Single-Monolayer Inkjetted Oligothiophene Organic TFTs Exhibiting High Performance and Low Leakage

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Introduction

Organic thin film transistors (OTFTs) have garnered substantial interest due to their potential applications in flat-panel displays and low-cost RFID tags. Both these applications require modest mobilities and, in particular, low-leakage, as they include low-power analog circuits. The highest performance in organic materials has been demonstrated via evaporated small molecules. However, soluble organic semiconductors are particularly attractive as a dramatic reduction in the cost of processing can be achieved using solution methods such as additive print-based patterning. Most printed results to date have been achieved using soluble polymers; such devices typically have mobilities $<10^{-2}$ and on-off ratios $<10^5$. Recently, several groups have demonstrated the use of soluble small molecule precursors that can be deposited from solution and then thermally annealed to regenerate their insoluble semiconducting forms. We recently developed a similar system using novel oligothiophenes where thermolysis of spun-cast films leads to highly crystalline film formations exhibiting high field-effect mobilities[1]. Here, for the first time, we demonstrate a novel property of this material; upon inkjetting of dilute solutions, the material reorganizes upon heating to form repeatable and controllable *monolayer* films. Resulting TFTs retain the high mobilites of their thicker counterparts, but exhibit superb leakage characteristics, with on/off ratios as high as 10^8.

Experimental

All devices were fabricated on n-type wafers with 100 nm thermal SiO_2 gate dielectric and gold source/drain electrodes. Our novel oligothiophene, **EtB12T6,** was used as the active layer. **EtB12T6** (Fig. 1) is initially soluble, but undergoes a conversion at 180°C to form a rigid oligothiophene with strong packing characteristics. This conversion temperature is compatible with several plastics. For comparison, devices were spun-cast from 3 mg/mL solutions in chloroform, and inkjet printed at 2-3 mg/mL in anisole. All films were heated under nitrogen at 180°C for 20 minutes to induce thermolysis of the material.

Results and Discussion

Spun cast films of **EtB12T6** were uniform and amorphous, but convert into a polycrystalline film with clear molecular terracing after thermolysis (Fig. 2). Converted films have average thickness > 20 nm. Resulting devices exhibited mobilities > 0.07 cm^2/Vs with on/off ratios $>10^5$. Inkjetted devices were formed on gold pads with channel lengths from 2 um to 10 um. Working devices required as little as a single drop, although devices up to 32 drops thick also exhibited transistor characteristics. AFM images show that single drop devices consist of a single monolayer, without the terraces imaged in thicker films (Fig. 3). The transition between the film and underlying substrate was sharp and distinct with a step of ~3 nm, corresponding to the length of a single molecule. Two to four drop devices also predominately had a minimum film thickness across the channel of a monolayer, although molecular terraces were frequently imaged along the channel.

The resulting monolayer devices exhibited field-effect mobilities > 0.06 cm^2/Vs, approaching that of the best spun-cast devices (Fig. 4). The resulting on/off ratios exceeded 10^8 (Fig. 5), among the highest reported for solution processed organic semiconductors. The absence of subsurface conduction paths dramatically improves swing (Fig. 6). Both drain-induced barrier lowering and gate-induced drain leakage are also suppressed (Fig. 7). The latter is indicative of low defect density in the monolayer. Hence the resulting monolayer devices exhibit the superior gate control expected with ideal minimal body thickness. Since on-current flows mainly at the gate interface while leakage current flows throughout the thickness of the body, reducing the body thickness produces a dramatic improvement in off-state performance without any significant degradation in on-state behavior. The ability to form such high-quality monolayers is uniquely demonstrated using our novel oligothiophene; the excellent packing and strong tendency towards reorganization into crystalline configurations allows the formation of monolayers out of the substantially thicker and non-uniform printed droplets. This enables the demonstration of excellent electrostatic behavior.

Conclusions

Through the use of a novel oligothiophene precursor, we have demonstrated organic TFTs exhibiting relatively high mobility while simultaneously retaining ultra-low leakage and excellent on-off ratios. The unique tendency of this material to self-assemble into a crystalline morphology allows non-uniform printed droplets to reorganize into high-quality monolayers. The resulting structure provides excellent electrostatic characteristics, ideal for low power analog applications.

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[1] Murphy, et. al. *J. Am. Chem. Soc.* **2004**, *126*, 1596-1597.

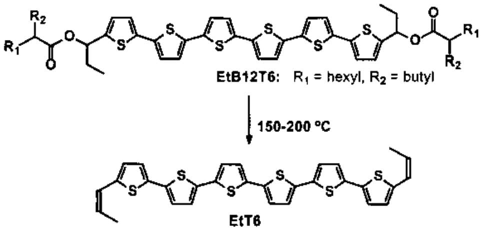

Figure 1: The soluble oligothiophene ***EtB12T6*** *converts to the rigid molecule* ***EtT6*** *with strong packing characteristics upon thermolysis. The precursor is soluble due to the bulky end-chains.*

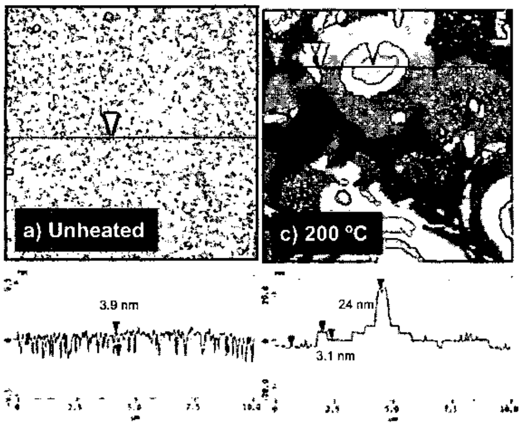

Figure 2: AFM images of unheated and heated spun-cast films, showing molecular terrace formation.

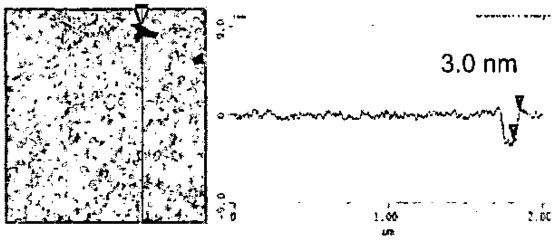

Figure 3: AFM image of a void in printed monolayer device. Thickness was verified to be exactly one monolayer. Coverage over large area was generally highly defect free, producing a high yield of monolayer devices.

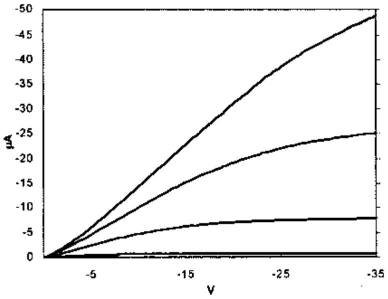

Figure 4: I-V curves for a (W/L) = 250/3 um printed monolayer device. V_G *= 0 to –35 in steps of –8.75 V.*

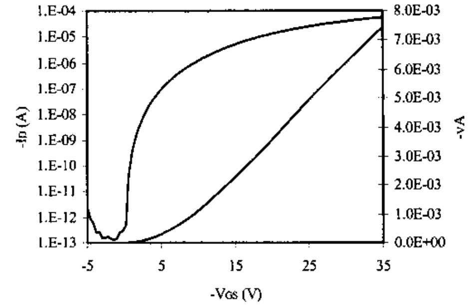

Figure 5: I-V curves for a (W/L) = 250/3 um printed monolayer device. I_D*-*V_G *curve with* V_D *= -35V.*

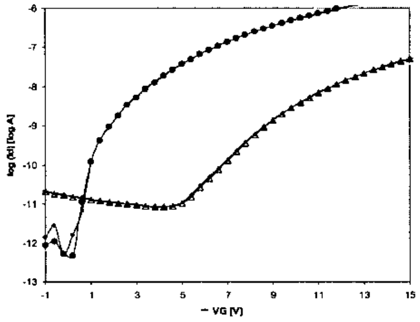

Figure 6: Comparison of a typical monolayer printed device (circle) and a typical spun-cast device (triangle) showing dramatic improvement in on-off ratio and swing.

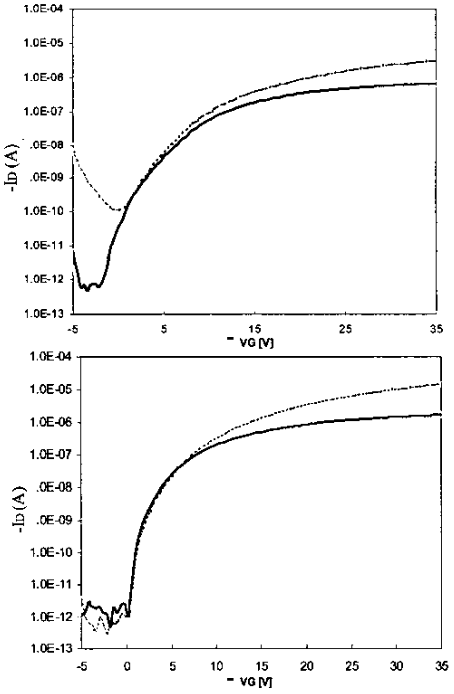

Figure 7: Comparison of spun-cast (top) and printed monolayer devices (bottom) showing improvement in both DIBL and GIDL in the monolayer device. This attests to the high quality of the printed monolayer. V_D *= -4 V (solid) and –35 V (dashed).*