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ARTICLE · SEPTEMBER 2010

DOI: 10.1063/1.3491815

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Citation: Appl. Phys. Lett. **97**, 133303 (2010); doi: 10.1063/1.3491815
View online: http://dx.doi.org/10.1063/1.3491815
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v97/i13
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Air-stable n-type organic thin-film transistor array and high gain complementary inverter on flexible substrate

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(Received 5 May 2010; accepted 29 June 2010; published online 27 September 2010)

Air-stable n-type organic thin-film transistor (TFT) arrays and a complementary inverter circuit were fabricated on a flexible substrate. A benzobis(thiadiazole) (BBT) derivative-based TFT showed excellent air- stability and performances such as an electron mobility of over 0.1 cm^2/V s, a large ON/OFF ratio over 10^8 when combined with a cross-linkable olefin-type polymer gate dielectric. In addition, an organic complementary inverter that combined the BBT derivative and a pentacene TFT demonstrated a sharp switching behavior and a high gain of over 150. We attribute these excellent characteristics to a combination of the low-lying lowest unoccupied molecular orbital level of n-type semiconductor material and the low interface trap of the gate dielectric. © *2010 American Institute of Physics*. [doi:10.1063/1.3491815]

The performance of organic thin-film transistors (OTFTs) has been significantly improved over the past decade. Recent reports of high-performance OTFTs and their application to a wide range of electron devices—including flexible displays, integrated circuits, and sensors—suggest the potential advantages of OTFTs in the fabrication of flexible electronics.[1] However, the air stability and operation reliability of OTFTs are still unsatisfied. p-type organic semiconductor (OSC) materials attained both a high hole mobility and stability when compared to Si TFTs under ambient air conditions;[2,3] by contrast, high performance, and air stability is still under investigation for n-type OTFTs. To achieve low-power complementary logic circuit, the development of air-stable n-type OTFT with high performance is crucial. Recently, studies on air-stable n-type TFTs based on relene bisimide,[4] perylene bisimide,[5–7] and naphthalenetetracarboxylic diimide[8] were reported but there has been little study done concerning the characteristics and stability of n-type TFTs with practical device dimensions. In many cases, channel lengths of the TFT were large (over 50 μm) and the devices were fabricated in top-contact configuration. Performance of the OTFT was generally degraded when the channel length was decreased due to a large contact resistance[9] and a space charge limited current.[10] The development of high performance n-type OTFTs with short channel lengths is key when considering practical applications in such devices as logic circuits and displays.

In addition to the OSC material itself, the gate insulating materials and the interface condition between the OSC and the dielectric film also affect the overall stability of OTFTs.[11,12] Choosing the appropriate materials and minimizing the interface trap density at the gate dielectric is essential to enhance the OTFTs' stability and performance. In terms of the gate dielectric, polymer materials are the most favorable candidates for low-cost and solution process. In particular, low-k and hydrophobic polymer gate dielectrics, which do not contain hydroxyl groups, are known to offer stable and hysteresis-free OTFT operation.[11,13] Excellent transistor performances with polymer gate dielectrics, such as cross-linkable poly(4-vinylphenol)[14,15] and amorphous fluoropolymer,[16–18] have been reported.

In this study, we describe air-stable n-type OTFT arrays and complementary inverter circuits with short channel length on a flexible substrate. We used a recently developed n-type OSC material based on a benzobis(thiadiazole) (BBT) derivative with trifluoromethylphenyl groups (FPTBBT) to improve the electron injection and air stability. This derivative has a lowest unoccupied molecular orbital (LUMO) level of 5.05 eV and a narrow energy gap of 1.2 eV.[19] A low-temperature cross-linkable olefin-type polymer was used as the gate dielectric. Combining these two distinguishing materials, we attempt to address the above issues.

Figure 1(a) shows molecular structure of the FPTBBT

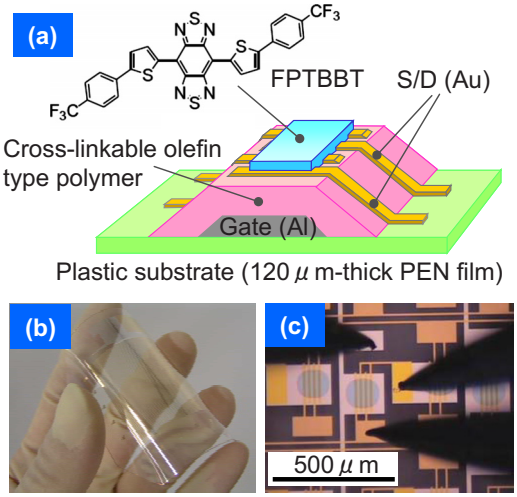

FIG. 1. (Color online) (a) Molecular structure of FPTBBT derivative and schematic cross-section of FPTBBT-based n-type TFT with BC configuration and (b) photograph of FPTBBT-based TFT array on flexible substrate. 64×64 matrix array was fabricated in 3 in. area. (c) Optical microscope image of fabricated array structure. Channel length and width are 5 μm and 200 μm, respectively.

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derivative and the device structure of a bottom-contact (BC) n-type TFT with the olefin-type polymer gate dielectric. A photograph of the fabricated 64×64 matrix array on the flexible substrate is also shown in Fig. 1(b). These arrays were prepared by using a simple three-step lithography process. The maximum processing temperature is 120 °C. 120 μm thick PEN film was used as the flexible substrate. After cleaning the substrate, a 100 nm thick SiO_2 layer that acts as the barrier and the adhesion layer was formed by a sputtering method at room temperature. Photolithography-defined 30 nm thick aluminum (Al) was used as a gate electrode. We spin-coated a cross-linkable olefin-type polymer derivative as the gate dielectric. ZOP-202 from the Zeon Co. was dissolved in diethylene glycol ethyl methyl ether in the ratio of 1:5 and then spin-coated at 2000 rpm for 60 s on the entire substrate. Next, the film was cured at 120 °C on a hotplate for 2 h in ambient air conditions, yielding a 180 nm thick film (measured by an optical interference method). This olefin-type polymer dielectric has many advantages, including a low curing temperature, high transparency, high solvent resistance, very low hygroscopicity, and low dielectric constant. This material does not contain hydroxyl groups in its main skeleton. From the atomic force microscopy measurement, we found the surface roughness of the spin-coated film was very smooth and the rms value was below 0.3 nm. From high frequency (1 kHz) capacitance-voltage measurement, the dielectric constant of the dielectric film was estimated to be 2.7. Compatibility of wettability and low surface energy of the gate dielectric are also crucial when applying the polymer material to the integration process. This olefin-type polymer dielectric exhibited a relatively high water contact angle of 78° as well as a hydrophobic surface while maintaining excellent wettability for common organic solvents.

The source/drain (S/D) electrode of a 30 nm thick Au was directly evaporated on the dielectric and patterned by a wet-etching method. A small linewidth of 5 μm was used to minimize the capacitive gate/source overlap. The photolithography process often leads to contaminations and defects at the surface of the polymer gate dielectric, so to eliminate residues and obtain the intrinsic hydrophobic surface, the surface of the channel area was cleaned and the device was annealed at 110–120 °C after the S/D electrode patterning. Finally, 50 nm thick FPTBBT film was evaporated at room temperature and patterned. All electrical measurements were performed in ambient air (the relative humidity ~50%) under dark conditions using a Keithley 4200-SCS semiconductor parameter analyzer and a SUSS semiauto proving system.

Figures 2(a) and 2(b) illustrates the typical output and transfer characteristics measured in saturation with V_{DS}=−15 V for the BC n-type TFT array with the short channel length L=5 μm. The fabricated devices exhibited pronounced saturation curves, a steep onset with a near zero turn-on voltage, and a low V_T of 5.2 V. High electron mobility—over 0.1 $cm^2/V\,s$—was obtained from the slope of plots of $(I_{DS})^{1/2}$ versus V_{GS} in the saturation region. The linearity at the low V_{DS} in Fig. 2(a) indicates an Ohmic-type injection, which is attributed to the low injection barrier between the work function of the S/D electrode and the LUMO energy of the FPTBBT derivative. The BC-TFT arrays also showed a low off-current under 10^{-13} and very large I_{ON}/I_{OFF} ratio of over 10^8 in ambient air, which is two to three orders of magnitude higher than those previously reported in n-type TFTs. This is attributed to the low leakage current of the dielectric film. n-type OTFTs often lack operational stability due to ambient oxidation or charge carrier trapping; electron carriers are particularly likely to be trapped at the semiconductor/gate dielectric interface. These traps are generated by interfacial chemical functionalities/species such as hydroxyl groups and ambient oxidants such as oxygen and water.[13,20,21] From the Fig. 2(b), the fabricated TFT showed a negligible small hysteresis with respect to the gate bias swing. The hysteresis behavior was caused by electron traps such as hydroxyl groups or mobile ions at the semiconductor/dielectric interface.[22] Our results suggested that the olefin-type polymer dielectric possess a minimal density of OH groups and impurities. We also estimated the subthreshold slope SS and the interface trap density D at the semiconductor/dielectric interface. Small SS of 0.45 V/decade and D=5.4×10^{11} $cm^{-2}\,eV^{-1}$ were obtained from the slope of the log I_{DS}-V_{GS} curve in the subthreshold region. These results indicate that our device has superior dielectric-semiconductor interface qualities.

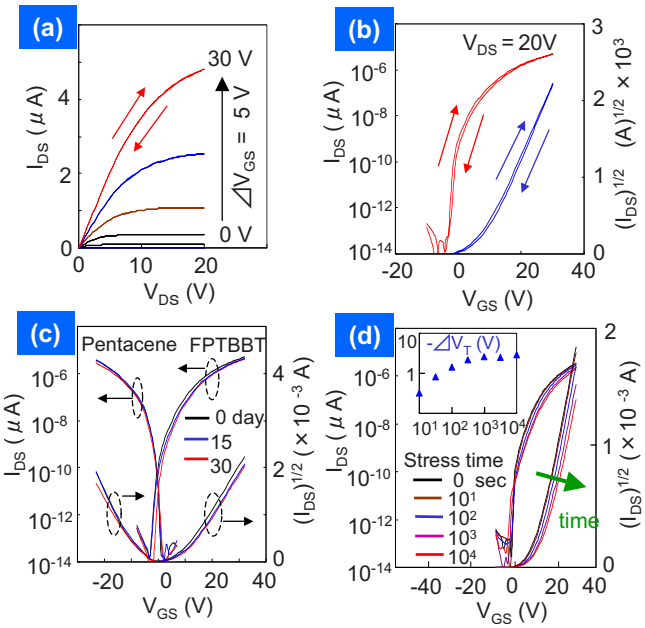

FIG. 2. (Color online) Electrical characteristics of fabricated FPTBBT-based n-type TFT array with L=5 μm on plastic substrate. Measurements were performed under ambient air dark conditions. (a) Output characteristics and (b) transfer characteristics. (c) Long-term air stability (stability of pentacene-based TFT is also shown as a reference). (d) Variation in transfer curves under constant bias stress of V_{GS}=20 V and V_{DS}=5 V (inset shows stress induced ΔV_T as a function of stress time).

We measured the long-term air stability and dc bias stress instability on the device without any encapsulation layer to determine the reliability of the fabricated TFT array. To avoid ambiguous results, each measurement was performed on a neighboring fresh device.[23] Figure 2(c) shows the measured transfer curve as a function of air exposure day. The stability of a p-type pentacene-based TFT with the same dimensions and the gate dielectric is plotted in the figure as a reference. After 1 month, the fabricated FPTBBT-based TFT array showed excellent air stability without any significant degradation of performance. Although the electron mobility was slightly decreased from 0.1 to 0.088 $cm^2/V\,s$ and a small V_T shift of 0.9 V was observed, the I_{ON}/I_{OFF} ratio and the subthreshold slope remained almost completely un-

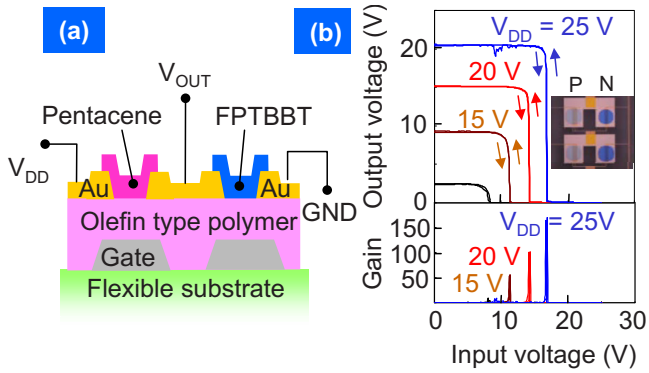

FIG. 3. (Color online) Air-stable complementary inverter circuit based on FPTBBT and pentacene on flexible substrate. (a) Schematic structure of complementary inverter circuit. (b) V_{out}-V_{in} characteristics and gain curves with various V_{DD}.

changed. We attribute this excellent stability to both the high resistance property to ambient oxidation of the semiconductor material and the low interface trap density of the gate dielectric. As the figure clearly shows, the pentacene TFT exhibited a similar tendency and excellent stability: the shift of V_T and the increase in off-current remained almost completely unchanged after 1 month. It is known that pentacene TFTs with SiO_2 gate dielectrics are degraded under ambient air storage conditions by oxidization or charge trapping;[24,25] our results indicate that using an olefin-type polymer gate dielectric provides excellent interface quality and thus improves the air stability. Figure 2(d) shows the transfer curves of the n-type TFT array before and after stressing with a constant V_{GS} of 20 V and a constant V_{DS} of 5 V for 10^5 s. The inset shows bias stress-induced threshold voltage shift ΔV_T as a function of stress time. Despite the short channel length (L=5 μm), the fabricated n-type TFT showed the good operational reliability. Although a small positive ΔV_T of 2.9 V was observed, the variation of the I_{ON}/I_{OFF} ratio and the mobility were very small after the stress. The main cause of the ΔV_T can possibly be attributed to the absorption and diffusion of H_2O into the OSC film.[26]

To demonstrate the usability of air-stable n-type OTFTs in circuit applications, we fabricated an organic complementary inverter circuit on a flexible substrate. The fabricated inverter was composed of a short channel pentacene and an FPTBBT-based TFT with a photolithography-defined gate and S/D electrodes. Channel length of the both transistors are 5 μm. A buffered inverter with two inverters was implemented to decrease the output impedance of the circuit.[27] Figure 3 shows (a) the schematic structure and (b) the V_{OUT}-V_{IN} characteristics of the fabricated inverter. Our inverter exhibited excellent output switching operation with a steep curve, negligible hysteresis, and a high signal gain of up to 160 within the relatively low supply voltages ranging from 15 to 25 V. The performance of the inverter was almost unchanged after 1 week in ambient air.

In summary, we fabricated an air-stable n-type short channel OTFT array based on the BBT derivative with a cross-linkable olefin-type polymer gate dielectric. The fabricated OTFT exhibited a high electron mobility over 0.1 $cm^2/V\,s$ and a very large ON/OFF ratio over 10^8 under ambient air storage conditions. We achieved excellent air stability and operational reliability by using a BBT derivative with a low LUMO level and a gate dielectric with low interface trap density. The olefin-type polymer gate dielectric also exhibited good compatibility with both of p- and n- type OSC materials. This combination of OSC materials and the polymer gate dielectric is promising for future use in various flexible electronics applications.

The authors would like to thank K. Sugitani, T. Kato, and H. Oomori of Zeon Co. for providing polymer dielectric material and for various discussions.

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