Organic Field-Effect Transistors with Reversible Threshold Voltage Shifts for Memory Element

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Abstract - We introduce an charge-accepting layer on a poly(methyl methacrylate) (PMMA) dielectric to investigate the reversible threshold voltage ($V_{th}$) shifts in all-polymer n-channel organic field-effect transistor (OFET) using an organic semiconductor of an poly(N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)) (P(NDI2OD-T2)). Top contact drain-source with a bottom-gate contact structure device exhibited a unipolar property with n-channel behavior. Furthermore, the existence of poly(3-hexylthiophene) (P3HT) films as a charge-accepting-like storage layers resulted in a reversible $V_{th}$ shifts upon the application of external gate bias ($V_{bias}$). Hence, all-polymer organic transistor with the charge-accepting layer exhibited a large memory window ($\Delta V_{th} \sim 10.7$ V) for write and erase electrically without major degradation in saturation mobility ($\mu_{sat} = 1.8$-$2.8 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$).

Keywords - organic semiconductor, n-channel, organic field-effect transistor (OFET), nonvolatile memory

I. INTRODUCTION

Research on organic semiconductor materials for their broad range of applications in the electronic industry has revolutionized the fields of electronics. Organic semiconductors have been the subject of interest for the past few years [1]. During this decade, the use of organic semiconductors has seen a spectacular evolution which provides a unique opportunity to enable low-cost, flexibility, solution processable, and easier fabrication procedure in electronic applications. However, organic materials became more than a curiosity when it was recognized to have excellent electronic properties compared with inorganic semiconductors. Recently, there has been impressive progress in the development of electronic devices, particularly high performance organic field-effect transistors (OFETs) which been utilized in sensors, light-emitting displays, memory elements, and integrated circuits [2-5]. In conventional silicon technology, research and development for silicon nonvolatile memory is fueled by the serious drawback in the physical limitation of the device structure toward nanosized transistors. Hence, this could be an alternative or complement technology to the conventional semiconductor technology in order to support fabrication at the nano-scale for nano-devices.

II. BACKGROUND AND LITERATURE REVIEW

Despite major development in the OFETs based on p-channel organic semiconductors, there are still problems concerning the development of n-channel organic transistors due to the selection of n-channel organic semiconductor materials, which are limited to a very small number of molecules and polymers [6]. There are also serious drawbacks in the implementation of organic electronic devices, including poor solubility, difficulty of synthesis and unstable transistor operation under the ambient atmosphere. A number of strategies have been developed to obtain OFETs that exhibit n-channel transistor behavior. The strategies are (1) use of combination of organic semiconductor and electrode material for which electrons can be efficiently injected into the LUMO, (2) elimination of electron traps from the transistor by passivating the dielectric interface and/or by operating the OFET in oxygen-free environment, and (3) development of functionalization of conjugated compounds with fluorine-rich substituents for air-stable organic n-channel OFETs [7,8]. However, since the first air-stable n-channel OFETs based on naphthalenedi-carboxylic diimides was reported [9], a large number of n-channel organic semiconductors have been based on either naphthalene diimide (NDI)- or perylene diimide (PDI)-based polymers for organic transistors [10-13]. Therefore, clearly n-channel organic semiconductors have an important role in the continuing development of organic semiconductor-based circuits and electronic products.

Initial attempts at nonvolatile organic memory were reported involving p-channel OFET memory with charge storage in polymer electret [14] and nanoparticle-embedded gate dielectrics [15]. H. E. Katz et al. demonstrated a top-gate/top-contact OFET device configuration using combination of semiconductors 1,4-bis(5-phenyl-2-thienyl)benzene (PTTPT) and N,N'-bis(1H,1H-perfluorooctyl) naphthalene-1,4,5,8-tetracarboxylic diimide (F15-NTCDI) with hydrophobic polymer as polarizable gate dielectric or electrets to operate as nonvolatile memory device. A quasi-stable threshold voltage shift was obtained upon the application writing voltage via the gate relative to...
a common source and drain voltage. The stored voltages are the result of injected static and/or induced dipole orientation at or between the two dielectric interfaces. Thus, the effectiveness of the hydrocarbons as charge storage media is consistent with the known performance of such materials as electrets [14]. Meanwhile, K. -J. Baeg et al. fabricated an OFET memory using solution-processed poly[9,9-dioctyfluorenyl-2,7-diy]-co-(bithiophene)] (F8T2) nanofloating gate memory with a top-gate/bottom-contact device configuration. The device exhibited a reversible shift in the threshold voltage with a large memory window (ca. 30 V) during writing and erasing operation voltage of 80 V of gate bias. The reliable memory characteristics was achieved by the incorporation of thin Au nanoparticles (Au-NPs) as charge storages for negative charges at the interface between polystyrene and cross-linked poly(4-vinylphenol) [15]. However, recently, nonvolatile n-channel organic memory using a block copolymer-nanoparticle hybrid system has been reported [16]. W. L. Leong et al. demonstrated programmable-erasable properties with a large memory window (~9–11 V) using n-channel (perfluorinated copper phthalocyanine) OFETs memories where in-situ synthesized gold (Au) nanoparticle in self-assembled polystyrene-block-poly-4-vinlypyridine (PS-b-P4VP) block copolymer nano-domains as charge storage elements. Thus, the use of n-channel organic semiconductors has become important for the continuous development of OFETs with memory element.

In this study, we demonstrate fabrication and characterization of solution processed all-polymer OFETs with heterojunction thin films of P(NDI2OD-T2) and poly(3-hexylthiophene) (P3HT). Moreover, we also present all-polymer organic transistor based on P(NDI2OD-T2) as an n-channel active layer with a charge-accepting layer on poly(methyl methacrylate) (PMMA) organic dielectric for memory element.

III. DEVICE CONCEPT AND FABRICATION

A. Organic semiconductor solutions

The poly[[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diy]-alt-5,5'-bis(2,2'-bithiophene)] [P(NDI2OD-T2)] was purchased from Polyera Corporation under the trade name of ActiveInk N2200. Molecular structure of P(NDI2OD-T2) is shown in Fig. 1(a). The P(NDI2OD-T2) is highly soluble in chlorinated solvents and for this work, P(NDI2OD-T2) was diluted in chloroform without further purification to form 0.5 wt% solution. The LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) energy levels of P(NDI2OD-T2) are approximately 4.0 eV and 5.6 eV below the vacuum level, respectively, as shown in Fig. 2.

B. Fabrication of organic field-effect transistors

A (100)-oriented B-doped p+-type si wafer (< 0.1 Ω cm) was used as the substrate and gate contact. The substrates were rinsed ultrasonically in deionized water, ethyl alcohol, acetone, and then methyl alcohol, and cleaned by the standard RCA cleaning procedure. Poly(methyl methacrylate) (PMMA) with molecular weight of 120 000, was purchased from Sigma Aldrich and was diluted in dichloromethane to form a 0.05 wt% solution. The HOMO and LUMO energy levels of P3HT are approximately 4.8 eV and 3.0 eV below the vacuum level, respectively, as shown in Fig. 2.

Figure 1. Molecular structure of P(NDI2OD-T2) and P3HT.

The P3HT with regioregularity of 98.5% was purchased from Rieke Metals. Molecular structure of P3HT is shown in Fig. 1(b). This conjugated polymer is one of the most widely used p-type semiconductors, especially in organic solar cells. For this work, P3HT was diluted in dichloromethane to form a 0.05 wt% solution. The HOMO and LUMO energy levels of P3HT are approximately 4.8 eV and 3.0 eV below the vacuum level, respectively, as shown in Fig. 2.

Figure 2. Energy band diagram of P(NDI2OD-T2) and P3HT.
dielectric layer to form the charge trapping layer, followed by spin coating of P(NDI2OD-T2) in chloroform solution at 5000 rpm to form the n-channel active semiconducting layer. 0.1 ml of each solution was filtered through a 0.2 μm syringe filter prior to deposition. Finally, a gold (Au) film was deposited through a designated shadow mask in a vacuum chamber for the top source and drain contacts. The channel dimension of these devices was $W/L = 2.5 \text{ mm}/50 \mu\text{m}$. The schematic structure of the bottom gate with top drain-source contact structure n-channel OFETs is shown in Fig. 3. The electrical measurements of the devices were measured in a probe station with a computer-controlled automatic electrical analyzer at room temperature in the dark under the ambient atmosphere.

The device shows a typical output curve of a field-effect transistor (FET) and undoubtedly indicates that only electrons are accumulated at the semiconductor-dielectric interface and the current flow from the source to the drain through the channel region when positive gate voltages ($V_g$) are applied. Therefore, the OFET is functioned in the n-channel operation in accumulation mode with increasing positive drain current ($V_{ds}$).

A bottom source-drain with a bottom-gate structure ambipolar organic field-effect transistors (OFETs) based on a bulk heterojunction layer of P(NDI2OD-T2) and P3HT have been reported [17], in which the p-channel and n-channel semiconductor layers have to be deposited using orthogonal solvents in order to prevent mixing of the layers. The top contact structure device based on heterojunction thin films did not interfere with the nature of charge transport, as the devices were found to behave as n-channel operation mode similarly to the unipolar P(NDI2OD-T2)-OFETs [10]. In fact, only electrons are accumulated at the semiconductor-insulator interface. However, a partial redissolution of the deposited P3HT layer occurs at the P(NDI2OD-T2)-P3HT interface upon the spin-coating of P(NDI2OD-T2) solution. Thus, the presence of very thin P3HT domains in P(NDI2OD-T2) could slow down the holes, and cause more electrons to travel into the active semiconductor layer inducing an increase in the drain current. On the other hand, the P3HT film could also provide additional protection to the NDI-based polymer from possible degradation by oxygen and humidity, thus preventing from device performance decline. Furthermore, the relative position of LUMO level of P(NDI2OD-T2) with respect to the gold work function cannot be considered as an Ohmic contact due to the presence of an injection barrier. Thus, in our experiments the electron injection is only slightly limited, allowing low current output (in range of nA order). In addition, the injection barrier can be further reduced by the application of top-gate structure OFETs.

IV. DEVICE CHARACTERIZATION RESULTS

A. Output characteristics

Figure 4 shows representative output characteristics of OFETs with P3HT film on the highly doped p-type silicon substrate, respectively.

B. Transfer characteristics

Figure 5 shows the transfer characteristics of the P(NDI2OD-T2)-OFETs with P3HT film at a constant positive $V_{ds}$ ($V_{ds} = +20 \text{ V}$). Transistor parameters such as charge carrier mobility ($\mu$), threshold voltage ($V_{th}$), on/off current ratio ($I_{on}/I_{off}$), and subthreshold slope (SS) are $1.1-2.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 30.6–34.6 V, 10², and 3.5 V/dec, respectively. The charge carrier mobilities of these devices were extracted in either the linear or saturation region using the standard transistor equation for FETs [18]. In fact, the mobility was in the range of the reported values for other unipolar OFETs based on NDI-polymer [10], and typically, spin-coated n-channel polymer devices displayed mobility in the range of $10^{-2}-10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This result indicates that the additional P3HT layer influenced the performance of the
n-channel P(NDI2OD-T2)-OFETs. In addition, the \(I_{ON}/I_{OFF}\) was relevant and the SS was also in the range of 0.1-10 V/dec, which is typical of conventional OFETs [19].

Figure 5. Semilogarithmic plots of both drain current and square root of drain current versus gate voltage showing the transfer characteristics of all-polymer OFET.

C. Memory element

An external gate bias (\(V_{bias}\)) was applied to the gate contact to cause reversible shifts in \(V_{th}\) in order to determine whether the device can sense for memory state, i.e. write and erase states, which is similar to the characteristics described by S. Tiwari et al. for nonvolatile memory [20].

The initial transfer characteristic was clearly shifted in a negative direction after the application of external \(V_{bias} = -60\) V (writing voltage) for \(T_{bias} = 5\) min. The shift in the \(V_{th}\) (\(\Delta V_{th}\)) or memory window was observed to be 10.7 V. Thereafter, the application of an external \(V_{bias} = +60\) V (erasing voltage) for \(T_{bias} = 5\) min caused the positively shifted transfer characteristic to return nearly to its initial position. The device parameters after the application of external bias; \(\mu_{sat} = 2.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}, V_{th} = 30.6\) V (initial), \(\mu_{sat} = 1.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}, V_{th} = 19.9\) V (negative external bias), and \(\mu_{sat} = 1.9 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}, V_{th} = 27.5\) V (positive external bias).

Before application of external gate bias, electrons were injected into the LUMO level of P(NDI2OD-T2) and forming charge accumulation later at the P(NDI2OD-T2)-P3HT interface and thus, the device exhibited electron-only (n-type) transport. The writing voltage caused negative shifts in \(V_{th}\) which indicates that positive charges are stored from the channel into the P3HT-charge-acceptor layer. The applied gate bias simultaneously facilitates charge transfers by reducing the potential barrier at the P(NDI2OD-T2)-P3HT interface. Hence the charges are efficiently transferred into the P3HT, which mostly positive charges are accumulated and trapped into the donor-like trap capability of P3HT, resulted in the changes of charge distribution at the P(NDI2OD-T2)-P3HT interface.

Figure 6. Transfer characteristics obtained upon application of different external gate bias conditions at constant positive \(V_{ds} = +20\) V for all-polymer OFET, \(V_{bias} = 0\) V (initial state), \(V_{bias} = -60\) V was applied for \(T_{bias} = 5\) min (write or “1” state), and \(V_{bias} = +60\) V was applied for \(T_{bias} = 5\) min (erase or “0” state).

Figure 6 shows the transfer characteristics of the P(NDI2OD-T2)-OFETs with a P3HT-charge storage layer following the application of an external \(V_{bias}\), which exhibited a significant shift depending on the polarity of the \(V_{bias}\). Furthermore, this cause the \(I_{DS}\) shifts in the negative direction, which corresponding to the occurrence of “1” state. On the other hand, the reversibility of the \(V_{th}\) shift in a positive direction was caused by an erasing operation of negative \(V_{bias}\), which indicates that the positive charges trapped in P3HT to detraps and transfer back into P(NDI2OD-T2) film, which cause a non-equilibrium charge distribution in the active semiconductor layer. This generates the recombination process with negative charges to overcome the non-equilibrium condition and eventually the recombination caused the decrease in the electron charge carrier transport in the P(NDI2OD-T2) film. Thus, the detrapped of negative charges from P3HT is responsible for the reversible \(V_{th}\) shifts in the opposite direction which corresponding to the occurrence of “0” state. Therefore, the position of the transfer curve in the device could be controlled by the proper selection of applied external \(V_{bias}\) with a certain amount of time bias.
The threshold voltage can be related to the work function difference of metal and semiconductor, the doping concentration, the interfacial charge density and the bulk potential [21]. Thus the number of transferred charges, i.e., interface trap density, \( N \), can be estimated from the shift in threshold voltage after the occurrence of “1” state according to

\[
N = \frac{\Delta V_{th} \cdot C_i}{\varrho}
\]  (1)

where, \( \varrho \) is electronic charge and \( C_i \) is capacitance per unit area. The observed threshold voltage shift of 10.7 V resulted for interface charge trap density of \( 2.1 \times 10^{11} \) charges/cm\(^2\). The result provide that memory window can be obtained by using the P3HT as the charge traps or charge storage layer, compared to our previously reported PCBM based pentacene-OFETs memory and also the interface trap is comparable to the first nanocrystalline-silicon (nc-Si) nonvolatile memory device reported by S. Tiwari et al. [22]. Here, one should distinguish the memory behavior upon bias-stress effects in OFETs by defect states or impurities in semiconductor and/or gate dielectrics, which also lead to \( V_{th} \) shifts [23]. Although this external effect would enhance to be opened the memory window, it cannot be controllable to use as a practical memory as well as not permanent [24].

V. CONCLUSIONS

We fabricated and characterized all-polymer OFETs based on P(NDI2OD-T2) as an active layer, P3HT as a charge-accepting layer, and PMMA as an organic gate dielectric. Furthermore, we also demonstrated memory element in all-polymer OFETs in which P3HT functioned as the charge storage layer. The all-polymer OFETs manifested a memory window of 10.7 V (\( \Delta V_{th} = 10.7 \) V) upon the application of an external gate bias without suffering any major degradation of performance properties. The incorporation of P3HT chains onto the PMMA dielectric films as charge storage sites for holes resulted in a reversible shift in the threshold voltage. After successfully demonstrating the n-channel organic transistor memory, currently we are working on the investigation of the design and fabrication of an organic nonvolatile integrated circuit memory element capable of storing both positive and negative polarity pulses to define distinguishable memory states, i.e., dual-polarity nonvolatile memory, for application in a neural circuit memory element. However, further improvement of the device performance is needed, especially the reliability of the memory operation, lowering of the high operating voltage and retention time, in order to complement our p-channel organic transistor memory with an electron-acceptor layer.

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