Charge transfer and trapping properties in polymer gate dielectrics for non-volatile organic field-effect transistor memory applications

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**A B S T R A C T**

We investigate here charge transfer and trapping characteristics of various chargeable polymer dielectric layers, polystyrene (PS), poly(4-vinyl naphthalene) (PVN), and amorphous fluoropolymer (Teflon® AF) in non-volatile pentacene field-effect transistor (FET) memory devices. Non-volatile memory properties, i.e., the degree of threshold voltage ($V_{th}$) shifts (memory window), the programming and erasing bias, and the retention time, strongly depended on the selection of a charge storage layer, due to its electronic and dielectric properties. The pentacene FETs with PVN or PS showed reversible positive and negative $V_{th}$ shifts by an application of external gate bias. In Teflon® AF device, most significant positive $V_{th}$ shift was obtained indicating a efficient electron injection whereas showed inefficient erasing characteristics via hole injection and storing due to a high electronegative properties of fluorine units in the dielectric.

This result indicates importance of a selection of the chargeable polymer dielectric to obtain efficient organic non-volatile memory with a long retention time.

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1. Introduction

The impressive progress in organic light emitting diodes has triggered the development of other organic devices such as organic field-effect transistors (OFETs) and organic photovoltaics (OPVs), due to their advantage for solution processable low cost manufacturing [1]. Organic memory is one of the emerging areas due to not only fundamental study of charge storage in organic molecules for a high-end, high density molecular memory devices but also high possibility applying in various commercial applications that need information storage at a low cost. One practical example would be a low density memory in radio frequency identification (RFID) tag for item level tagging onto plastic substrates. Several types of organic memory devices have recently been demonstrated, both of the diode structure (organic electrically bistable devices, [2,3] organic–inorganic hybrid memory, [4,5] and molecular electronic memory [6]) and the transistor structure (organic field-effect transistor (OFET) memory with ferroelectric or chargeable gate dielectrics) [7–12].

The functionality of OFET memory arises from field-effect modulation by spontaneous polarization in the polymeric ferroelectric layer or trapped charges in the chargeable polymer dielectrics. Therefore, the configuration is more attractive than other types of organic memory devices because of its non-destructive readout, architectural compatibility with complementary metal oxide semiconductor (CMOS) like circuits, absence of cross-talk problems, and single transistor applications in aspects of stable information storage, device integration and scalability [13]. A few attempts to develop OFET memory have been reported [7–12], and we have also demonstrated stable, non-volatile memory characteristics using chargeable gate dielectrics, i.e., polyelectrets in OFETs [10]. In spite of this progress, details of the operating mechanism such as charge storing sites, charging and discharging process in dielectric are not fully understood [14].

In this paper, we study on a charge transfer and trapping characteristics in non-volatile OFET memory with various chargeable polymer gate dielectrics including polystyrene (PS), poly(4-vinyl naphthalene) (PVN), and amorphous fluoropolymer (Teflon® AF), i.e., polymer electrets in particular the relationship between electrical properties of chargeable polymer dielectrics and the charge storage mechanism. The memory characteristics strongly depended on the unique electronic and dielectric properties of the polymer electrets, and those properties played key roles in stable OFET memory operations.

For the fabrication of polymer electret memory (PEM) devices, a prime-grade silicon wafer ($n \pm Si$) with a 100 nm thick thermally grown oxide was used as substrate. Pentacene (Sigma–Aldrich), PS (Sigma–Aldrich, weight-average molecular weight $M_w = 280$...
kg/mol), PVN (Sigma–Aldrich, $M_w = 175$ kg/mol), and Teflon® AF 16000 (Dupont) were purchased and used without further purification. The polymer electret films (ca. 30–35 nm) were spin-coated using a solution in toluene (PS and PVN) and hexafluorobenzene (Teflon® AF), and after then the samples were dried in a vacuum oven at 90 °C overnight. For active channel layers, 50 nm thick pentacene film was deposited on room temperature substrate in a conventional high vacuum thermal evaporation (<10⁻¹⁰ Torr) with a deposition rate of 0.2–0.3 Å/s. The PEM devices were finished by a metal shadow mask to form source and drain electrodes on pentacene thin film. The devices had a channel length and width of 50 µm and 1.5 mm, respectively. The fabricated bottom-gate/top-contact PEM device configuration is represented in Fig. 1b. The electrical characteristics of these PEM devices were measured with a KEITHLEY 4200-SCS in dark and nitrogen conditions at room temperature.

PS, PVN, and Teflon® AF (amorphous fluoropolymer) were selected to study the dependence of a chargeable dielectrics on memory properties due to its unique electric and dielectric properties. The PS is a commonly used dielectric polymer that was used here as a reference material for comparison with the memory properties due to its large extension of $pi$-orbital than PS, possessing a smaller energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) than that of PS. We could expect better performance memory with a small bandgap. Teflon® AF is an amorphous fluoropolymer having highly electronegative fluorine units in its polymer backbone. Therefore, more efficient electron withdrawing ability and easy electron trapping was anticipated than that of PS and PVN. On the other hand, the deep HOMO level of Teflon® AF can make hole trapping difficult as shown in Fig. 3c.

The pentacene PEM devices showed typical $p$-channel OFET characteristics. The fundamental device parameters such as the field-effect mobility ($\mu_{\text{FET}}$), the threshold voltage ($V_{\text{TH}}$), and the on/off ratio ($I_{\text{on}}/I_{\text{off}}$), were obtained from the conventional characterization equation for OFETs at the saturation region [15]. The overall device performance of PEMs with Teflon® AF was relatively low (the $\mu_{\text{FET}}$ is ca. 0.02 cm² V⁻¹ s⁻¹), which might be due to poor adhesion property of pentacene molecules to ultrahydrophobic Teflon® AF surface. However, PEM devices with PS and PVN all showed reasonably good OFET characteristics (the $\mu_{\text{FET}}$ was ca. 0.4 and 0.6 cm² V⁻¹ s⁻¹ for the devices with PS and PVN, respectively). Moreover, the OFET characteristics could be further improved either by interfacial engineering between the pentacene and polymer gate dielectrics or by optimization of pentacene crystal growth conditions [16].

The $V_{\text{TH}}$ of OFETs with an additional polymer electret layer can be systemically controlled by application of an external gate bias in a short time scale, which could be used as a non-volatile organic transistor memory [17]. These reversible shifts in $V_{\text{TH}}$ could be explained by mobile charge transfer from an organic semiconductor and deep-trapping in polymer dielectric layers or interfaces. The PEM devices with PS, PVN, and Teflon® AF layers also exhibited similar shifts in $V_{\text{TH}}$ upon application of external gate fields. However, the overall memory characteristics, i.e., the amount of shift in $V_{\text{TH}}$ (memory window), its direction in shifts, and the on/off ratio strongly depended on the used polymer dielectric layer. For an intuitive comparison of these polymer electrets in PEMs, the memory window was measured by the application of the same gate biases of 70 V and −70 V in a relatively short time scale (ca. a few ms) for programming and erasing, respectively (Fig. 2).

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**Fig. 1.** (a) Various polymer electret materials: PS, PVN, and Teflon® AF and (b) device configuration of the bottom-gate/top-contact PEM device.

**Fig. 2.** Systematic and reversible shifts in the $V_{\text{TH}}$ of PEMs with various polymer electret materials: (a) PS, (b) PVN, and (c) Teflon® AF. The transfer curves were obtained at $V_g = −15$ V (saturation region) (1st, 3rd $V_g$ sweeps: after application of $V_g = 70$ V, and 2nd, 4th $V_g$ sweeps: after application of $V_g = −70$ V for a few ms).
The PS device had a memory window and an on/off ratio of about 30 V and $10^5$, respectively. The PVN device exhibited further significant shifts in $V_{Th}$ in both the positive and negative directions meaning easier programmable and erasable than the PS device. The measured memory window and on/off ratio for PVN device were 55 V and $10^6$, respectively. In contrast to the PS and PVN devices, the Teflon® AF device showed significant shifts of more than 30 V only in the positive direction meaning easy electron trapping, but no further shift in the negative direction, and it was difficult to restore it to its original state (easily programmable and hardly erasable).

The amount of shifts in $V_{Th}$ that were obtained after application of programmed gate bias for a short period of time (a few ms) is represented in Fig. 3a. Significant shifts in $V_{Th}$ for programming of the PEM devices were initially only observed above a certain threshold condition. The Teflon® AF device had the lowest critical gate voltage for programming ($V_{Th}^{Prog}$), about 30 V, and the other PEM devices with PS and PVN showed quite similar $V_{Th}^{Prog}$ at about 40 V. Above this point, the transfer curves started to show remarkable shifts, and the amount of shift in $V_{Th}$ was also exponentially increased by applying the $V_{Th}^{Prog}$. The material dependence of $V_{Th}^{Prog}$ could be explained by the difference of energy barriers for a charge transfer and trapping between the pentacene and the polymer electret layers. The energy barrier for a charge transfer and trapping is defined as an energy gap between the LUMO of pentacene and the LUMO of the polymer electret. Although the exact values of the LUMO and HOMO for the polymer electrets cannot be directly measured for this study, the relative energy barrier might be estimated from these $V_{Th}^{Prog}$ values. Obviously, the overall HOMO and LUMO gap in PVN would be smaller than that of PS, owing to the longer $\pi$-conjugation length of naphthalene units in the side chain of PVN than the benzene ring in the side chain of PS, resulting in the low LUMO and high HOMO levels. Thus, the $V_{Th}$ was more easily and markedly shifted in PVN device by the application of the same gate bias due to the lower energy barrier (see Fig. 3c).

Teflon® AF has a strong electron withdrawing group in its polymer backbone, and thus definitely has lower LUMO and HOMO levels than those of PS and PVN. Therefore, it induced the lowest energy barrier for electron transfer between the pentacene and Teflon® AF and caused the largest shifts in $V_{Th}$ of the PEM devices.

The degree of shift in $V_{Th}$ upon the application of a reverse gate bias for an erasing process was also obtained. In Fig. 3b, the PEM devices with various polymer electret layers exhibited different erasing characteristics. The PEMs required different values of erasing biases to be completely restored to their initial states. Similar to the programming characteristics, the PVN device showed easy recovery to its original state at relatively low gate bias (ca. 30 V), and the $V_{Th}$ was further significantly shifted more than 30 V to the negative direction by the application of higher reverse gate bias (above ~40 V). On the other hand, the PS and Teflon® AF devices need a higher reverse gate bias for erasing process than the PVN device. In the PS device, ~60 V of gate bias was required to completely restore the transfer curve to its initial state. Moreover, much higher gate bias (~70 V) was needed to fully remove the trapped charges for Teflon® AF because of the large injection barrier height for hole between HOMO energetic level of pentacene and Teflon® AF (Fig. 3c). The erasing characteristics in our PEM devices can be explained by a counter charge injection mechanism. The trapped electrons in polymer electrets were compensated for by the injected counter charges (holes) via reverse gate bias for erasing. Therefore, erasing characteristics in PEM devices depends on the HOMO level difference between the semiconductor and polymer electret. We can conclude that the lower programming and erasing voltage in PVN devices results from the smaller difference of energetic levels from pentacene than other electrets. One interesting result is the memory characteristics in Teflon® AF device. The Teflon® AF devices showed a highly efficient electron injection and storing, but difficult hole injection and storing for erasing process at the same time due to its very low lying HOMO level resulting in inefficient counter charge injection.

Once mobile charges are injected, most of the charges are rapidly deep-trapped in the polymer electrets on a very fast time scale [18,19]. Therefore, the levels of deep-trap sites and the bulk and surface conductivity of polymer dielectrics to dissipate the trapped charges would determine charge stability for a long retention time of the non-volatile memory [18]. In a retention test, the on-current states of PEMs with PS and PVN were more stably sustained for a longer time than that of the Teflon® AF device (Fig. 4). The estimated retention time, i.e., the time required to decrease the on-current to 50% of the initial current state, of PEMs with PS, PVN, and Teflon® AF was about 120, 60, and 7 h, respectively. From these results, Teflon® AF could be considered to have shallower charge trapping levels and relatively higher surface and bulk conductivity.
than PS and PVN devices. In addition, the decay of the on-current state for the PS, PVN, Teflon\textsuperscript{AF} devices also exhibited non-exponential characteristics: a relatively strong initial decay and a subsequent slower decay. This behavior was consistent with the model for long-term trapped charge decay in most polymer electrets [20]. However, the information from this study was not sufficient to conclude the exact charge trapping characteristics for the PEM devices, so more intensive work would be necessary in this respect.

In conclusion, charge transfer and trapping phenomena in non-volatile organic transistor memory devices with PS, PVN, or Teflon\textsuperscript{AF} as chargeable gate dielectrics were investigated. The PEM devices with additional polymeric layers between pentacene and Si\textsubscript{O}\textsubscript{2} gate dielectric showed significant and reversible shifts in the $V_{Th}$ upon application of external gate bias on a short time scale. Moreover, the memory window, programming and erasing characteristics, and retention properties were quite different, depending on unique electronic and dielectric properties of the polymer dielectrics. Among the used polymer dielectric materials, a PVN-based PEMs showed efficient charge transfer and trapping phenomena, which mainly resulted from the lower injection barriers for charge transfer. The injected charges in gate electrets were sustained for more than 100 h. These findings suggest that more optimized PEM devices could be fabricated once the energy levels and conductivities of polymer electrets are systematically considered.

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