Flexible low-voltage organic transistors based on a novel, high-mobility organic semiconductor

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Organic thin-film transistors (TFTs) are of interest for a variety of large-area electronics applications, such as flexible active-matrix displays and conformable sensor arrays [1]. Among the challenges in the development of high-performance organic TFTs, especially on flexible polymeric substrates, is to realize organic TFTs that simultaneously provide a large field-effect mobility, a large on/off current ratio, and a steep subthreshold swing.

The reason why a large field-effect mobility is desirable is that it determines the maximum frequency at which a field-effect transistor can be operated [2]. In organic TFTs the largest field-effect mobilities are typically obtained by using organic semiconductors that condense into thin films with a favorable crystal structure and a low defect density; such as pentacene, dioctyl-benzothienobenzothiophene (C_8-BTBT), and dinaphtho-thienothiophene (DNTT) [3].

The on/off current ratio is the ratio between the on-state drain current and the off-state drain current of the transistor. Maximizing the on-state drain current is desirable, because this maximizes the rate at which intrinsic and parasitic capacitances are charged and discharged during rapid switching events. Minimizing the off-state drain current is important, since this minimizes the charge leakage and hence the loss of information from the display or sensor element during the frame refresh time. While the on-state drain current is directly proportional to the field-effect mobility, the off-state drain current can be minimized by avoiding charge leakage through the semiconductor and through the gate dielectric of the transistor. Charge leakage through the semiconductor can be minimized by choosing a semiconductor with a large HOMO-LUMO gap (to block the undesired injection of minority carriers from the drain contact) and by purification of the semiconductor (to eliminate bulk impurities). Avoiding charge leakage through the gate dielectric is straightforward if the gate dielectric is either sufficiently thick (to eliminate direct tunneling and to minimize Fowler-Nordheim tunneling and Ohmic currents) or grown at a sufficiently high temperature (to produce a dense, defect-free insulator). For example, organic TFTs with SiO_2 gate dielectrics grown at temperatures above 800 ºC or using spin-coated polymer gate dielectrics with a thickness of several hundred nanometers can have on/off current ratios as large as 10^{10}.

However, high process temperatures interfere with the goal of manufacturing organic TFTs on flexible polymeric substrates (which typically have a glass transition temperature below 150 ºC), and thick gate dielectrics usually have a rather small capacitance per unit area, which results in a large operating voltage and a poor subthreshold swing. The reason for the latter is that the subthreshold swing is determined by the ratio between the density of trap states at the semiconductor/dielectric interface and the capacitance per unit area of the gate dielectric. Organic TFTs on polymeric substrates that provide low charge leakage, low operating voltages, and a steep subthreshold swing therefore require a gate dielectric that is dense, defect-free, has a large capacitance per unit area, and can be produced at temperatures below about 150 ºC. To realize flexible organic TFTs that simultaneously provide a large field-effect mobility, a large on/off current ratio, and a steep subthreshold swing we have therefore combined a novel high-mobility organic semiconductor with a high-capacitance gate dielectric that is based on a thin, oxygen-plasma-grown aluminum oxide layer and a solution-processed organic self-assembled monolayer, both of which are obtained at temperatures below 100 ºC.

The transistors were fabricated on 125-µm-thick, flexible, transparent polyethylene naphthalate (PEN) film. Aluminum gate electrodes with a thickness of 20 nm were deposited by thermal evaporation in vacuum through a polyimide shadow mask and briefly exposed to an oxygen plasma to create an AlO_x layer with a thickness of 3.6 nm, followed by immersing the substrate in a 2-propanol solution of tetradecylphosphonic acid in order to form a 1.7-nm-thick self-assembled monolayer (SAM) on the AlO_x surface. The result is a dense AlO_x/SAM gate dielectric with a thickness of 5.3 nm and a capacitance of 800 nF/cm^2 that allows the TFTs to operate with relatively low voltages of about 2 to 3 V [1-3]. A 20-nm-thick layer of the organic semiconductor 2,9-didecyldinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (C_{10}-DNTT; chemical structure shown in Fig. 1a) that was recently developed at Hiroshima University and was purified by temperature-gradient sublimation prior to use was then vacuum-deposited at a substrate temperature of 80 ºC and patterned using a shadow mask. Compared with the more common organic semiconductors pentacene and DNTT, the decyl substituents in C_{10}-DNTT force the molecules into a tighter solid-state packing with enhanced overlap of the delocalized molecular orbitals, which creates the possibility for larger carrier mobilities in the plane parallel to the substrate surface. C_{10}-DNTT also has a relatively large HOMO-LUMO gap of almost 3 eV that is beneficial for achieving a small off-state drain current and hence a large on/off current ratio.

However, the long aliphatic substituents protruding from the conjugated core of the C_{10}-DNTT molecules also impede the charge transport in the vertical direction and hence the efficient exchange of charge carriers between the C_{10}-DNTT molecules and the Au source and drain contacts located on top of the semiconductor layer. Strategies to alleviate this effect and provide improved charge exchange, reduced contact resistance, and increased effective field-effect mobility include the introduction of area-selective contact doping at the interface between the semiconductor and the metal contacts [2]. Therefore, a 1-nm-thick layer of the strong organic molecular dopant NDP-9 that has been developed by Novaled [2], a 2-nm-thick layer of the non-alkylated organic semiconductor DNTT [3], and another 1-nm-thick layer of NDP-9 were sequentially deposited onto the C_{10}-DNTT layer through a shadow mask prior to depositing the Au source and drain contacts through the same shadow mask. By depositing the NDP-9 / DNTT / NDP-9 stack and the Au contacts through the same shadow mask, the doping effect is confined to the contact regions of the transistors, which is important to maintain a large on/off current ratio (see Fig. 1b for a schematic cross-section of the completed TFTs).

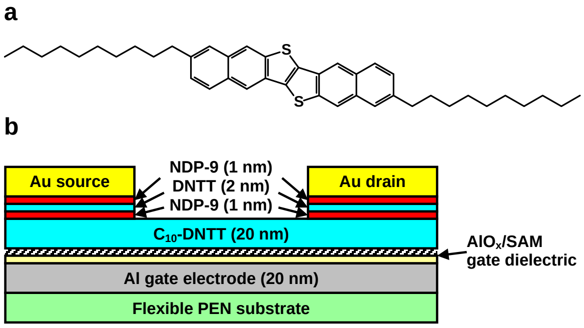

Figure 1:
(a) Chemical structure of the organic semiconductor C_{10}-DNTT.
(b) Schematic cross-section of the C_{10}-DNTT transistors with NDP-9 contact doping.

Figure 2 shows the current-voltage characteristics of a C_{10}-DNTT TFT with NDP-9 contact doping on a flexible PEN substrate. The TFT has a channel length of 30 µm, a field-effect mobility of 4.3 cm^2/Vs, a maximum gate current of 0.4 pA, an off-state drain current below 0.1 pA, an on/off current ratio of 10^8, and a subthreshold swing of 68 mV/decade. To our knowledge these are the largest on/off current ratio, the steepest subthreshold swing, and the second-largest field-effect mobility reported for a flexible organic TFT. Researchers at Nanyang Technological University Singapore recently reported a field-effect mobility of 6.4 cm^2/Vs for flexible pentacene TFTs which also operate with low voltages (3 V), but these TFTs show a somewhat larger off-state drain current (100 pA), a smaller on/off current ratio (2×10^5), and a less steep subthreshold swing (160 mV/decade).

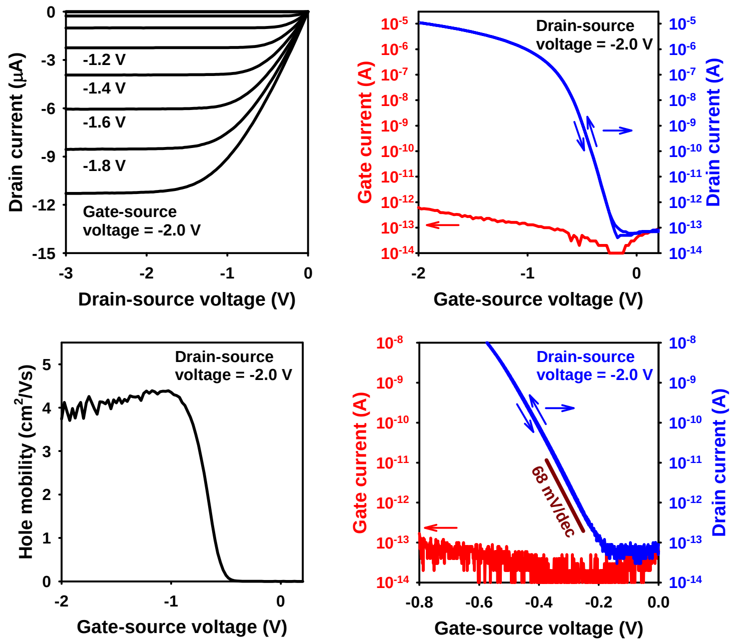

Figure 2:
Electrical characteristics of a flexible C_{10}-DNTT TFT with a channel length of 30 µm and a channel width of 100 µm. The transistor has a field-effect mobility of 4.3 cm^2/Vs, an on/off current ratio of 10^8, and a subthreshold swing of 68 mV/decade.

To evaluate the dynamic performance of the flexible C_{10}-DNTT TFTs we have designed and fabricated 5-stage ring oscillators composed of unipolar inverters based on a saturated-load design. The static transfer characteristics of such an inverter are shown in Fig. 3a. Figure 3b shows the signal propagation delay per stage as a function of the supply voltage measured for flexible ring oscillators with two different design rules. When the TFTs have a channel length of 30 µm and a gate-to-contact overlap of 30 µm, the signal delay measured at a supply voltage of -3 V is 25 µsec per stage (blue data points in Fig. 3b), whereas when the TFTs have a channel length of 10 µm and a gate-to-contact overlap of 15 µm (which are the smallest lateral dimensions attainable with our polyimide shadow masks), the signal delay measured at a supply voltage of -3 V is 5 µsec per stage (red data points in Fig. 3b). This is the shortest signal delay reported for an organic ring oscillator at supply voltages below 7 V.

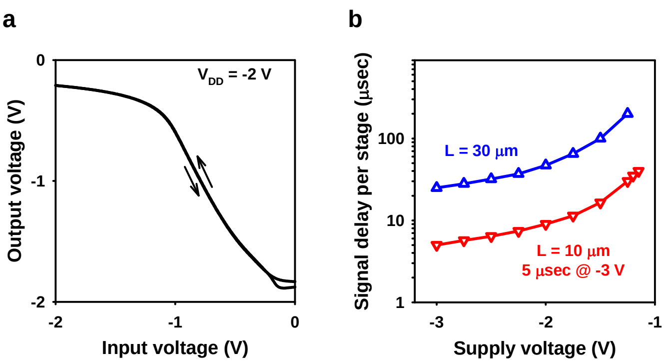

Figure 3:
a) Static transfer characteristics of an inverter with saturated load based on C_{10}-DNTT TFTs on a flexible PEN substrate.
b) Signal propagation delay as a function of supply voltage of flexible 5-stage ring oscillators based on C_{10}-DNTT TFTs with channel lengths of 30 µm and 10 µm.

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[2] *Ante, F., D. Kälblein, U. Zschieschang, T. W. Canzler, A. Werner, K. Takimiya, M. Ikeda, T. Sekitani, T. Someya, and H. Klauk.* Small **7**, 1186-1191 (2011).

[3] *Zschieschang, U. , F. Ante, D. Kälblein, T. Yamamoto, K. Takimiya, H. Kuwabara, M. Ikeda, T. Sekitani, T. Someya, J. Blochwitz-Nimoth, and H. Klauk.* Org. Electronics **12**, 1370-1375 (2011).

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