# C-7-1 (Invited)

Towards Printed Organic Electronics: Semiconductor Materials Design for Plastic Transistors

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## Introduction

Silicon technology is wonderful for numerous microelectronic applications, but for large-area devices such as displays, it may become unjustifiably and prohibitively expensive. Integrated circuits composed of plastic thin film transistors (TFTs) and components are attractive alternatives for these applications as they can potentially be manufactured at significantly lower cost via solution processes (e.g., coating, stamp, printing, etc.) in ambient conditions. The plastic circuits are also compatible with flexible substrates, thus enabling design of compact, lightweight, flexible, and structurally inspiring electronic devices. However, most of the current semiconductor materials are either insoluble in common organic solvents, which renders solution processing not possible, or sensitive to air and cannot therefore be processed in ambient conditions to provide high performance characteristics. The general consensus is that for low-cost manufacturing, both the solution processability and ambient stability are the necessary requirements. This paper discusses current organic semiconductor materials issues, challenges, and progress for plastic TFTs as well as our development of polythiophenes with sufficient air stability to enable solution processing at ambient to provide TFTs with excellent transistor characteristics.

#### General:

The objectives of our current research are two-fold: (1) to understand the issues of current organic semiconductor materials and establish a structureproperty correlation to guide our structural design effort; and (2) to design solution processable organic semiconductor materials that possess sufficient air stability to enable fabrication of organic or plastic transistors in ambient conditions with the required functionality.

The polythiophene semiconductors were prepared from structurally symmetrical thiophene monomers using various known polymerization techniques depending on the intended polymers. Final polythiophene products were purified by first dedoping, then extraction with appropriate organic solvents, and dried in vacuo before use.

Our materials processing and device fabrication were all conducted in ambient conditions without precautionary measures being taken to exclude oxygen, moisture and light. Experimental bottom-gate TFT devices were built on n-doped silicon wafer with a thermal SiO2 layer. The wafer was used as the gate electrode while the SiO2, gate dielectric. The dielectric surface was modified with a self-assembled monolayer (SAM) of octyltrichlorosilane (OTS) using common procedures. For the staggered top-contact device, a semiconductor layer was first deposited on the OTS-modified SiO<sub>2</sub> layer by spin coating a dilute solution of polythiophene in a suitable solvent and then vacuum dried to give a 20-50 nm-thick semiconductor layer. Subsequently, the gold source and drain electrodes were deposited by vacuum evaporation through a shadow mask, thus creating a series of TFTs with various channel length (L) and width (W) dimensions. For the coplanar bottom-contact device, the gold source and drain electrodes were first deposited on the OTS-modified  $\mathrm{SiO}_2$  surface before the semiconductor layer was spin coated upon. For some devices, further thermal annealing was carried out to achieve optimum microstructural orders and orientation in the semiconductor channel layers.

TFTs were characterized using Keithley SCS-4200 semiconductor characterization system in ambient conditions. Patterned transistors with channel length of 60 or 165  $\mu$ m and channel width of 1 or 5 mm were used for I-V measurements. For the transfer curves, the gate voltage (Vg) was swept from +10 or +20V to -40, -60, or -80V with the source-drain voltage (Vd) being held at -40, -60, or -80V for saturated regime and at -1, -2 or -4 V for linear regime. At least 30 points were recorded for each curve. For the output curve, Vd was swept from + 2V to -40, or -60V with Vg varied from +20 or +10V to -40 or -60V.

The mobility in the saturated and linear regimes was extracted from the following equations:

Linear regime 
$$(V_d \ll V_g)$$
:  $I_d = V_d C_i \mu (V_g - V_T) W/L$   
Saturated regime  $(V_d > V_g)$ :  $I_d = C_i \mu (W/2L) (V_g - V_T)^2$ 

where  $I_d$  is the drain current, W and L are respectively the semiconductor channel width and length,  $C_i$  is the capacitance per unit area of the gate dielectric layer, and Vg and  $V_T$  are respectively the gate voltage and threshold voltage.  $V_T$  of the device was determined from the relationship between the square root of  $I_d$  at the saturated regime and Vg of the device by extrapolating the measured data to  $I_d = 0$ .

Current on/off ratio  $(I_{\rm on}/I_{\rm off})$  was calculated from the ratio of the current in the accumulation mode over the current in the depletion mode.

#### Discussion

Most small organic molecular semiconductors such as pentacene are generally not suitable for solution processing due to lack of solubility. Some oligothiophenes are solution processable, but the TFT devices fabricated with these materials using solution processes do not generally provide high mobility. An apparent exception is the recently reported soluble pentacene precursor derivative. The latter could be solution processed into TFT semiconductor layers, and when thermally retro-converted to pentacene, provided high mobility.<sup>1</sup> This pentacene precursor technique may be highly sensitive to fabrication conditions and film quality as an earlier similar approach had provided significantly lower mobility.<sup>2</sup>

We focused our studies on regioregularly substituted polythiophene derivatives for their solution processability and self-organization capability. However, high-performing polythiophenes such as regioregular poly(3-hexythiophene) (P3HT) are extremely sensitive to air.<sup>3</sup> High mobility of 0.05 – 0.1 cm<sup>2</sup>/V.s had been reported but only when the device fabrication was carried out in an inert atmosphere.<sup>4</sup> In ambient conditions, both the mobility and current on/off ratio were substantially lower, and the performance degraded rapidly. This ambient instability of regioregular P3HT can be attributed to its coplanar lamellar structure in condensed phase, arising from intermolecular side-chain alignment. As a result, extensive  $\pi$ -delocalization occurred, leading to formation of an electron-rich system which is prone to oxidative doping.

To achieve sufficient air stability for ambient processability while providing functionally useful transistor performance, regioregular polythiophenes of this nature need to possess an effective conjugation length that delicately balances air stability versus transistor characteristics. An effective approach to accomplish this objective is to introduce specific structural perturbations to the polythiophene systems to disrupt their extended  $\pi$ -conjugation. Our structural design studies were accordingly guided by these principles: (1) long side-chain for solution processability; (2) structural regularity for molecular self-organization; and (3) perturbation to the extensive  $\pi$ -conjugation system to achieve a delicate balance between air stability and transistor functionality.

The following are the basic structural building blocks for our regioregular polythiophenes:



The R-substituted thienylene unit (I) was utilized to provide solution processability and when R's were regioregularly positioned on the polymer backbone, serve to induce and facilitate molecular self-assembly. The other structural units (II), (III) and/or (IV) were incorporated to control the polymer  $\pi$ -conjugation to achieve, through rotational freedom, torsional barrier, and/or segmentation of  $\pi$ -conjugation, an effective  $\pi$ -conjugation length for air stability and transistor functionality. D is a saturated or a non-thienylene unsaturated linkage.

The first polymer that we studied was a simple poly(terthiophene), PTT (1), which carries two alkyl side-chains in the central thienylene moiety of the repeating terthiophene units.<sup>5</sup>



Spectroscopic data of (1) showed that a bathochromic shift from solution to thin film, suggesting that molecular self-organization occurred in the solid state. When used as a channel semiconductor layer in a TFT device, (1) provided a saturated mobility up to about  $0.01 \text{ cm}^2/\text{V}$ s and current on/off ratio of  $10^5$ . These results were comparable to those of P3HT devices fabricated under ambient conditions except that the PTT devices possessed far greater ambient stability. The PTT-device gave a high initial current on/off ratio with no significant degradation in transistor performance even after standing over a month in air in the dark. On the other hand, the P3HT-devices exhibited a lower initial on/off ratio, and essentially irreversibly lost their FET activity in about two weeks under similar conditions.

A modified poly(terthiophene) system  $(2)^6$  was studied with the objective of achieving higher molecular orders for transistor performance. Indeed, the placement of the alkyl side chains on the two terminal thienylene units had led to higher mobility. Mobility up to about 0.016 cm<sup>2</sup>/V.s and current on/off ratios of 10<sup>6</sup> were obtained with the devices fabricated from (2).



The best TFT performance however was obtained from a novel class of smectic liquid crystalline polythiophenes (3). This was a regioregular polythiophene system with appropriate built-in structure features that enhanced its resistance to oxidative doping in air. At the same time, it was a system with the capability of forming highly ordered lamellar  $\pi$ -stacks (5) via side-chain interdigitation, and face-to-face  $\pi$ - $\pi$  stacking (4). Under appropriate conditions, the lamellar stacks could also be induced to orient themselves normal to the supporting substrate.



XRD analysis of a pressed pellet of (3) showed two diffraction peaks at 7.38° and 21.46° 2 $\theta$ , characteristic of a smectic liquid crystal. DSC thermogram displayed two endotherms at about 125°C and 140°C on heating, corresponding respectively to the side-chain and main-chain melting. Figure 1a shows the XRD patterns of a thin film of (3): the lower trace corresponds to the "as-cast" thin film, while the upper trace, the annealed thin film (at 135-

 $150^{\circ}\text{C}\text{)}.$  It can clearly be noted that higher structural orders were achieved after annealing.







TFT devices fabricated with (3) in ambient conditions as the semiconductor channel layers exhibited excellent transistor properties. The initial mobility was generally on the order of 0.02 to 0.05 cm<sup>2</sup>/V.s with a current on/off ratio of about  $10^6$ . After annealing at 135-150 °C, the mobility improved significantly to about 0.05 to 0.14 cm<sup>2</sup>/V.s with a current on/off ratio of about  $10^7$ . Both the mobility at the linear regime and saturated regime provided about the same values. In addition, little or no hysteresis and bias stress effects had been observed with these devices.

#### Conclusions

We have shown that through incorporation of proper structural features and control of  $\pi$ -conjugation of regioregular polythiophenes, an optimum balance of ambient stability and transistor functionality can be achieved. Our regioregular polythiophenes have exhibited excellent all-round polymer transistor properties.

#### Acknowledgements

The author wishes to thank Dr. Yiliang Wu, Ms. Ping Liu, and Ms. Sandra Gardner of the Printed Organic Electronics Group at Xerox Research Centre of Canada for their contributions to this work. The collaborations with Dr. Robert Street and his team at Palo Alto Research Center, Inc are gratefully acknowledged. Partial financial support of this work is provided by the National Institute of Standards and Technology through an Advanced Technology Grant 70NANB80H3033.

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