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Fabrication of Electrically Bistable Organic Semiconducting/Ferroelectric Blend Films by Temperature Controlled Spin Coating

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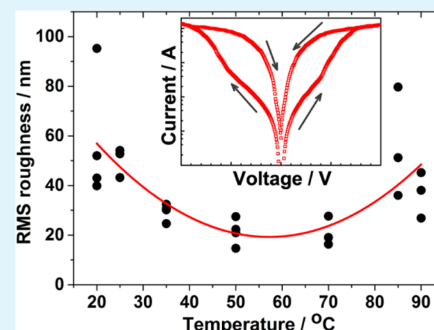
ABSTRACT: Organic semiconducting/ferroelectric blend films attracted much attention due to their electrical bistability and rectification properties and thereof the potential in resistive memory devices. During film deposition from the blend solution, spinodal decomposition induced phase separation, resulting in discrete semiconducting phase whose electrical property could be modulated by the continuous ferroelectric phase. However, blend films processed by common spin coating method showed extremely rough surfaces, even comparable to the film thickness, which caused large electrical leakage and thus compromised the resistive switching performance. To improve film roughness and thus increase the productivity of these resistive devices, we developed temperature controlled spin coating technique to carefully adjust the phase separation process. Here we reported our experimental results from the blend films of ferroelectric poly-(vinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) and semiconducting poly(3-hexylthiophene) (P3HT). We conducted a series of experiments at various deposition temperatures ranging from 20 to 90 °C. The resulting films were characterized by AFM, SEM, and VPFM to determine their structure and roughness. Film roughness first decreased and then increased with the increase of deposition temperature. Electrical performance was also characterized and obviously improved insulating property was obtained from the films deposited between 50 and 70 °C. By temperature control during film deposition, it is convenient to efficiently fabricate ferroelectric/semiconducting blend films with good electrical bistability.



KEYWORDS: *resistive switching, ferroelectric/semiconducting blend films, spin coating, phase separation*

INTRODUCTION

Resistive random-access memory (RRAM) is a type of nonvolatile random-access memory that works by changing the resistance across a dielectric solid-state material often referred to as a memristor.[1] RRAM has attracted much attention due to its various advantages such as high storage density, nonvolatility, and ease of production. The ultimate memory structure is simple where the storage medium is sandwiched between rows and columns of metal electrode lines, which forms a cross-bar array. The big obstacle of the realization of true cross-bar array is the existence of cross talk. To avoid this, it requires electrical isolation of the discrete cells. The common solution is to integrate resistive memory elements with transistors[2] or diodes,[3] which will surely lead to the complex of production of RRAM.

The development of organic semiconducting/ferroelectric blend films can well solve this problem of cross talk.[4] During the deposition of organic semiconductor and ferroelectric polymer P(VDF-TrFE), the copolymer of vinylidene fluoride and trifluoroethylene, from the blend solution, phase separation occurs due to spinodal decomposition, resulting in a discrete semiconducting phase embedded in a continuous ferroelectric phase. The semiconducting phase penetrates the whole films forming conducting paths whose electrical performance can be modulated by the polarization of the surrounding ferroelectric phase. Furthermore, by careful selection of the top and bottom electrodes and the modification of interfaces between electrode and blend films, it is possible to get polarization-tuned rectifying property which well solves the cross talk problem.[5] Organic semiconducting/ferroelectric blend films make it possible to fabricate cross-talk-free resistive memories with simple process. However, during the common spin coating process, spinodal-decomposition-induced phase separation also results in an extremely rough surface, even comparable to the film thickness. As a consequence, the high roughness of the blend film results in large electrical leakage and thus compromises the resistive switching performance which leads to the low fabrication yield of such resistive devices.[6] Because organic semiconductors and ferroelectric polymers seem to obey upper critical solution temperature (UCST) behavior, which means that with the increase of process temperature, both phases gradually get miscible. It is expected to improve film roughness by increasing deposition temperature, although to some extent, the phase separation would be weakened. On the basis of such a consideration, Li et al. developed wire-bar coating technique to deposit P(VDF-TrFE) and poly(9,9-

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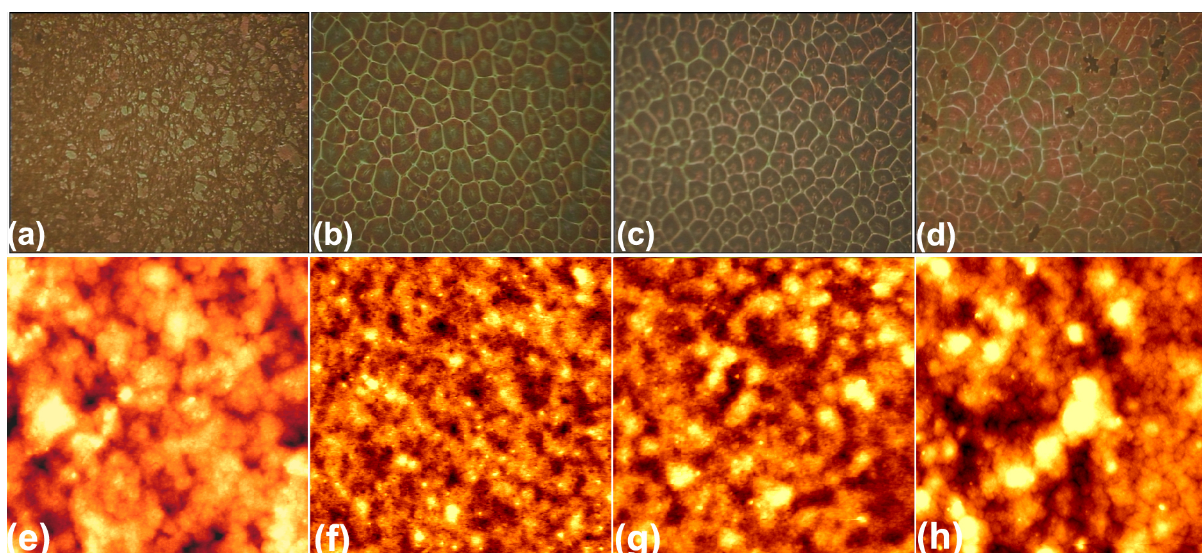

Figure 1. (a−d) Optical and (e−h) AFM images of P3HT/P(VDF-TrFE) blend films spin coated at environmental temperatures of (a,e) 20, (b,f) 50, (c,g) 70, and (d,h) 90 °C, respectively. The area for all optical images was 0.33 × 0.25 mm^2, while all AFM images were scanned in 20 × 20 μm^2.

dioctylfl uorenyl-2,7-diyl) (PFO) phase separated films at relatively high temperature, such as 50 °C, and get obviously improved film roughness.[6] However, wire-bar coating is not a usual technique for organic thin film preparation and spin coating technique is preferred in current industries.[7] To develop a spin coating method to deposit blend films at controlled temperature is highly expected. Here we report our work on the fabrication of phase separated P(VDF-TrFE) and poly(3-hexylthiophene) (P3HT) blend films by modified and temperature controlled spin coating technique. The films spin coated under various temperatures were characterized by optical (OM), scanning electron (SEM), and atomic force (AFM) microscopes, and their electrical performance was determined by current−voltage measurements. Our experimental observations indicated that P3HT/P(VDF-TrFE) blend films spin coated at 50−70 °C show improved film roughness and leakage current and thus resistive performance.

■ RESULTS AND DISCUSSION

Optical and AFM images of the as-coated P(VDF-TrFE)/P3HT blend films are shown in Figure 1a−h, where blend films were deposited under environmental temperatures of 20, 50, 70, and 90 °C, respectively. Blend film coated at lower temperature, such as 20 °C, shows a much disordered surface (Figure 1a), and the corresponding AFM image (Figure 1e) indicates an extremely coarse surface with root-mean-square (rms) roughness R_{rms} as large as 39.97 nm. The difference in height between the highest and lowest points in the whole AFM image, defined as R_{max}, is about 243 nm, which is comparable to the film thickness and tends to result in large current leakage and device failure thereof. With the increase of deposition temperature, both ferroelectric and semiconducting phases gradually get miscible and hence form films with improved roughness, as can be proved from both OM and AFM results of the blend films coated at 50 and 70 °C. Both OM images of Figure 1b,c show more organized structure with patterns like tortoise shells. AFM results of Figure 1f,g show further improved film roughness with R_{rms} of 14.7 and 16.3 nm for films deposited at 50 and 70 °C, respectively. R_{max} values also greatly decrease from 243 to 104.3 nm for the 50 °C deposited one and 92.6 nm for the 70 °C deposited one. However, with further increase of deposition temperature, such as 90 °C, too fast evaporation of organic solvent tends to cause rough surfaces again during the formation of blend films, which counteracts the contribution of improved miscibility to film roughness. Furthermore, at such high temperature, the phase separation may be greatly inhibited, resulting in the loss of conducting paths. The OM image in Figure 1d is obtained from blend film deposited at 90 °C, which also shows kind of tortoise-shell-like patterns but with some "dirty" points. The corresponding AFM image in Figure 1h shows some large clusters resulting in increased film roughness. The R_{rms} and R_{max} of such a 90 °C deposited film are 38.06 and 263 nm, respectively.

We also comprehensively analyzed film roughness deposited at various temperatures, and the results are shown in Figure 2,

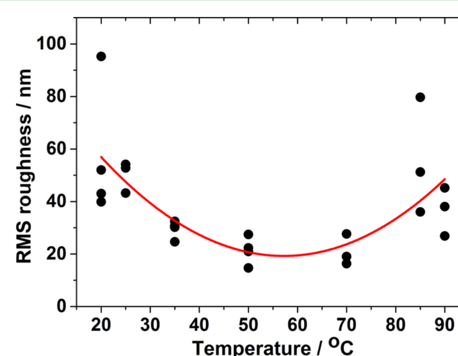

Figure 2. RMS roughness analyses of blend films deposited at various environmental temperatures. At each temperature, at least three samples were prepared and then images by an AFM in an area of 20 × 20 μm^2 for roughness analyses. Red line is used to guide eyes.

where for each deposition temperature, at least three blend films were spin coated and the corresponding surface roughness was determined by imaging an area of 20 × 20 μm^2 by an AFM and then calculating its RMS roughness. Statistically, film roughness shows obvious temperature dependence. With the increase of deposition temperature, RMS roughness first

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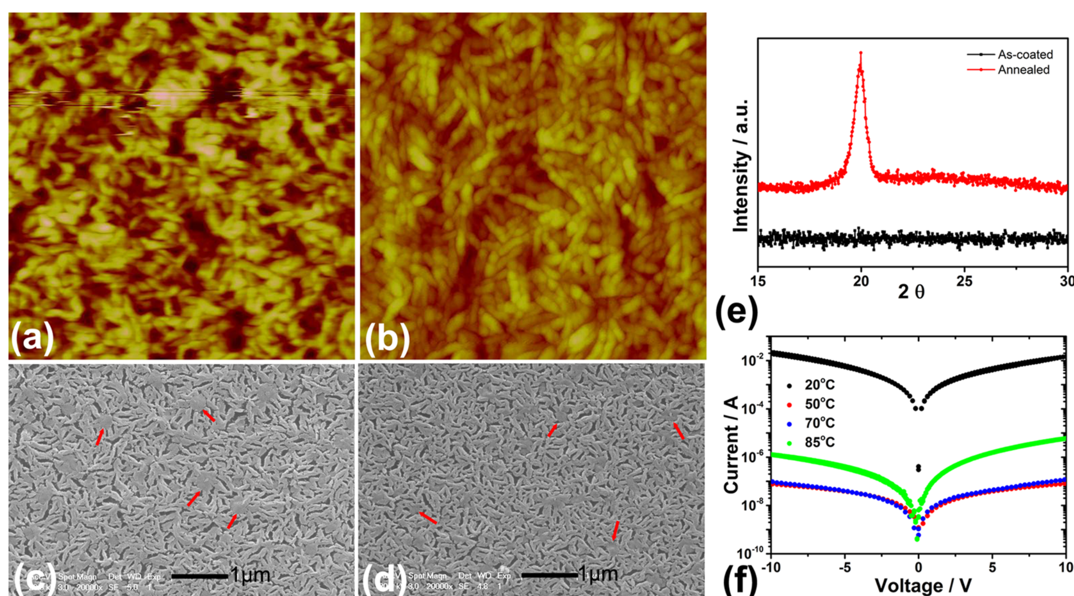

Figure 3. AFM (a,b), SEM (c,d), XRD (e), and leakage characteristic (f) analyses of the annealed P3HT/P(VDF-TrFE) blend films initially coated at environmental temperature of (a,c) 20 and (b,d) 50 °C, respectively. The as-cast films were deposited from 3.0 wt % THF solution and annealed at 135 °C for 5 h. Scan size for both AFM images was 5 × 5 μm^2. Some of P3HT domains are indicated by red arrows in SEM images.

gradually decreases from 40 to 95 nm at 20 °C to 14 to 26 nm at 50–70 °C and then inversely increases with further increase of deposition temperature. Furthermore, the calculated RMS roughness shows larger discretization at relatively lower, such as 20 °C, and higher, such as 85 °C, temperatures, which further indicates the great nonuniformity of film roughness obtained at too low or too high deposition temperatures.

To improve the degree of crystallinity in ferroelectric films, blend films were required to be annealed between their Curie and melting temperatures. AFM, SEM, and XRD were used to determine the influence of annealing treatment on structure and crystalline phases in blend films. In Figure 3e are shown the XRD spectra of blend films before and after annealing treatment. The as-cast film shows negligible crystalline characteristics, while, after thermal annealing at 135 °C for 5 h, one crystalline peak at $2\theta = 19.98°$ occurs which comes from the superimposition of (200) and (110) reflections, indicating the existence of crystalline β-polar phase in P(VDF-TrFE) film.[8] 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.

The typical morphologies of the annealed blend films are characterized by AFM and SEM, which are shown in Figure 3 for annealed blend films initially deposited at 20 and 50 °C. Both annealed samples show needle-like domains which are typical P(VDF-TrFE) structure for well-crystallized P(VDF-TrFE) films by thermal annealing.[9] From AFM imaging, it is hard to distinguish ferroelectric and P3HT phases. Note that during imaging the annealed blend film deposited at 20 °C, we carefully selected an area with relatively low roughness. However, the film surface in Figure 3a still shows large protrusions and some depressions, while the annealed film initially deposited at 50 °C (Figure 3b) shows much smooth surface completely covered with needle-like crystallites. SEM analyses are usually used to distinguish both ferroelectric and semiconducting phases,[10] which were also conducted on our P3HT/P(VDF-TrFE) blend films spin coated at various environmental temperatures to separate both phases and also to determine the dimension of semiconducting phase. Both images in Figure 3c,d show two phases: needle-like one and featureless one. Such needle-like domains are proved by AFM measurements shown in Figure 3a,b, while the featureless domains are usually attributed to P3HT phase.[10] Some of these P3HT domains are indicated by red arrows in both SEM images. Therefore, both SEM images indicate obvious phase separation with discrete P3HT phase surrounded by continuous ferroelectric phase. The diameters of P3HT domains are about 320–400 and 220–270 nm for 20 and 50 °C deposited blend films, respectively. This observation also indicates that with the increase of deposition temperature, the dimension of P3HT domains tends to be decreased, as may be due to the improved miscibility with the increase of deposition temperature.

Current leakage characteristic was also determined from annealed blend films deposited at various environmental temperatures. Current–voltage (I–V) measurements were performed in N_2 filled glovebox and under dark environment. P3HT/P(VDF-TrFE) blend films were deposited from 3.0 wt % THF solution at various temperatures and then annealed at 135 °C for 5 h. Typical I–V characteristics are shown in Figure 3f, where the deposition temperatures are also indicated. Obviously films deposited at 50 and 70 °C show the lowest leakage current, probably due to the well improved surface roughness which has been discussed above. Blend film deposited at 20 °C shows the worst insulating property. At voltage of 10 V, the leakage current of 20 °C deposited blend film is about 5 orders of magnitude higher than that of 50 °C (or 70 °C) deposited film, while blend film deposited at relatively higher temperature, such as 85 °C, also displays worse insulating property with leakage current 1 order of magnitude higher than that 50 °C (or 70 °C) deposited film. Such I–V measurements indicate strong roughness dependence, as was also discussed for wire-bar coated PFO/P(VDF-TrFE) blend films.[6]

From all these experimental observations on the surface roughness in Figures 1 and 2 and leakage characteristic in

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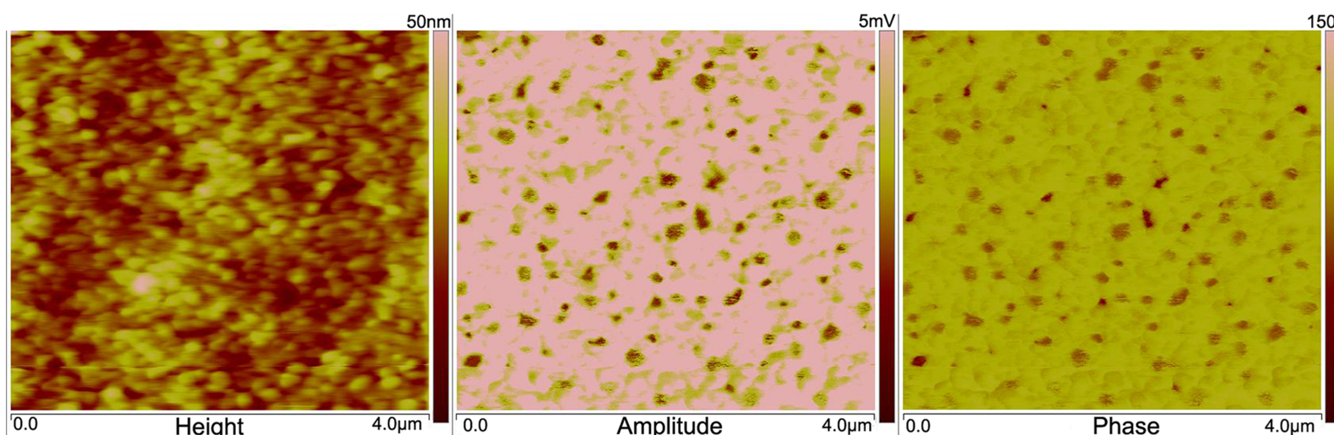

Figure 4. VPFM results of 1:10 P3HT/P(VDF-TrFE) blend film spin coated at 50 °C from 1.0 wt % solution onto Ag-deposited glass substrate and then annealed at 132 °C for 3 h.

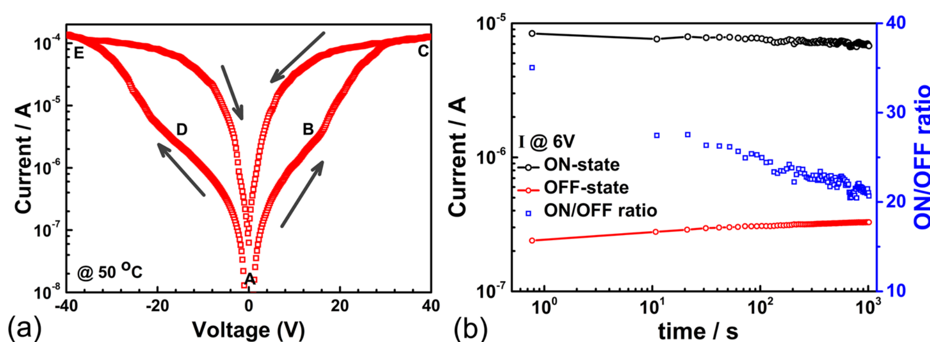

Figure 5. (a) Current−voltage and (b) retention characteristics of P3HT/P(VDF-TrFE) blend film spin coated from 3.0% THF solution at 50 °C. Arrows in (a) indicate the direction of the voltage sweeping. Before retention measurements, a voltage of +40 V (−40 V) was applied for 10 s to drive the blend film into ON (OFF) state, and then retention was measured at 6 V in next 10^3 s.

Figure 3, it is preferred to deposit blend films at proper high temperature, here 50−70 °C, in order to get relatively smooth surfaces and thus low leakage current.

The continuous P(VDF-TrFE) phase in such blend films is ferroelectric and its electrical dipoles can be switched by the applied poling voltage higher than the coercive voltage, as pure P(VDF-TrFE) films do. However, due to the existence of semiconducting P3HT domains which result in large leakage current, ferroelectric polarization process, i.e., polarization−voltage hysteresis loops, is hard to be well characterized by macroscopic measures, such as a typical Sawyer−Tower circuit. Fortunately, vertical piezoresponse force microscopy (VPFM) measurements satisfy such a requirement by determining nanoscale polarization reversal in ferroelectric phase of such blend systems. In fact, VPFM is widely used for study of ferroelectric films, including both inorganic and organic ferroelectrics.[11] V. Khikhlovskyi et al. have reported their VPFM study on P(VDF-TrFE)/F8BT (poly[(9,9-din-octylfluorenyl-2,7-diyl)-*alt*-(benzo[2,1,3]thiadiazol-4,8-diyl)]) blend films and observed ferroelectric reversal in P(VDF-TrFE) phase.[12] Besides the nanoscale measurements of ferroelectricity in ferroelectric phase, VPFM could be further performed for phase separation investigation. From VPFM amplitude images, it is possible to determine the piezoelectric property by measuring the vibration of film thickness induced by alternating driving voltage applied between the conductive probe and bottom electrode of the sample, while from VPFM phase images we can distinguish the polarization states (the orientation of electrical dipoles) in ferroelectrics. Different from the ferroelectric materials, semiconducting P3HT does not possess observable ferroelectric and piezoelectric properties. Under the excitation of alternating voltage, no vibration signals can be detected from the nonpiezoelectric P3HT phase. Therefore, from VPFM phase and amplitude images, it is expected to separate the ferroelectric and semiconducting phases. The typical VPFM results are shown in Figure 4, where P3HT/P(VDF-TrFE) blend film was spin coated at 50 °C from 1.0 wt % solution onto Ag-deposited glass substrate and then annealed at 132 °C for 3 h. During VPFM measurements, a conductive probe was electrically grounded and voltage was applied to the bottom Ag electrode. The whole area of 4.0 μm × 4.0 μm was first polarized by voltage of −10 V, and then VPFM was operated at contact mode with driving voltage of 3 V and frequency of 200 kHz. The height image shows film surface covered with small grains with diameter of tens of to several hundred nanometers. In height image it is hard to separate both phases. VPFM amplitude image shows some dark spots and light surrounding. Dark spots indicate extremely lower amplitude than the light surrounding, implying no observable piezoelectric vibration can be detected at these dark areas. Thus, these dark spots are regarded as nonpiezoelectric semiconducting P3HT domains embedded in continuous light surrounding phase. Obviously the continuous light surrounding is piezoelectric and should be regarded as P(VDF-TrFE) phase. In VPFM phase image, some dark spots are also obviously distinguished from the smooth surrounding. The phase

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difference between the dark spots and the surrounding is about 70°. Note that these dark spots in both VPFM amplitude and phase images are of one to one correspondence, indicating these spots are not due to experimental errors. The observed phase difference also indicates the existence of both piezoelectric and nonpiezoelectric phases. All these analyses further prove our understanding that these discrete spots should be attributed to the semiconducting phase and the surrounding to the ferroelectric phase. The dimensions of these P3HT domains are between 100 and 180 nm, a little smaller than the values from SEM analyses, which may be due to the lower P3HT/P(VDF-TrFE) concentration of 1.0 wt % than the concentration of 3.0 wt % in SEM measurements.[13]

Finally, resistive measurements were provided for blend films deposited at 50 °C. Note that here we does not provide the results from the films deposited at low temperature, such as 20 °C, because, as we have discussed above, blend films deposited at low temperature have extremely large surface roughness which tends to induce large leakage current and result in much low fabrication yield of resistive devices. Thus, from such low-temperature-coated blend films, on a few samples we can get electrical performance with good resistive switching characteristics, as reported elsewhere,[4,5] while in most cases large leakage current conceals resistive switching and even results in electrical breakdown. However, blend films deposited at 50 °C show obviously improved surface roughness and thus decreased leakage current. We have measured about 30 such devices, among which about 25 ones show good resistive switching performance, indicating high fabrication yield of resistive devices. Typical electrical measurements are shown in Figure 5, where P3HT/P(VDF-TrFE) blend films were spin coated from 3.0% THF solution at 50 °C and then annealed at 135 °C for 5 h. Before I−V measurements, the blend film was first poled negative by a voltage of −40 V for 10 s and then I−V measurements shown in Figure 5a were performed with the voltage swept between ±40 V. The obvious butterfly shape hysteresis loop indicates the resistive switching performance of such 50 °C deposited blend films. The current ON/OFF ratio at 6 V is about 31.3, superior to that obtained from room-temperature-coated films reported elsewhere.[4] Both butterfly wings are almost symmetric due to the symmetric top and bottom Ag electrode structure. By careful selection of asymmetric electrode structure, it is expected to get diode-like rectifying property which can be tuned by ferroelectric polarization. The retention characteristic of such 50 °C deposited blend films was also determined, and the typical result is shown in Figure 5b. Before retention measurements, a DC bias of +40 V (−40 V) was applied for 10 s to drive the blend film into ON (OFF) state, and then retention performance was determined at bias of 6 V in next 10^3 s. The ON-state current slightly decreases from 8.4 to 6.8 μA, while the OFF-state current degrades from 0.24 to 0.33 μA, resulting in the degradation of ON/OFF ratio from 35 to 21. Such resistive devices show good retention performance.

Resistive switching mechanism of such ferroelectric/semiconductor blend films have been well characterized experimentally and theoretically. In such blend films, current can only flow through the semiconducting channels, while the ferroelectric phase is insulating. Usually resistive switching is attributed to the result from modulation of the charge injection barrier, i.e., the difference between the work function of the electrode and the highest occupied molecular orbital (HOMO) energy of the semiconductor, at the semiconductor−electrode interfaces.[4,12,14] Numerical simulations showed that the stray field of the polarization charges in the ferroelectric phase modulated the charge injection from an electrode into the organic semiconductor and switched charge transport between injection limited (ILC) and space charge limited (SCLC) current.[15] 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.[4] Charge transport is injection limited due to this large injection barrier, and the sequent device current is low. When the ferroelectric phase is polarized to the right direction which can efficiently decrease the injection barrier at the Ag/P3HT interfaces, charge transport is switched to SCLC 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,[4,14] resulting in still low current. Thus, a bistable resistive switch is obtained.

The butterfly loop in Figure 5a is always expected for such a bistable resistive switching mechanism. As for the positive sweeping voltage, when the voltage sweeps from A to B, the ferroelectric phase stays still at the preset negative polarization state, the injection barrier still exists and low ILC current is observed; with further increase of the sweeping voltage from B to C, the voltage is high enough to cause polarization reversal from negative to positive polarization state and the injection barrier is efficiently reduced and charge transport is switched from ILC to SCLC mode, resulting in larger current; when the voltage sweeps backward from C to A, the ferroelectric phase remains at positive polarization state and larger SCLC current is still observed. Thus, one wing of the butterfly loop appears. The same analysis can be performed when negative voltage is swept, finally resulting in the whole butterfly loop.

■ CONCLUSION

In summary, by modified and temperature controlled spin coating technique, we prepared P3HT/P(VDF-TrFE) blend films with improved roughness at deposition temperature between 50 and 70 °C, which was proved by AFM analyses. SEM and PFM measurements were conducted to distinguish both ferroelectric and semiconducting phases and also to determine the dimension of P3HT domains. Leakage current characteristic was also measured to study the influence of surface roughness. Current−voltage measurements further determined the resistive switching characteristic and retention property of blend films deposited at 50 °C. These experimental observations proved the feasibility of improving the fabrication yield of organic semiconducting/ferroelectric blend resistive devices by increased coating temperature between 50 and 70 °C.

■ EXPERIMENTAL SECTION

Ferroelectric polymer P(VDF-TrFE) (VDF/TrFE molar ratio: 70/30) and organic semiconductor P3HT were purchased from Kunshan Hisense Electronic Co. and Sigma-Aldrich, respectively, and used as received. The blend solution was prepared by codissolving P(VDF-TrFE) and P3HT in tetrahydrofuran (THF) with weight ratio of 3.0%. P(VDF-TrFE):P3HT ratio was 10:1 by weight. Temperature-controlled spin coating was conducted in a nitrogen-filled glovebox. Commercial spin coater was modified so that the spin stage was enclosed in an environmental temperature controlled chamber. Before spin coating, the precleaned glass substrates were put onto the spin stage and the environmental temperature in the chamber was heated to and then kept at the preset temperature, usually between room

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temperature and 90 °C, for half an hour. Then the blend solution was spin coated at 700 rpm onto the glass substrates under such a controlled environmental temperature. 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 glovebox. The averaged film thickness was about 280 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 Ag stripes were thermally deposited via hard mask onto glass substrates, then P(VDF-TrFE)/P3HT blend films were spin coated from 3.0 wt % THF solution onto Ag bottom electrodes at preset environmental temperature and then annealed at 135 °C for 5 h. Finally, top Ag stripes were deposited onto blend film/Ag structure forming an effective electrode area of 0.04 mm^2. I−V measurements were performed in a N_2-filled glovebox by a Keithley 6487 sourcemeter. As for samples used for VPFM (vertical piezoresponse force microscope) measurements, Ag electrodes were predeposited onto glass substrates, then P(VDF-TrFE)/P3HT blend films were spin coated from 1.0 wt % THF solution onto Ag bottom electrodes at preset environmental temperature. Finally blend films were annealed at 132 °C for 3 h. VPFM (Nanoscope V, Bruker) was operated on such blend film/Ag structure in order to distinguish ferroelectric and semiconducting phases. During all VPFM measurements, the conductive probe was electrically grounded and the applied voltage was applied to the bottom Ag electrodes. VPFM was operated in contact mode with driving amplitude of 4 V and frequency of 200 kHz.

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Notes

The authors declare no competing financial interest.

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