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Retention Time and Depolarization in Organic Nonvolatile Memories Based on Ferroelectric Semiconductor Phase-Separated Blends

Kamal Asadi, Jurjen Wildeman, Paul W. M. Blom, and Dago M. de Leeuw

Abstract—Resistive switches have been fabricated using a phase-separated blend film of ferroelectric random copolymer poly(vinylidene fluoride-co-trifluoroethylene) with the organic semiconductor regio-irregular poly(3-hexylthiophene) (rir-P3HT). Spin-coated blend films have been contacted with symmetrical Ag top and Ag bottom electrodes, yielding switching diodes. The ferroelectric polarization modulates the injection barrier, yielding an injection-limited OFF-state and a space-charge-limited ON-state. To study the effect of depolarization, an additional polyphenylenevinylene-type semiconductor layer with the highest occupied molecular orbital energy that is comparable to that of rir-P3HT has been inserted in the diode stack. When the ad-layer is the injecting contact, the current modulation ratio goes to unity. The origin is a decrease in the effective band bending at the contact with increasing ad-layer thickness. When the counter electrode at the blend interface is the injecting contact, the diode can be switched, but the ON-state is only stable when an electric field that is larger than the coercive field is applied. Upon field removal, the ferroelectric depolarizes, and the current drops to that of an unpoled pristine diode. The depolarization is confirmed by capacitance–voltage and retention time measurements. To realize bistable diodes with excellent retention times, the thickness of the semiconducting wetting layer may not be at most 10 nm.

Index Terms—Depolarization, ferroelectric, nonvolatile memory, resistive switch, retention time.

I. INTRODUCTION

FLEXIBLE and organic electronics have emerged as a promising technology for low-cost large-area microelectronic applications by providing inexpensive lightweight capable ubiquitous components that can be printed onto plastic, glass, or metal foils. Contactless radio frequency identification transponders have already been demonstrated [1]. The digital code was stored in a hardwired or mask read-only memory

matrix. The envisaged applications, such as electronic barcodes or smart labels, however, require dynamic nonvolatile memories that can be repeatedly written and read. Various memory technologies are being investigated, e.g., those based on ferroelectricity [2], metal–organic–semiconductor–metal junctions [3], charge-trapping effects in field-effect transistors [4], [5], and electromechanical switches [6]. A promising concept is the use of a phase-separated blend of a ferroelectric polymer and organic semiconductor. The polarization field of the ferroelectric modulates the injection barrier at the metal–semiconductor contact [7]. The two binary states of the ferroelectric can then be probed by a change in resistance. The reported current modulation is orders of magnitude, the programming cycle endurance is more than 1000 cycles, and the data retention time is more than a week [8].

The blend memory concept has many desirable features such as the use of an unpatterned storage medium in a cross-point array that does not need strict alignment; a cell size of only $4F^2$, where F is the minimum feature size; a nondestructive readout; and bistable-rectifying diodes that prevent cross talk. Crucial for any application, however, is data retention. Ferroelectric polarization gives rise to a depolarization field, just like for classical dielectrics [9], [10]. In the absence of an externally applied field, the depolarization field negates ferroelectric polarization. To stabilize the polarization and, hence, to retain the stored logic state, one therefore needs to supply compensation charges at the surfaces of the ferroelectric.

To substantiate the effect of depolarization in ferroelectric blend diodes, we took the approach that was suggested by Batra *et al.* [11] by inserting an additional semiconductor layer in between the blend and the electrode. We systematically varied the thickness and measured the diode capacitance as a function of voltage, current modulation, and data retention. We present a qualitative interpretation of the depolarization.

II. DEVICE FABRICATION

The resistive switches were fabricated using a blend of ferroelectric random copolymer poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] (65%–35%) (purchased from Solvay) with regio-irregular poly(3-hexylethiophene) (rir-P3HT) (purchased from Reike Metals). The blending ratio of rir-P3HT:P(VDF-TrFE) was fixed at 10 : 90 in weight. P(VDF-TrFE) was used as received. Rir-P3HT was purified before use [8]. We note that resistive switching is universal; rir-P3HT was chosen for internal consistency with previous publications

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Fig. 1. Schematic representation of current transport in resistive switches that is based on semiconductor–ferroelectric phase-separated blends. The right electrode is grounded; bias is put on the left electrode. The direction of the voltage axis is to the left to illustrate the switching of the corresponding contact. (a) Chemical structure of the compounds that are used. (b)–(c) Blend-only diodes. (d)–(e) Diodes with an additional semiconductor layer in between the ferroelectric blend and the electrode. Both thick and thin ad-layers are represented. (b)–(c) (Dotted line) The first measurement. The diodes switch at the coercive field E_c . The fully drawn curves show the permanent transport at lower biases. ON and OFF indicate a space-charge-limited contact and an injection-limited contact, respectively. The contacts in (d)–(e) are either nonswitching or depolarized. The corresponding schematic JV sweep is included below of each cartoon for different polarization states.

[7], [8]. For the additional semiconducting layer, we used a random symmetric copolymer poly(2,5-bis(2-ethylhexyloxy)-co-2,5-bis(2-methylbutyloxy)-1,4-phenylenevinylene) (BEH-BMB-PPV). The chemical structures of the compounds are presented in Fig. 1(a). BEH-BMB-PPV was synthesized according to a literature procedure [12]. The precursor was carefully purified from hexane three times by crystallization, and the obtained polymers were purified by a second precipitation from acetone. Molecular weight $M_n = 1.0 \times 10^5$ (g mol⁻¹), with a polydispersity of $M_w/M_n = 2.8$, was determined by gel permeation chromatography that is measured in trichlorobenzene at 135 °C and calibrated with polystyrene standards.

To prevent intermixing, the two layers were spin coated from orthogonal solvents. The ferroelectric blend materials were codissolved in tetrahydrofuran (THF). The solubility of BEH-BMB-PPV can be tuned by the copolymer ratio of BEH and BMB parts [13]. By using a ratio of 1:5, the copolymer can be processed from CHCl_3 , whereas it is insoluble in THF [13].

For the diode fabrication, we evaporated Ag (40 nm) on clean glass substrates with Cr (1 nm) as adhesion layer. Onto the Ag electrode, thin films of BEH-BMB-PPV with different thicknesses ranging from 0 to 70 nm were spin coated after filtration of the solution through 5- μm polytetrafluoroethylene (PTFE) filters. Blend films of about 150 nm were spin coated onto the Ag electrode or onto the BEH-BMB-PPV ad-layer after filtration of the solution through 1- μm PTFE filters. Before applying the Ag top electrode (70 nm), the substrates were annealed at 140 °C in order to enhance the crystallinity of the ferroelectric P(VDF-TrFE) [14]. A Keithley 2400 source meter was used to measure current transport. To switch, the diode pulses of ± 20 V with 10-ms duration were applied from an Agilent 8114A pulse generator. CV measurements were performed using an Agilent 4284A LCR meter. All the preparation processes and electrical measurements were carried out in nitrogen-filled glove boxes.

III. CURRENT TRANSPORT

The operation and current–voltage characteristics of diodes with and without additional semiconductor layer are schematically presented in Fig. 1(b)–(e). The blend phase separates upon spin coating. Bicontinuous rir-P3HT domains are formed within the P(VDF-TrFE) matrix [15], [16]. Ag is a bad injecting contact for holes in rir-P3HT. The hole injection barrier, i.e., the difference between the work function of Ag and the highest occupied molecular orbital (HOMO) of rir-P3HT, is about 0.6–0.7 eV [7], [8]. We note that any other electrode material that yields the same injection barrier can be used. For a pristine diode, the transport, therefore, is injection limited, and the current density is low. We now pole the ferroelectric by applying a field that is larger than the coercive field E_c . At one electrode, the polarization charge is negative, whereas, at the counter electrode, the polarization charge is positive. The negative polarization charge is compensated by the metal and, partially, by accumulated holes in the semiconductor. The resulting band bending effectively lowers the injection barrier at the respective electrode, and the injected current becomes space charge limited. This electrode, i.e., the left electrode in Fig. 1(b), therefore, is called ON. At the counter electrode, the polarization charge is positive. Because we use a p-type semiconductor, the ferroelectric polarization charges cannot be compensated for by the semiconductor. The compensation charges, i.e., electrons are supplied only by the metal. In this case, the injection barrier at the counter electrode, i.e., the right electrode in Fig. 1(b), remains high. The current injection from this electrode is low and injection limited, and therefore, this electrode is called OFF.

The ferroelectric polarization is stable as the compensation charges are present at both electrodes. In summary, the JV curves of poled diodes are asymmetric. One electrode is ON, whereas the other is OFF. The diode turns on at the coercive field of the ferroelectric, and the current remains high at lower biases. When the ferroelectric is poled in the opposite direction than in Fig. 1(b), the mirror image of the JV curve, as shown in

Fig. 2. Switching characteristics of a *rir*-P3HT:P(VDF-TrFE) 10:90 blend-only diode at electric fields that are lower than the coercive field of the ferroelectric. Pulses of ± 20 V are applied to set the diode into the ON- and OFF-states. For each state, we presented the forward and backward sweep, showing that there is no hysteresis in the current transport through the semiconductor phase.

Fig. 1(c), is obtained. The ferroelectric polarization is stabilized by countercharges, and depolarization is not expected.

As an illustration, switching characteristics of a blend diode without ad-layer are presented in Fig. 2. Only one contact is shown. The diode can be polarized at biases above ± 20 V, corresponding to a coercive field of ± 50 MV $\cdot$ m $^{-1}$. The diode can be put in an ON-state and an OFF-state. The current in the OFF-state is injection limited, and the current in the ON-state is space charge limited. The current modulation is about two orders of magnitude. The switching bias of ± 20 V is too high for practical application. However, we note that low voltage operation of the ferroelectric diodes can be inferred from the low-operation voltages of organic ferroelectric capacitors and ferroelectric transistors [17], [18]. Electrochemistry, as driving mechanism for bistability, can be ruled out because switching occurs exactly at the coercive field.

Subsequently, an additional BEH-BMB-PPV layer was inserted in between the Ag electrode and the ferroelectric blend. The BEH-BMB-PPV is a p-type semiconductor with the HOMO energy level and hole mobility comparable to that of *rir*-P3HT [13]. The offset between the HOMO of BEH-BMB-PPV and that of *rir*-P3HT at their corresponding interface is negligible and does not interfere with the hole transport through the whole stack.

The current transport was measured as a function of the thickness of the BEH-BMB-PPV ad-layer for both ferroelectric polarization. We first discuss the diode when the ferroelectric is poled negative, as shown in Fig. 1(d). The Ag electrode in direct contact with the blend, which is the left electrode in Fig. 1(d), is then in the OFF-state, as previously discussed. The current is injection limited and independent of the thickness of the ad-layer.

The current density using the Ag electrode–ad-layer as injecting contact is presented in Fig. 3 as a function of ad-layer thickness. The current density was nondestructively measured at a constant field of 15 MV $\cdot$ m $^{-1}$, which is well below the co-

Fig. 3. Evolution of the on-state and the OFF-state current density of diodes as a function of thickness of an additional BEH-BMB-PPV semiconductor layer. The diodes were polarized using an electric field that is larger than the coercive field of P(VDF-TrFE) and nondestructively readout at a low field of 15-MV $\cdot$ m $^{-1}$ well below the coercive field. (Dashed lines) Guide to the eye.

ercive field of about 50 MV $\cdot$ m $^{-1}$. The current density slightly increases first for a very thin ad-layer thickness of about 10 nm and then rapidly drops. The current density versus the voltage for the thin and thick ad-layers is schematically presented in Fig. 1(d). The origin of the drop in current density is the effective band bending at the Ag electrode–ad-layer interface that depends on the ad-layer thickness. Holes are injected from the Ag electrode, transported through the semiconducting ad-layer, and accumulated at the ad-layer–blend interface, where they compensate the negative ferroelectric polarization. The accumulated holes lead to band bending. The amount of band bending is largest at the ad-layer–blend interface and then decreases as the distance from this interface to the Ag electrode–ad-layer interface increases. Hence, for a very thin ad-layer, the remaining band bending at the Ag electrode is still sufficient to lower the injection barrier. The current is space charge limited; the diode is in the ON-state.

The current density is calculated using the whole device area and is not corrected for the effective semiconductor area. In the blend-only diodes, the effective area is about equal to the weight percentage of *rir*-P3HT, viz., 10% of the device area, whereas, for the diodes with an ad-layer, the whole device area is semiconducting. For very thin ad-layers, the device's current density in the ON-state, therefore, slightly increases as compared to blend-only diodes.

The band bending extends over a distance in the order of the thickness of the accumulation layer in field-effect transistors, viz., 10 nm [19]. As the ad-layers thicken, the remaining band bending at the Ag electrode rapidly decreases. The effective injection barrier, therefore, increases with increasing ad-layer thickness. The current density in the ON-state then rapidly drops. Hence, the resistance switching at the ad-layer electrode is called thickness limited.

The current transport of the diode in reverse polarization is presented in Fig. 1(e). The Ag electrode–ad-layer contact, i.e., the left contact in Fig. 1(e), is in the OFF-state. The current is injection limited. Fig. 3 shows that the OFF-state current

density slowly increases with increasing ad-layer thickness. This current increase is expected because the current density is calculated for the total device area, instead of being corrected for the effective semiconductor area, which is similar to what was previously discussed. We note that, for thick ad-layers, the injection barrier at the Ag/ad-layer contact is expected to be independent of the sign of the ferroelectric polarization. This is confirmed by Fig. 3, showing that, for thick ad-layers, the current density in the ON-state [see Fig. 1(d)] is identical to that in the OFF-state [see Fig. 1(e)].

The top Ag contact is in the ON-state. Similar to what is previously discussed for blend-only diodes, the negative ferroelectric polarization is compensated for by holes that are accumulated in the *rir*-P3HT semiconductor phase of the blend, eliminating the injection barrier. However, we note that, here, due to the presence of the ad-layer, the ferroelectric polarization is only stable as long as an electric field that is larger than the coercive field is applied; in the *JV* characteristics, there is hardly any hysteresis. The remnant polarization is negligible. Upon field removal, the ferroelectric depolarizes, as will be discussed in Section IV.

IV. DEPOLARIZATION AND RETENTION

The spontaneous alignment of electric dipoles in a ferroelectric gives rise to a depolarization field that opposes the net dipole moment in the material. In a capacitor, the ferroelectric polarization is compensated for by charge carriers in the metallic electrodes. The polarization field, then, is eliminated. However, as pointed out by Black *et al.* [20], the addition of a linear capacitor in series with a ferroelectric capacitor prevents full compensation of the polarization. A depolarization field remains, i.e., the magnitude of which depends on the relative values of the capacitances. As a consequence, the remnant polarization decreases. More importantly, any remaining depolarization field can drastically reduce the retention time [21].

The diode in Fig. 1(e) is not a simple series connection of a linear and a ferroelectric capacitor but a series connection of two *RC* networks. Hence, the depolarization cannot be quantitatively analyzed. We explain the origin of the experimentally observed depolarization as follows. At the right Ag contact in Fig. 1(e), the negative ferroelectric polarization is compensated for by accumulated holes in the *rir*-P3HT semiconductor phase of the blend. In order to compensate the positive polarization on the other side, electrons are required. However, the BEH-BMB-PPV ad-layer is a p-type semiconductor that shows inferior electron injection from silver and poor electron-transporting properties [22]. The electron density at the ad-layer–blend interface is too low to compensate the ferroelectric polarization. The polarization is only stable at electric fields that are above the coercive field. As soon as the field strength decreases, the ferroelectric depolarizes. The diode is again in the pristine state. The original band alignment at both contacts is restored, and the current density is injection limited.

To experimentally confirm the depolarization of the ferroelectric in the presence of the BEH-BMB-PPV layer, *CV* measurements were performed. Fig. 4 shows the *CV* characteristics of the blend-only diode. The butterfly shape is due to the

Fig. 4. *CV* measurements of (black square) a *rir*-P3HT:P(VDF-TrFE) 10:90 blend-only diode and (red circle) a diode with an additional 68-nm BEH-BMB-PPV layer. The butterfly shape of the blend-only diode unambiguously demonstrates the presence of both ferroelectric polarization states, whereas the diode with additional semiconductor layer depolarization of the ferroelectric obstructs the positive ferroelectric polarization state.

nonlinear dielectric response of the P(VDF-TrFE) to the electric field [23]. The maxima that is observed near the coercive field of P(VDF-TrFE), i.e., $\pm 50 \text{ MV} \cdot \text{m}^{-1}$, corresponds to polarization reversal [23]. The symmetric shape unambiguously demonstrates the presence of both polarization states in the blend-only diode.

For diodes with a BEH-BMB-PPV ad-layer that is not symmetric but is asymmetric, *CV* characteristics are obtained. Fig. 4 shows that hysteresis is only measured in one bias polarity, corresponding to Fig. 1(d). The response is then comparable to that of a blend-only diode.

In the opposite polarity, corresponding to Fig. 1(e), there is only little hysteresis. The ferroelectric P(VDF-TrFE) can be polarized above the coercive field. The remnant polarization is negligible, and the ferroelectric depolarizes during the *CV* measurements. The fast depolarization originates from the lack of electrons at the interface between the ad-layer and the blend to stabilize the positive ferroelectric polarization. The depolarization field is not compensated, which therefore prevents remnant ferroelectric polarization [9]. We note that a comparable behavior has been observed in metal–ferroelectric insulator–semiconductor diodes [24]. *CV* measurements showed that these ferroelectric metal–insulator–semiconductor diodes switch between a polarized ON-state and a depolarized OFF-state [21]. A polarization in the OFF-state could not be remanently stabilized due to lack of charge-compensating electrons in the p-type semiconductor.

The ferroelectric depolarization limits the data retention time of programmed diodes. Both blend-only diodes and diodes with a semiconducting ad-layer were programmed in the ON-state. The current density, which is nondestructively measured at a field that is lower than the coercive field, is presented in Fig. 5 as a function of time. For the blend-only diode, the current is constant, which is in good agreement with the reported retention times of more than a week. For diodes with an ad-layer, the retention time is limited by the experimental resolution. Already, after half a second, the diode is back in the OFF-state, and the current is low. The depolarization of the

Fig. 5. Retention time measurements. The current density in the ON-state is measured at $-20 \text{ MV} \cdot \text{m}^{-1}$ and presented as a function of time. (Green square) Blend-only diode. The current density is constant with time, which is in good agreement with the reported retention time measurements [8]. (Red circle) Diode with a 68-nm-thick additional semiconducting BEH-BMB-PPV layer. The current density was measured for the electrode that is in direct contact with the blend [the left electrodes in Fig. 1(d) and (e)]. The time resolution of the experimental setup is a few hundred milliseconds. Therefore, the depolarization of the ON-state is schematically represented (dashed red-line). The low current density shows that the diode readily depolarizes.

ON-state to the depolarized state is, therefore, schematically presented by a dashed line. Within the time resolution of the experiment, the current drops to that of the unpolarized pristine diode.

The data retention time, which is crucial for any application, is dominated by the ferroelectric depolarization. We have shown that the thicker the ad-layer, the larger the depolarization field. This implies that, in the processing of the blend, any semiconducting wetting layer should be avoided at the interface between the injecting contact and the ferroelectric. As shown in Fig. 3, the wetting layer may not be thicker than 10 nm. Experimentally, we have shown using scanning transmission X-ray microscopy [16] that the semiconducting wetting layer is at most 4 nm. This explains the excellent retention time of optimized bistable diodes.

V. CONCLUSION

Resistive switches have been fabricated using a phase-separated blend of the ferroelectric random copolymer P(VDF-TrFE) (65%–35%) with the semiconductor rir-P3HT. The diodes have been contacted with Ag top and Ag bottom electrodes. The ferroelectric polarization has been compensated for by charge carriers in the rir-P3HT semiconductor. The resulting band bending lowers the injection barrier. Depending on the poling of the ferroelectric, the diode switches between an injection-limited OFF-state and a space-charge-limited ON-state.

Ferroelectric polarization gives rise to a depolarization field. When not compensated, the depolarization limits remnant polarization and data retention time, which is crucial for any memory application. Depolarization has been investigated by inserting an additional polyphenylenevinylene-type semiconductor layer with the HOMO energy that is comparable to that of rir-P3HT. When the ad-layer is at the injecting contact,

the current density for very thin ad-layers slightly increases, compared to blend-only diodes due to a larger effective device area. For thicker ad-layers, the remaining band bending at the injecting electrode decreases with increasing ad-layer thickness. Consequently, the current rapidly drops, and for ad-layer thickness that is larger than about 60 nm, there is no current modulation left. On the other hand, when the electrode at the blend interface is the injecting contact, the diode can be poled into a conducting ON-state and a resistive OFF-state. There are, however, not enough electrons in the p-type semiconductors to stabilize the positive ferroelectric polarization. The ferroelectric polarization is only stable at electric fields that are larger than the coercive field. Upon field removal, the ferroelectric depolarizes, and the current drops to that of an unpoled pristine diode. The depolarization is confirmed by CV and retention time measurements.

To realize bistable diodes with excellent retention times, the thickness of the semiconducting wetting layer may not be at most 10 nm.

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