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Ultra-low voltage air-stable polyelectrolyte gated n-type organic thin film transistors

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Complementary circuits, processing digital signals, are a cornerstone of modern electronics. Such circuits require both p- and n-type transistors. Polyelectrolytes are used as gate insulators in organic thin film transistors (OTFTs) to establish an electric double layer capacitor upon gate bias that allows low operational voltages (<1 V). However, stable and low-voltage operating n-channel organic transistors have proven difficult to construct. Here, we report ultra-low voltage n-channel organic polymer-based transistors that are stable in ambient atmosphere. Our n-type OTFTs exhibit on/off ratios around 10^3 for an applied drain potential as low as 0.1 V. Since small ions are known to promote electrochemical reactions within the semiconductor's channel bulk and typically slow down the transistor, we use a solid polycationic gate insulator that suppresses penetration of anions into the n-channel semiconductor. As a result, our n-channel OTFTs switch on in under 5 ms and off in less than 1 ms. © 2011 American Institute of Physics. [doi:10.1063/1.3626587]

Organic transistors hold the promise for solution processable, disposable, low-cost, ubiquitous electronic circuits for a wide range of applications.¹ These transistors have been explored for a variety of applications such as addressing, driver circuits for displays, radio frequency identification (RFID) tags, and pressure sensing elements.^{2,3}

The electronic performance of organic thin film transistors (OTFTs) has been considerably improved in recent years both in terms of speed and power consumption.⁴⁻⁷ Complementary circuits that include p- and n-type transistors operating at low voltage offer low static power consumption, which is of particular importance for distributed or single-use applications. Complementary circuits have additional advantages such as a high degree of noise immunity. Moreover, as compared to other classes of digital circuit solutions, a complementary technology allows for fabrication of high density circuits.^{7,8} One strategy to reach low operating voltages is to utilize electrolytes as the gate insulator in OTFTs. In such gating configurations, one takes advantage of the exceptionally high capacitance (10-100 $\mu\text{F}/\text{cm}^2$) generated by the electrical double-layer (EDL) formed at the semiconductor-electrolyte interface.⁹⁻¹¹

Up to now, electrolyte-gated polymer-based transistors have mainly been demonstrated with hole transporting channels, because electron transporting organic semiconductors are typically unstable in air and at humid conditions. However, an air-stable n-type conjugated polymer with high electron mobility was recently synthesized: poly[N,N'-bis(2-octyldecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene) ([P(NDI2OD-T2)]_n, commercialized as ActivInk™ N2200 by Polyera®). A field effect electron mobility of 0.85 cm^2/Vs has been reported for this material.^{12,13}

In the present study, we have used this n-type organic semiconductor together with a polycation gate insulator to manufacture OTFTs. The motivation for using a polycation gate insulator in a n-channel OTFT stems from the good per-

formance recently achieved in p-channel OTFT equivalents incorporating a polyanion as the gate insulator.¹⁴ The immobile ionomers prevent electrochemical reaction at the semiconductor-electrolyte interface. The polycation is synthesized by mixing poly(vinylbenzyl chloride) (PVBC) dissolved in tetrahydrofuran (THF) with dimethylbenzylamine (DMBA) at 80 mol. % per monomer unit PVBC (see Figure 1 for chemical structure).

The amine of the DMBA reacts with the carbon-chlorine bond on the PVBC through a nucleophilic substitution. The reaction produces quaternary ammonium cations within the polymer chains including chloride counterions. The charged polymer precipitates in THF but can be re-dissolved in an aqueous solution. 1,4-diazabicyclo[2.2.2]octane (DABCO) (5 mol. % per monomer unit PVBC) is then added to the solution as a thermal crosslinker. This polyelectrolyte system is referred to as poly(vinyl dimethyl dibenzyl ammonium chloride) (PVDMDBAC).

We fabricated an EDL capacitor by spin coating a 120 nm film of PVDMDBAC (from a 5 wt. % 50/50% H₂O/1-propanol solution) atop gold electrodes patterned on glass substrate. The polyelectrolyte is then annealed to promote cross-linking between the difunctional DABCO and residual benzyl chloride groups in the polymer. Finally, we vacuum deposited a 600 μm layer of titanium on top of the polyelectrolyte layer. The polyelectrolyte capacitor stack is then characterized using impedance spectrometry (novocontrol alpha high resolution dielectric analyzer); the results are given in Figure 2. The large value of the capacitance per area [15 $\mu\text{F}/\text{cm}^2$] at lower frequencies, together with a phase angle close to -90° , indicates that an electrical double layer is generated at the metal-electrolyte interfaces (see Figure 2) as the chloride ions accumulate at the positively polarized electrode. The EDL is formed in less than 100 μs (assuming the formation starts at a phase angle of -45°).

The ability of the polycation to achieve such high capacitance values suggests that it is possible to use the material as the gate insulator in fast-switching n-type OTFTs operating at low voltages. Interestingly, the capacitance

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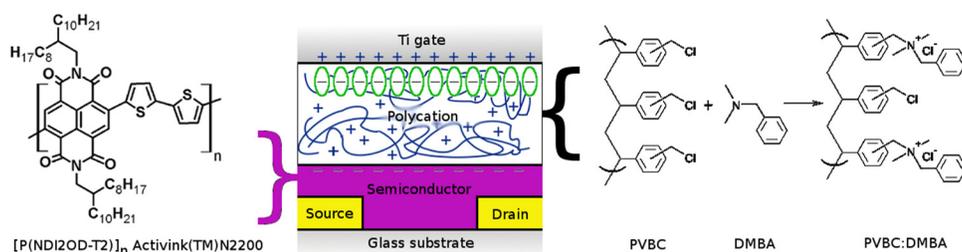


FIG. 1. (Color online) A schematic cross-section of the OTFT, with the chemical structures of the different layers.

remains significantly high even at relatively high frequencies [$4 \mu\text{F}/\text{cm}^2$ at 10^5 Hz for a 120 nm film] before it quickly drops as the frequency is increased further. This decrease in capacitance indicates a change of regime in the polarization of the cationic polyelectrolyte.¹⁴ At those higher frequencies, ionic motion predominates and the impedance acquires a typical resistive character (the phase angle is close to zero at 3×10^5 Hz).

Fabrication of n-type polyelectrolyte-gated OTFTs includes a delicate manufacturing step: the deposition of a hydrophilic electrolyte on a hydrophobic organic semiconductor.¹⁵ Despite the very hydrophobic character of $[P(NDI2OD-T2)]_n$, we were able to obtain a polycation film on top of the semiconductor. The presence of the cross-linker apparently stabilizes the semiconductor-polycation interface.¹⁵ To manufacture the transistor device, we spin-coated the $[P(NDI2OD-T2)]_n$ semiconductor (15 nm thick) from chloroform solution on a glass substrate pre-patterned with source and drain gold electrodes (vacuum-deposited at 10^{-6} Torr and patterned using photolithography, channel length = $3 \mu\text{m}$, and channel width = $2000 \mu\text{m}$). Subsequently, the semiconductor is annealed at 90°C for 90 s in nitrogen atmosphere. The PVDMDBAC is then spin-coated on top of the semiconductor, followed by annealing at 90°C for 60 s. Finally, a 600 nm layer of titanium is vacuum-deposited (8×10^{-7} Torr) as the gate electrode.

From the transfer curve (see Figure 3), we observe current modulation of three orders of magnitude on/off ratio at low drain voltages ($V_d = 0.1$ V). A saturation current occurring in sub-0.1 V range is consistent with previously reported

polymer polyelectrolyte gated OTFTs with similar channel length/width ratios.⁴ The mobility is extracted from the following transconductance equation $\frac{\partial I_d}{\partial V_g} = \frac{W}{L} C_i \mu V_d$ and yields a value of $0.0033 \text{ cm}^2/\text{Vs}$, which is two orders of magnitude lower than the calculated mobility for $[P(NDI2OD-T2)]_n$ OTFTs that include a thin oxide dielectric layer as the gate insulator.¹² This large difference in mobility could be attributed to an increase in the density of charge traps along the semiconductor-polyelectrolyte interface due to the polar nature of the polyelectrolyte and the presence of grain-boundaries.^{9,15,16} Further, the current-voltage output characteristics display little hysteresis (see Figure 4) and saturation occurs at very low drain voltage throughout the entire gate voltage region. These polycation-gated n-type OTFTs exhibit a fast transient response. The transient characteristics were measured by applying a 1 kHz square-shaped pulse to the gate at the same time as the output current was recorded. The drain current was monitored by measuring the voltage drop over a $10 \text{ k}\Omega$ resistance connected in series with the drain electrode. Figure 5 displays the transistor data; the transistor turns on (off) within 70% of the full response in less than 0.5 ms (0.1 ms) for a drain voltage of 0.25 V. The inset in Figure 5 shows the drain current transient response subtracted from capacitive charging current (i.e., $I_d [V_d = 0.2 \text{ V}]$ minus $I_d [V_d = 0 \text{ V}]$). This subtraction removes the stray capacitance contribution and provides an estimate of the actual time needed to open and close the channel; in this case approximately 3 ms. This observation is supported by the impedance data shown in Figure 2. Indeed, the EDL is formed within 0.5 ms. This is the fastest air-stable n-type transistor operating at such low voltages to date.

We theorize that these devices operate in field effect mode when operated at speeds faster than 1 kHz. This is possible due to the hefty immobile polycationic chains in PVDMDBAC that cannot penetrate into the negatively

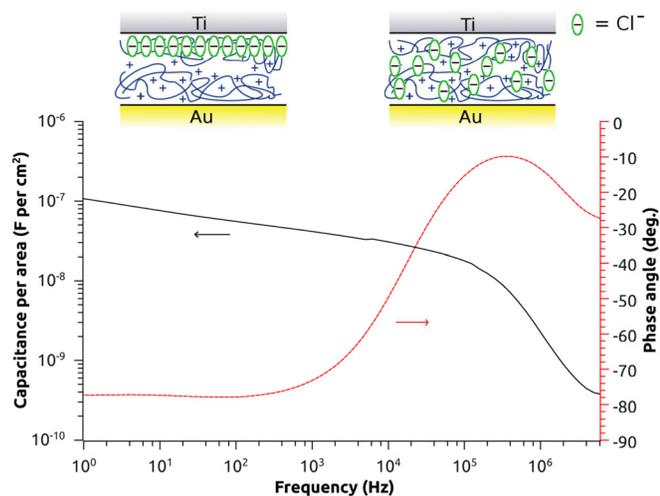


FIG. 2. (Color online) Capacitance and phase angle versus frequency. The mobile (chloride) anions migrate towards the top electrode starting from 1000 Hz, creating an electrical double layer capacitor.

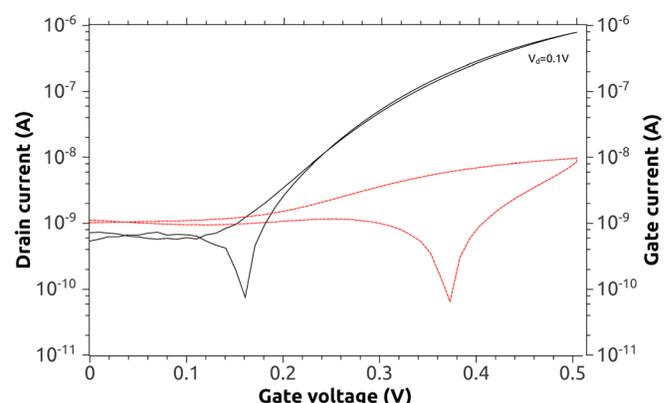


FIG. 3. (Color online) Transfer characteristics of the drain current versus gate voltage at a drain voltage of 0.1 V.

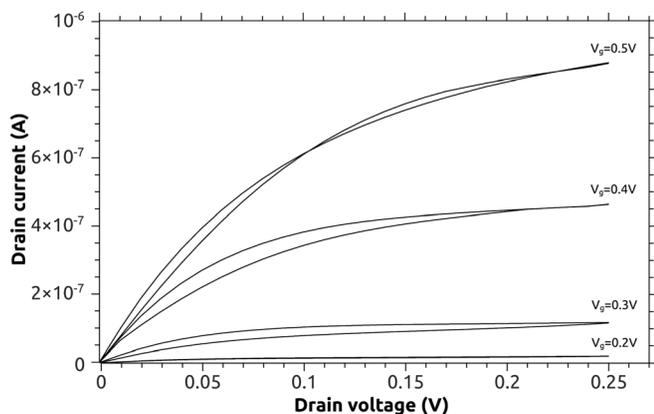


FIG. 4. Output characteristics of the drain current.

charged semiconductor channel.¹⁷ To investigate the robustness of these polycation-gated OTFTs, we ran them in ambient atmosphere for more than 3000 s with a gate voltage of 0.2 V and a drain voltage of 0.25 V continuously applied. Figure 6 shows that the recorded drain current stays within 80% of the maximal measured value. This indicates that the n-type semiconducting properties of the $[P(\text{NDI}2\text{OD}-\text{T}2)]_n$ polymer are not dramatically affected by any of the oxidative processes commonly observed in ambient atmosphere for n-type organic semiconductors. We note, however, a relatively slower transient response of the transistor after it was exposed for this extended biasing.

In summary, we have used a highly polarizable cross-linked polycation as the gate insulator in air-stable, low-voltage operating OTFT, which switches at speeds comparable to those reported for p-OFETs gated via polyanionic electrolytes. This work ushers in the possibility to fabricate air-stable fully organic complementary circuits with ultra low operational voltages that run at a speed exceeding 1 kHz.

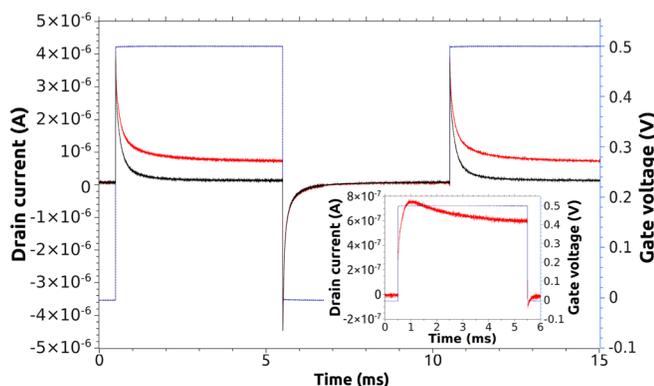


FIG. 5. (Color online) Transient measurement that shows the drain current's response to a 0.5 V square-shaped pulse. The dashed line (red) represents the drain current when the drain voltage is zero. The full line (red) is the current when the drain voltage is set to 0.2 V. The inset shows the subtracted response ($I_d [V_d = 0.2 \text{ V}]$ minus $I_d [V_d = 0 \text{ V}]$).

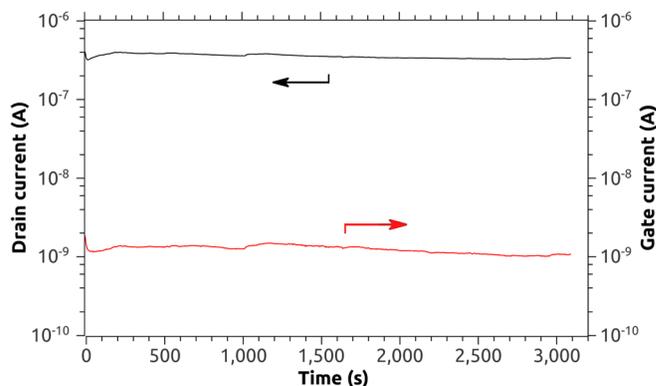


FIG. 6. (Color online) Stability measurement showing the drain (and gate) current's response as a function of time. This measurement was conducted in ambient atmosphere (with 40% relative humidity), with a drain voltage of 0.25 V and a gate voltage of 0.4 V.

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