Top-gate Organic Field-effect Transistors Fabricated on Shape-memory Polymer Substrates

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ABSTRACT

We demonstrate top-gate organic field-effect transistors (OFETs) with a bilayer gate dielectric and doped contacts fabricated on shape-memory polymer (SMP) substrates. SMPs exhibit large variations in Young's modulus dependent on temperature and have the ability to fix two or more geometric configurations when a proper stimulus is applied. These unique properties make SMPs desirable for three-dimensional shape applications of OFETs. The electrical properties of OFETs on SMP substrates are presented and compared to those of OFETs on traditional glass substrates.

Keywords: Organic transistors, shape-memory polymer, bilayer gate dielectric

1. INTRODUCTION

Organic field-effect transistors (OFETs) have been intensively developed, and their characteristics and processibility have dramatically improved: carrier mobility (μ) values in some OFETs are now even higher than those in amorphous silicon thin-film-transistors (a-Si TFTs) [1]; threshold voltage values (V_{TH}) have been decreased to near zero [2], which enables low-voltage driving of OFET circuits; high operational and environmental stability has also been reported [3], particularly in top-gate bilayer OFET geometries; and new fabrication methods, such as inkjet-printing [4], have been developed.

As the basic properties of OFETs are approaching the required performance for the realization of commercially viable products, applications of OFETs have become an important topic of research. One desirable property of OFETs is the realization of flexible electronic devices, such as wearable electronics. Towards this goal, researchers have been exploring new flexible substrate materials, such as polyimide, poly(dimethylsiloxane) (PDMS), and polyestersulfone (PES). In recent years, shape-memory polymers (SMPs) – part of an emerging class of materials – have shown unique features, such as a variable Young's modulus dependent on temperature, low cure stress, and biocompatibility, as well as the capability of transfer by polymerization [5]. These features make SMPs good candidates as substrate materials for three-dimensional shape applications; for example, human body-embedded sensors can be achieved using a variety of stimuli-responsive SMPs [6]. Reeder *et al.* demonstrated the use of SMP substrates for biomedical applications by building high performance bottom-gate dinaphtho[2,3-*b*:2′,3′-*f*]thieno[3,2-*b*]thiophene (DNTT) OFETs on SMPs and the OFETs coated by SMPs [7]. In addition to the variable modulus of SMPs, the property of returning to the permanent shape in response to stimuli (shape recovery) can be also exploited for self-assembly electronics: Wang *et al.* showed self-wrapping polymers [8], Liu *et al*. demonstrated self-folding polymer sheets [9], and Lu *et al.* reported the electrical actuation with nanopaper-combined SMPs [10].

Here, we report on the direct fabrication of high-performance top-gate 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene)/poly(triaryl amine) (PTAA) OFETs on biocompatible, low cure stress SMP substrates, and compare their performance to that of OFETs fabricated on conventional glass substrates.

Organic Field-Effect Transistors XIV; and Organic Sensors and Bioelectronics VIII, edited by Iain McCulloch, Oana D. Jurchescu, Ioannis Kymissis, Ruth Shinar, Luisa Torsi, Proc. of SPIE Vol. 9568, 95680A

2. EXPERIMENTAL

Shape memory polymer substrates were fabricated as follows: tricyclodecane dimethanol diacrylate (TCMDA, Sigma-Aldrich), 1,3,5-triallyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (TATATO, Sigma-Aldrich), and 2,2-dimethoxy-2-phenyl acetophenone (DMPA, Sigma-Aldrich), a photocuring agent, were mixed in a vial with a composition ratio of 31 mol%, TCMDA and 0.1 wt.% DMPA followed by vortex mixing for 2 min. The vial was covered by aluminum foil to shield the solution from light exposure, and trimethylolpropane tris(3-mercaptopropionate) (TMTMP, Sigma-Aldrich) was added into the solution. After another vortex mixing for 2 min, the vial was sonicated for 5 min for removal of air bubbles inside the solution. All the chemicals were used without additional purification after purchase. Microscope glass slides of desired dimensions were cleaned by sonication in acetone, deionized water, and isopropanol for molding. In order to prevent the polymer from adhering to the glass molds during curing, we coated the surface of the glass slides with Rain-X (Illinois Tool Works Inc.). Two glass spacers of the desired thickness were placed along opposite sides of the bottom glass slide, and the unreacted polymer solution was casted on the bottom glass slide followed by rolling the top glass slide across the surface of the solution. The two glass slides, then, were clamped together with binder clips around the spacers. The mold was placed in the UV chamber for 45 min, spreading the unreacted polymer across the mold, and cured with 365 nm UV radiation for 1 h, followed by another 1 min of UV curing after removing the binder clips. Once the top glass slide was removed, the SMP substrate was post-cured in a vacuum oven for 12 h at 120 °C. The bottom glass slide was kept under SMPs providing rigid and flat backplane during the transistor fabrication process.

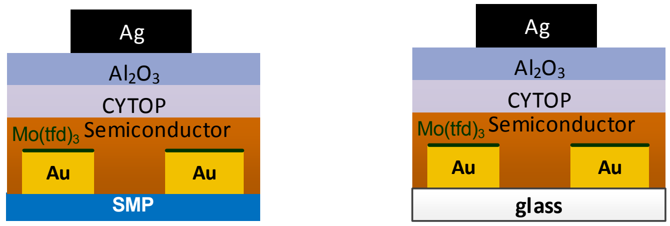
Bottom-contact top-gate TIPS-pentacene transistors were fabricated on both glass and SMP substrates as follows: glass substrates (Corning® Eagle2000TM) were cleaned by sonication in acetone, deionized water, and isopropanol for 5 min each. SMP substrates were used as fabricated without additional cleaning steps. Au (50 nm) was deposited on both substrates by a Denton e-beam evaporator at a deposition rate of 1 Å/s under 2×10^{-6} Torr at room temperature for the source/drain electrodes of OFETs with shadow masks. Molybdenum tris[1,2-bis(trifluoromethyl)ethane-1,2-dithiolene] ($Mo(tfd)_3$) [11] was deposited on top of the Au electrodes by a thermal evaporator through the same shadow mask at a base pressure of $<5 \times 10^{-7}$ Torr for contact doping. A 1:1 weight ratio of TIPS-pentacene (15 mg) and PTAA (15 mg) blend was dissolved in anhydrous 1,2,3,4-tetrahydronaphthalene for a concentration of 30 mg/mL. A 70 nm-thick TIPS-pentacene/PTAA layer was spin-coated at 500 rpm for 10 s with 500 rpm/s acceleration and 2000 rpm for 20 s with 1000 rpm/s acceleration, followed by annealing at 100 ºC for 15 min on a hot plate in a N_2-filled glove box. CYTOP (ASAHI GLASS, CTL-809M) diluted with a solvent (ASAHI GLASS, CT-SOLV180) (1:3.5 volume ratio) was spin-coated on top of the semiconductor layer at 3000 rpm for 60 s (acceleration of 10000 rpm/s) to produce a 35 nm-thick film. Samples were annealed at 100 ºC for 10 min on a hot plate inside the glove box. A 40 nm-thick Al_2O_3 film was grown in a Savannah 100 ALD system from Cambridge Nanotech. The film was deposited at a processing temperature of 110 ºC using alternating exposures of trimethylaluminum and water vapor. 100 nm-thick Ag gate electrodes were deposited by thermal evaporation through a shadow mask at a base pressure of $<5 \times 10^{-7}$ Torr. Current-voltage (*I-V*) characteristics of OFETs and the resistance of the patterned films were measured using an Agilent E5272A source/monitor unit in a N_2-filled glove box.

3. RESULTS AND DISCUSSION

Since the organic semiconductor layer is spin-coated on the substrates, we investigated the surface properties of the SMP substrates by contact angle measurements and by X-ray photoelectron spectroscopy (XPS). Figure 1 shows a water droplet on an SMP substrate. The measured water contact angle from three different locations was 35 (±1.9) °. The XPS measurement revealed the presence of sulfur, attributable to TMTMP, as well as that of carbon, oxygen, and nitrogen.

Figure 1. Water droplet on SMP substrate.

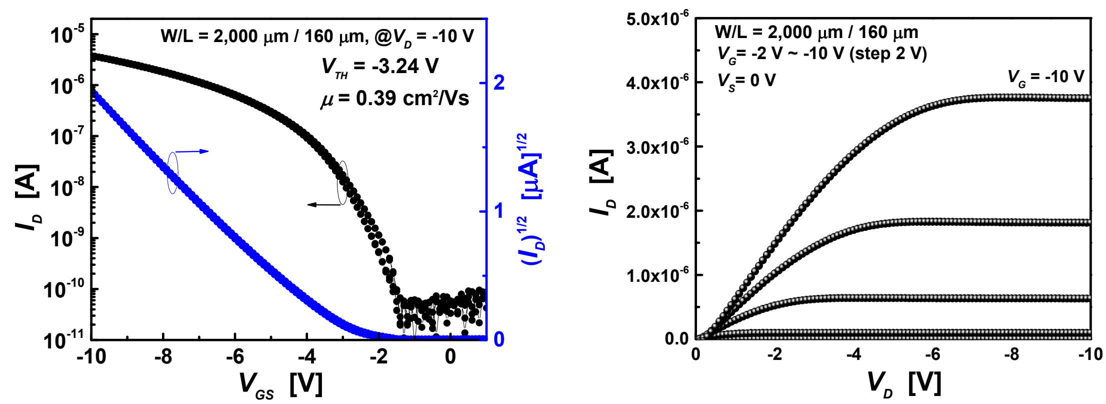
The fabricated top-gate TIPS-pentacene/PTAA OFETs have the vertical structure described in figure 2. The organic semiconductor layer is deposited directly on top of the substrate and the CYTOP/Al_2O_3 bilayer gate dielectrics are adapted for high-performance OFETs. Source and drain electrodes are contact-doped using $Mo(tfd)_3$ to improve charge injection and to reduce contact resistance parasitic effects [12].



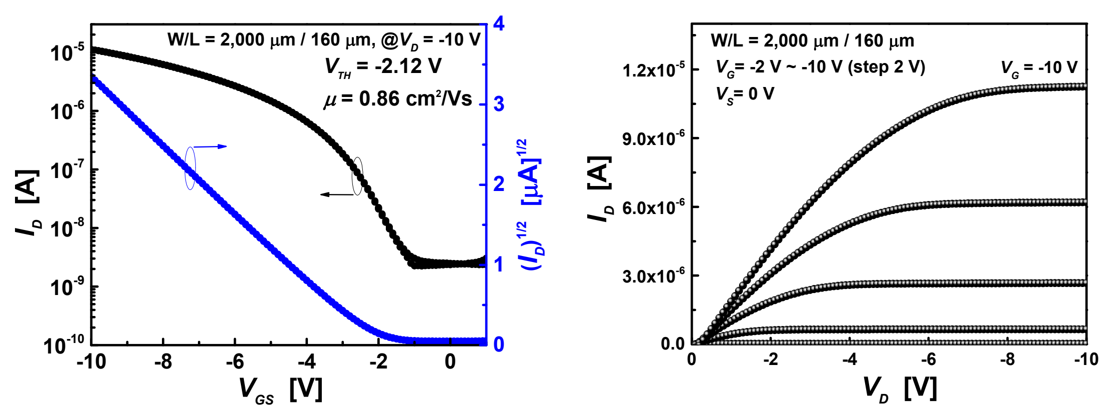
(a) (b)

Figure 2. Vertical structure of fabricated OFETs on (a) SMP and (b) glass substrates.

The fabrication yield for OFETs on SMP substrates was 31%, lower than the 69% yield obtained for OFETs on glass. The device failures on SMP substrates are mostly from dewetting of TIPS-pentacene/PTAA solution on SMP substrates and electrical shorting between gate and source/drain electrodes. Figure 3 shows the current-voltage transfer and output



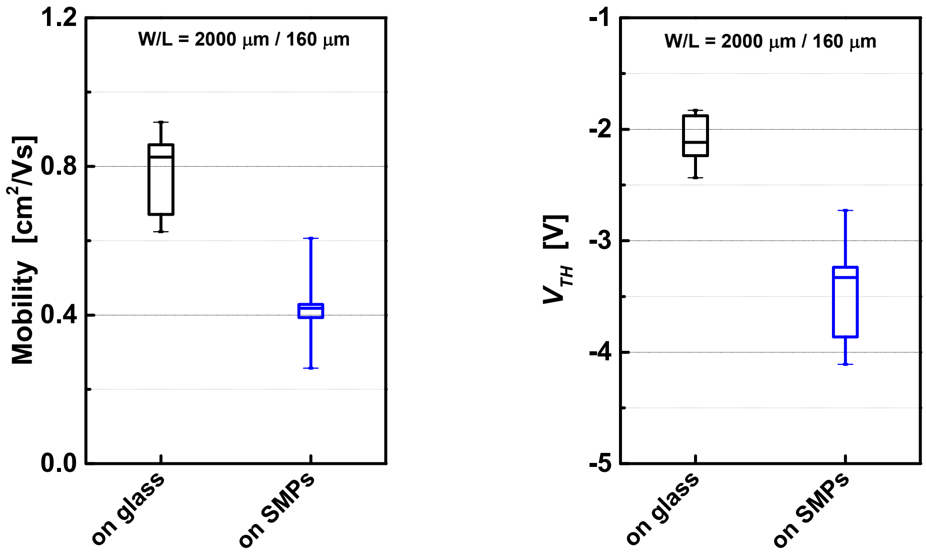
(a)



(b)

Figure 3. Current-voltage transfer (left) and output (right) characteristics of TIPS-pentacene/PTAA transistors on (a) SMP and (b) glass substrates

characteristics of fabricated OFETs on both SMP and glass substrates. As shown in figure 3(a), OFETs on SMP substrates follow the square law of typical field-effect transistors, and have average mobility values of 0.4 (±0.1) cm^2/Vs and threshold voltage values of -3.5 (±0.5) V (average values from six devices), while on glass, OFETs displayed mobility and threshold voltage values of 0.8 (±0.1) cm^2/Vs and -2.1 (±0.2) V, respectively (average values from 11 OFETs). OFETs on SMP substrates present a clear saturation region and low contact resistance as shown by their output curves. However, they also display small but measurable hysteresis effects in their *I-V* transfer characteristics, which did not appear in OFETs on glass substrates in the same batch.



(a) (b)

Figure 4. Comparison of (a) mobility and (b) threshold voltages of OFETs on SMP and glass substrates.

4. CONCLUSIONS AND FUTURE WORK

Shape-memory polymers have the potential to be used for wearable and bioimplantable electronics, and we successfully fabricated top-gate organic field-effect transistors directly on SMP substrates that have threshold voltages of -3.5 V with mobility values of 0.4 cm^2/Vs in average. The OFETs display overall good characteristics, albeit not as good as those of reference OFETs fabricated on glass. The reduced yield for OFETs on SMP substrates is found to be related to dewetting of the TIPS-pentacene/PTAA film. Preliminary data suggest that the impaired performance of the OFETs on SMPs, such as the hysteresis observed in the electrical characteristics, may correlate with the diffusion of impurities from SMPs into the organic semiconductor. These research results suggest that the top-gate OFETs can be directly fabricated on SMP substrates for soft electronics with good electrical performance and, at the same time, suggest the need for a proper buffer layer to address the wetting and impurity issues. Further optimization of the device geometry to include such buffer layers and detailed studies of the mechanical properties of OFETs on SMPs are currently under way.

5. ACKNOWLEDGEMENTS

This research is supported in part by the Academic Training Program of Samsung Display (S.C.). Research on electrical dopants used to reduce the contact resistance is funded in part by the Office of Naval Research (ONR) through programs

N00014-14-1-0126 and N00014-14-1-0580. The research is also supported by the DARPA Young Faculty Award Program and a DARPA Director's Fellowship (W.V.).

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Citation:

Choi, Sangmoo, Canek Fuentes-Hernandez, Cheng-Yin Wang, Andrew Wei, et al. 2015. "Top-gate organic field-effect transistors fabricated on shape-memory polymer substrates." Proc. SPIE 9568, Organic Field-Effect Transistors XIV; and Organic Sensors and Bioelectronics VIII, 95680A, doi:10.1117/12.2188684