Ferroelectric polymer P(VDF-TrFE) (VDF/TrFE molar ratio of 70:30) were purchased from Kunshan Hisense Electronic Co. and organic semiconductor P3HT and PMMA were from Sigma-Aldrich. All materials were used as received. P3HT and P(VDF-TrFE) were co-dissolved in tetrahydrofuran (THF) to form 4.0% by weight solution. Weight ratio of P(VDF-TrFE) to P3HT was fixed at 10:1. Then PMMA was added into such solution to form three-component blend solution. The amount of PMMA addition varied in order to determine its influence on structural and electrical characteristics of such three-component blend films. Temperature-controlled spin coating was conducted in a nitrogen-filled glove box. Commercial spin coater was modified so that the spin stage was enclosed in an environmental temperature controlled chamber. The blend solution was spin coated at 700 r/min onto the glass substrates under controlled environmental temperature of 50 °C. More detail on such a temperature-controlled spin coating could refer to Ref.[7]. To increase the crystallinity of ferroelectric phase, the as-cast blend films were further annealed at 135 °C for 5 h in this nitrogen-filled glove box. The averaged film thickness was about 380 nm, which was determined by AFM (Ultraobjective, Bruker). Film structure was characterized by SEM (XL30FEG, PHILIPS), XRD (X-ray Diffraction, D8, Bruker-AXS, Germany), and AFM. As for samples used for current-voltage (I-V) measurements, 0.2 mm wide and 50 nm thick Ag stripes were thermally deposited via hard mask onto glass substrates, then PMMA/P3HT/P(VDF-TrFE) blend films were spin coated from THF solution onto Ag bottom electrodes at 50 °C and then annealed at 135 °C for 5 h. Finally 50 nm thick top Ag stripes were deposited onto the top surface of blend film forming an effective electrode area of 0.04 mm². I-V measurements were performed in a N₂-filled glove box by a Keithley 6487 sourcemeter.

III. RESULTS AND DISCUSSION

To show the influence of PMMA addition on the structures and topologies of the blend films, AFM measurements were conducted. The results indicate that, with the increase of PMMA content, the RMS (root mean square) roughness of film surfaces gradually decreases. The typical morphologies of the PMMA/P3HT/P(VDF-TrFE) blend films are shown in Fig.1, where PMMA:P3HT:P(VDF-TrFE) weight ratio varied from 0:1:10 (Fig.1(a)) through 0.2:1:10 (Fig.1(b)) to 0.5:1:10 (Fig.1(c)). The surface of P3HT/P(VDF-TrFE) film without PMMA addition is covered by some clusters, which results in large roughness (Fig.1(a)); while, with the increase of PMMA content, the number of these clusters gradually decreases with improved surface roughness (Fig.1 (b) and (c)). RMS roughness of these blend films reduces from 14.04 nm (0:1:10) to 12.41 nm (0.2:1:10) to 9.64 nm (0.5:1:10). For all these as-coated blend films, we cannot distinguish all three phases from each other by AFM measurements.

To improve the degree of crystallinity in ferroelectric phase, blend films were required to be annealed between the Curie and melting temperatures of ferroelectric phase. AFM, SEM, and XRD were used to determine the influence of annealing treatment on structure and crystalline phases in blend films. Figure 2 (a) and (b) show the typical micro-structure of 0.2:1:10 PMMA/P3HT/P(VDF-TrFE) blend film, imaged by AFM and SEM, respectively. Film surface is covered with needle-like crystallite grains which are characteristic structure of ferroelectric phase. In the AFM image (Fig.2(a)), quasi-circular holes are discretely distributed on the whole surface, which may be attributed to the P3HT phase and/or large structural undulation of rough P(VDF-TrFE) surface. That is, according to AFM image, it is a little difficult or arbitrary to well distinguish both P3HT and P(VDF-TrFE) phases. However, from the SEM image in Fig.2(b), circular disc-like domains are also visualized which are discretely embedded in ferroelectric needle-like domains. These disc-like domains are attributed to semiconducting P3HT phase [3, 7]. Some of these P3HT domains are indicated by red arrows in Fig.2(b). PMMA phase cannot be distinguished from P3HT and P(VDF-TrFE) phases in both AFM and SEM measurements, which may be due to its small content and also due to its structural configuration with other phases. Figure 3(a)
FIG. 1 AFM images of as-coated PMMA/P3HT/P(VDF-TrFE) blend films with various PMMA:P3HT:P(VDF-TrFE) weight ratio of (a) 0:1:10, (b) 0.2:1:10 and (c) 0.5:1:10. Scan sizes for all three images were 10 μm x 10 μm.

shows the XRD spectra of blend films with various PMMA contents. Note that during XRD measurements, we did not observe any characteristic peaks of P3HT phases, probably due to their much lower weight ratio in the whole blend films and/or low crystallinity even after annealing treatment. Characteristic peak at 2θ≈20.1° comes from the superimposition of (200) and (110) reflections indicating the existence of crystalline β-polar phase of P(VDF-TrFE). Note that the XRD spectrum from 0.2:1:10 PMMA/P3HT/P(VDF-TrFE) blend film almost superimposes with that from the 0.5:1:10 PMMA/P3HT/P(VDF-TrFE) film. The XRD spectrum of 5:1:10 PMMA/P3HT/P(VDF-TrFE) film shows no observable crystalline peak indicating that P(VDF-TrFE) phase is hard to crystallize. Also, we can observe the continuous widening of the crystalline peak with increased PMMA content, which should be due to a reduction of crystallite sizes and the dilution of P(VDF-TrFE) content by PMMA addition. Currently it seems difficult to judge which one makes the major contribution. Most interesting is that, when PMMA content is less than 0.5:1:10, the intensity of the crystalline peak increases with increased PMMA content. This result implies an increase of the β-polar phase with the increase of PMMA content due to PMMA-induced crystallization. In fact, in the study of PMMA/PVDF composite films, Niu et al. also observed the continuously increased intensity of the crystalline peak until the PMMA content reached up to 30% [17]. However, overmuch PMMA addition, for example 5:1:10 of PMMA:P3HT:P(VDF-TrFE) in Fig.3(a), inversely inhibits the crystallization of ferroelectric phase due to the miscibility of PMMA and P(VDF-TrFE). Figure 3(b) shows the current leakage property for different PMMA addition. During the current-voltage (I-V) measurements of these annealed blend films, the voltage was swept from −5 V to 5 V, much lower than...
the coercive voltage of ferroelectric phase, and the consequent current was recorded. Obviously, with the increase of PMMA content, leakage current decreases from $5.9 \times 10^{-7}$ A to $2.1 \times 10^{-8}$ A at 5 V, corresponding to PMMA content from 0:1:10 to 1:1:10. Improved leakage current property is expected for the improvement of retention performance of such resistive memory devices.

Next, resistive switching performance was determined for these blend films with various PMMA contents. Typical results are shown in Fig.4 to indicate the evolution of resistive switching with PMMA addition. Before $I$-$V$ measurements, all blend films were first poled negative by a voltage of $-40$ V for 10 s and then $I$-$V$ measurements were performed by applying first positive sweeping voltages and then negative ones. Electrical fatigue measurements were also conducted on PMMA/P3HT/P(VDF-TrFE) blend films. Bipolar rectangular pulses with amplitude of 100 V and period of 0.1 s were applied to repeatedly switch the electrical property of such blend films between ON and OFF states. At pre-set fatigue cycles, rectangular fatigue pulse was removed and the resistive switching performance was recorded by applying sweeping voltage between $\pm 100$ V and then recording the resulting current.

Note that resistive switching mechanism of ferroelectric/semiconductor blend films have been well studied experimentally and theoretically [3, 18, 19]. In such blend films, current can only flow through the semiconducting phase, while ferroelectric phase is insulating. Resistive switching is attributed to the result from modulation of the charge injection barrier at the semiconductor-electrode interfaces. To build up an injection barrier between the electrode and semiconducting phase, here Ag electrode is intentionally selected, resulting in an injection barrier of the order of 0.6–0.7 eV [3]. Charge transport is injection limited due to this large injection barrier, and the consequent device current is low. When the ferroelectric phase is polarized to the right direction which efficiently decreases the injection barrier at the Ag/P3HT interfaces, charge transport is switched to space charge limited mode and higher device current is expected. However, when the ferroelectric is polarized to the opposite direction, the injection barrier remains constant or even slightly increases [3, 19], resulting in still low current. Thus butterfly loop is always expected for such a bistable resistive switching mechanism. When the voltage is swept along one direction, for example from $-100$ V to $100$ V shown in Fig.4(b), charge transport is switched from space charge limited in negative voltage range to injection limited mode in positive voltage range and the corresponding $I$-$V$ curve is asymmetric about zero voltage showing a diode property.

P3HT/P(VDF-TrFE) blend film without PMMA addition shows bad endurance to electrical stress (Fig.4(a)). When sweeping voltage is applied between $\pm 40$ V, $I$-$V$ curve shows obvious butterfly-shape hysteresis loop indicating good resistive switching performance (Fig.4(a)). However, if the sweeping voltage is further increased, for example, to $\pm 60$ V, electrical performance of such blend films gets unstable. For the first sweeping cycle (the red curve labeled as 60 V,1st in Fig.4(a)), the right wing of the butterfly loop still shows good resistive switching, while when the voltage starts the sweeping of the negative half cycle, though we finally get the left wing of the butterfly loop, the recorded data points get a little disordered resulting in uneven curve. Furthermore, after several cycles of the application of $\pm 60$ V voltage, for example the tenth cycle labeled as 60 V,10th in Fig.4(a), blend film is totally electrically broken down. In fact, in our measurements, even we swept $\pm 40$ V voltage for tens or hundreds of cycles, the blend films can also be broken down due to the continuous application of electrical stress (the data are not shown here).

When small amount of PMMA is added to form blend film with PMMA:P3HT:P(VDF-TrFE) weight ratio of 0.2:1:10, improved electrical performance is observed, as shown in Fig.4(b). As for such a blend film, even sweeping voltage is applied between $\pm 100$ V, stable resistive switching can still be observed (black curve in Fig.4(b). The current ON/OFF ratio at 12 V is about 33.2, similar to that of 31.3 obtained from P3HT/P(VDF-TrFE) blend film (Fig.4(a)), indicating that small amount of
PMMA addition does not degrade resistive switching performance. Such blend film also shows well improved endurance to electrical fatigue. Even after $10^6$ cycles of repeated switching between ON and OFF states by rectangular fatigue pulses with amplitude of 100 V and period of 0.1 s, stable butterfly-shape hysteresis loop can still be observed, though the ON/OFF ratio reduces to 15.3. The decrease of ON/OFF ratio may be due to polarization fatigue in ferroelectric phase. Polarization fatigue is the reduction in switchable polarization of ferroelectric films due to repeated electrical stress. The degradation of switchable polarization weakens its control on electrical property in semiconducting phase, resulting in decreased ON/OFF ratio. More details on polarization fatigue of ferroelectrics can refer to Ref.[20].

However, with further increase of PMMA content in such three-component films, resistive switching performance gets limited, as shown in Fig.4(c). The $I$-$V$ results were obtained from 0.5:1:10 PMMA/P3HT/P(VDF-TrFE) blend film. As for such a blend film with overmuch PMMA addition, slim butterfly-shape $I$-$V$ loops can be observed even at voltage sweeping between ±100 V, however, the ON/OFF ratio is only about 2.2 at 12 V. The film displays good endurance to repeated electrical switching. After $3\times10^5$ fatigue cycles, we can still observe the slim butterfly loop. The degraded ON/OFF ratio should be due to the layer separation between PMMA and P3HT phases, as will be discussed below.

Retention performance was also characterized for such blend films. Since in Fig.4 we have determined that overmuch PMMA addition could result in degraded resistive switching performance, here we only conducted retention measurements of blend films without PMMA addition and blend films with small PMMA content. Before retention measurements, a DC voltage of +40 V (−40 V) was applied for 10 s to drive the blend films into ON (OFF) state, and then retention property was measured at 6 V. Typical results are shown in Fig.5. As for P3HT/P(VDF-TrFE) blend film without PMMA addition, during the whole retention measurement of $10^3$ s, the ON-state current slightly decreases from 8.4 μA to 6.8 μA, while the OFF-state current degrades from 0.24 μA to 0.33 μA (Fig.5(a)), resulting in degraded ON/OFF ratio from 35 to 21 (Fig.5(b)). While, as for 0.2:1:10 PMMA/P3HT/P(VDF-TrFE) film, during the whole measurement of $4\times10^3$ s, the ON-state current nearly keeps constant and the OFF-state current degraded from 0.053 μA to 0.065 μA, resulting in a slightly decrease of ON/OFF ratio from 36.6 to 29.6. Both blend films show good retention performance. However, from Fig.5(b), 0.2:1:10 PMMA/P3HT/P(VDF-TrFE) film presents slower degradation of ON/OFF ratio than P3HT/P(VDF-TrFE) film, which implies that appropriate addition of PMMA can effectively improve retention performance of semiconducting/ferroelectric blend system. This improvement may be due to reduced leakage current after PMMA addition, as is determined in

![Graph](image-url)
The PMMA-addition-induced decrease of leakage current, as shown in Fig.3(b), can be attributed to two factors. First, as for phase III, PMMA addition effectively improves surface roughness and thus decreases leakage current, as have been approved in some work on PMMA/P(VDF-TrFE) blend films [8, 12, 13]. Second, PMMA-rich phase II is an insulating layer, which effectively limits the current from semiconducting P3HT-rich phase I.

In Fig.4, proper PMMA addition improved endurance to both high sweeping voltage and electrical fatigue (Fig.4(b)). In our model, small amount of PMMA deposits underneath P3HT layer resulting in layer phase separation. The existence of this insulating PMMA layer decreases the current flowing through P3HT-rich and PMMA-rich phases and thus reduces the possibility of electrical breakdown of P3HT-rich phase. Furthermore, note that the mechanism of resistive switching in semiconducting/ferroelectric blend films is ferroelectric polarization modulation of electrical property in semiconducting phase. Thus polarization fatigue of ferroelectric phase is one key factor to directly influence electrical fatigue characteristics in semiconducting/ferroelectric blend films. Experimental observation has proved that proper addition of PMMA into P(VDF-TrFE) can effectively improve the endurance to polarization fatigue of ferroelectric polymer films [12, 13]. Thus here PMMA addition into P3HT/P(VDF-TrFE) blend films improves the endurance to polarization fatigue in P(VDF-TrFE)-PMMA phase and consequently results in improved endurance to electrical fatigue of the whole blend films.

In Fig.4, overmuch PMMA addition tends to result in the loss of resistive switching characteristic in, for example, 0.5:1:10 PMMA/P3HT/P(VDF-TrFE) blend films. This should be attributed to the increase of layer thickness of PMMA-rich phase II. In our model, though most of PMMA is mixed with P(VDF-TrFE) to form phase III, there is still small amount of PMMA which forms phase II underneath P3HT-rich layer. The thickness of this PMMA layer is expected to influence the resistive switching property. The resistive characteristic of the whole blend films should be understood according to the series connection of both resistors: one is a variable resistor composed of P3HT-rich layer (phase I), the resistive characteristic of which is modulated by ferroelectric polarization, while the other is a constant resistor composed of PMMA layer (phase II). Here we neglect the contribution of the resistance of P(VDF-TrFE)-PMMA phase on the resistance of the whole blend films. When small amount of PMMA is added into P3HT/P(VDF-TrFE) films, for example PMMA:P3HT:P(VDF-TrFe) weight ratio of 0.2:1:10 in Fig.5(b), the thickness of phase II is expected to be so thin that PMMA layer shows much low resistance. Thus the series resistance is mainly determined by the resistance of P3HT layer. In this case, resistive switching characteristic is expected. With further increase of PMMA content, the thickness of phase II increases resulting in large resistance. In this case, the resistance from PMMA layer tends to weaken the resistive switching characteristic from P3HT layer, resulting in slim I-V hysteresis (Fig.4(c)).

In Fig.5, we observed improved retention property of logic resistive states due to PMMA addition. We know that resistive switching in such blend films is modulated by ferroelectric polarization in ferroelectric phase. Thus polarization retention is a key factor to determine the retention property of resistive states in semiconducting/ferroelectric blend films. It is well accepted that current leakage can greatly degrade polarization retention in ferroelectric films [21]. Since PMMA addition effectively decreases leakage current (Fig.3(b)), improved polarization retention in PMMA/P(VDF-TrFE) phase is expected [8, 12]. In fact, this improvement was also experimentally determined in ferroelectric-insulator-semiconductor capacitors [13]. Improved polarization retention results in improved retention of ON and OFF states in PMMA/P3HT/P(VDF-TrFE) blend films, as shown in Fig.5.

IV. CONCLUSION

We introduced PMMA into P3HT/P(VDF-TrFe) blend films in order to improve electrical performance of such blend films. Experimental measurements indicated that proper PMMA addition, such as weight ratio of 0.2:1:10 for PMMA:P3HT:P(VDF-TrFe), can effectively improve retention performance and also enhance the endurance of the blend films to electrical breakdown and electrical fatigue. However, overmuch PMMA addition tends to inhibit resistive switching property. Based on our structural and electrical observations of these blend films, we put forward a model trying to understand the configuration of three components in the whole blend films.
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