



# Air-stable polythiophene-based thin film transistors processed using oxidative chemical vapor deposition: Carrier transport and channel/metallization contact interface



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## ABSTRACT

Oxidative chemical-vapor-deposition (oCVD) provides a facile route to polymerize and deposit insoluble monomers in thin film form. Here, we report on oCVD polythiophene (PT)-based organic thin film transistors (OTFTs) that present both high mobility and excellent stability over time in air. The measured field effect mobility ( $\mu_{FE}$ ) is  $\sim 0.02 \text{ cm}^2/\text{V sec}$  with the low threshold voltage between  $-1 \text{ V}$  and  $0.3 \text{ V}$ . Additionally the PT OTFTs show no evidence of performance degradation after 3 months exposure in air. The transmission line model (TLM) enables the determination of the specific contact resistance ( $\rho_C$ ) of oCVD PT channel/metallization interface and reveals that  $\rho_C$  is improved with increasing gate bias. The oCVD PT channel conductivity ( $\sigma_{ch}$ ) and carrier density ( $p$ ) were evaluated from more than 100 devices using TLM measurements and the relation of  $\sigma_{ch} = qp\mu_{FE}$ . Carrier transport analysis suggests that the charge screening effect governs hole carrier mobility in the carrier density regime below approximately  $10^{18}/\text{cm}^3$  where an increase in carrier density leads to higher mobility. We also demonstrate photo-conductivity of oCVD PT through an increase in device on-state current and the field effect mobility when the PT OTFT is illuminated. Strategies to further enhance the performance of the materials and devices are also suggested.

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## 1. Introduction

Organic small-molecules and polymers that exhibit electrical conductivity have received significant attention for their application in various electronic and optoelectronic devices including thin film transistors (TFTs) and solar cells. The motivation for organic devices is lower cost, high mechanical flexibility, wide array of functionalities, and low processing temperatures compared to their inorganic counterparts [1–4]. In particular, TFT devices, whose various applications include active-matrix displays, chemical and gas sensors, and electronic papers, may benefit from these promising properties of organic semiconductors for the next-generation flexible device application. Many organic semiconductors, based on triisopropyl-silylethynyl [5,6], pentacene [7,8], poly(3-hexylthiophene) [9–11], poly(3-octylthiophene) [12], poly(4,8-dialkyl-2,6-bis(3-alkylthiophene-2-yl)benzo[1,2-b:4,5-

b']dithiophene) [13], poly(triarylamine) [14] and dihexyl-quaterthiophene [15], have been investigated and implemented in organic TFT (OTFT) devices as TFT channel material and demonstrated promising feasibility for the potential implementation in real-world optoelectronic devices. The field-effect mobility is an important figure of merit for OTFTs and is highly material-dependent. While the majority of field effect mobilities of OTFTs are in the range of  $10^{-4}$ – $1 \text{ cm}^2/\text{Vsec}$ , which is comparable or slightly lower than that of current-standard amorphous Si-based TFTs, some recent OTFT studies reported the field effect mobility greater than  $10 \text{ cm}^2/\text{Vsec}$ . Li et al. [16] utilized a conjugated alternating donor-acceptor moiety of *N*-alkyl diketopyrrolo-pyrrole as a p-type TFT channel and demonstrated printed OTFTs showing  $\mu_{FE}$  of  $\sim 10.5 \text{ cm}^2/\text{Vsec}$ . Minemawari et al. [17] fabricated a single crystalline organic semiconductor of 2,7-dioctyl[1]benzothieno[3,2-b][1] benzothiophene (C8-BTBT) by inkjet printing and the TFTs using C8-BTBT as a p-type channel demonstrated  $\mu_{FE}$  of  $\sim 16.4 \text{ cm}^2/\text{Vsec}$ . More recently, an off-center spin-coating method was introduced by Yuan et al. [18] in order to achieve a highly aligned, *meta*-stable crystal packing structure of C8-BTBT and the

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resulting OTFTs exhibited significantly high  $\mu_{FE}$  of  $\sim 25 \text{ cm}^2/\text{Vsec}$  (highest of  $43 \text{ cm}^2/\text{Vsec}$ ).

To date, organic channel materials in OTFT devices are mostly prepared by solution-based techniques such as spin-coating and dip-casting. However, when solvents are removed, de-wetting effects cause surface non-uniformity and, therefore, lack of reproducibility is often observed. In addition, it can be difficult with solution-based processes to precisely control film thickness, which is critical for optical (e.g., visible regime transmittance) and electrical (e.g., sheet resistance) properties. More fundamentally, since solution techniques require the solubility of materials, many promising, but insoluble, organic materials are not considered in practical device applications. For conjugated polymers, in particular, the main difficulty results from the rigid nature of the polymer backbone, making these materials largely insoluble in common organic solvents [19]. Solvent processing can also be a concern in device fabrication where care must be taken not to redissolve underlying layers.

Recently emerging oxidative chemical vapor deposition (oCVD) provides a simple and easy route to synthesize and deposit conjugated polymers at low temperatures ( $25\text{--}150 \text{ }^\circ\text{C}$ ) [20,21] irrespective of polymer solubility or the solvent compatibility with the substrate and underlying materials. The oCVD technique has shown considerable improvements over solution-based techniques in film uniformity over the large areas [21,22], electrical properties (e.g., conductivity [21], mobility [23]) and conformality for non-planar [24,25] and patterned [20,26] structures such as textiles and trench wafers. In addition, oCVD offers a facile approach to tune the doping level of the resulting polymers during deposition *in situ* by controlling substrate temperature [27] and varying oxidizing agents [28] and *ex situ* by post process acid treatments [22,23]. Moreover, oCVD offers the well-known processing benefits of vacuum processing, including parallel and sequential deposition, well-defined thickness control, and inline integration with other standard vacuum processes [29]. Recently, scalability of oCVD as a method for fabrication of thin films of conjugated polymers was successfully demonstrated [30]. Conducting polymer of PEDOT thin films were deposited on large area flexible substrates with dimensions of  $8.5'' \times 13''$  ( $21.5 \text{ cm} \times 33 \text{ cm}$ ) using a custom-built roll-to-roll oCVD. The average electrical conductivity was achieved as high as  $\sim 138 \text{ S/cm}$  and showed only 10% deviation of the conductivity over the entire substrates. Such scalability gives the oCVD technique promise for the potential real-world application in various large area and flexible electronic devices.

Although unsubstituted polythiophene (PT) has several promising properties such as high electrical conductivity as well as excellent environmental and thermal stability, its insoluble nature makes it challenging to be processed using conventional solution-based techniques. Therefore, the implementation of unsubstituted PT in organic electronic and optoelectronic devices has been quite limited. However, the volatility of thiophene monomer enables the use of oCVD to readily synthesize and deposit PT films. We previously reported the first demonstration of organic solar cells utilizing vapor-phase-synthesized PT as an electron donor [31]. More recently, the effect of working pressure during oCVD PT fabrication on the chemical, structural and electrical properties of the resulting oCVD PT thin films was investigated: an increase in conjugation length and a consequent enhancement in conductivity were observed. The first OTFT integrating polythiophene thin films as TFT channel was successfully fabricated using oCVD and these devices presented the field effect mobility ranging from  $10^{-4}$  to  $4 \times 10^{-3} \text{ cm}^2/\text{Vsec}$  as a function of chamber pressure during oCVD deposition.

To realize high performance oCVD PT-based OTFT devices, it is necessary to first study the fundamental performance of materials

and devices. In the present study, the specific contact resistance between PT channel and metallization is evaluated for the first time and the effect of the contact resistance on the performance of the TFT devices is systemically discussed using the transmission line model (TLM) measurements. Investigation on the relation between carrier density and carrier mobility allows for the establishment of the important carrier transport mechanism that is predominately governed by the charge screening effect. Promising photo conductivity and excellent device stability over time in air are also presented.

## 2. Experimental

### 2.1. oCVD polythiophene synthesis

PT films were deposited using oxidative chemical vapor deposition (oCVD) in a custom-built reactor described in detail elsewhere [32]. Briefly, monomer was held in a temperature-controlled glass jar outside of the reactor and feed into the chamber through an inlet port. A dry pump was used to achieve vacuum through an exhaust port opposite from the monomer inlet port. A throttle valve (MKS Instruments, Model 653B) was used to maintain pressures above 50 mTorr. A turbomolecular pump (Pfeiffer Vacuum, HiPace 300C) was used to achieve higher vacuum when necessary. A low temperature evaporation (LTE) point source (Kurt J. Lesker Co.) at the bottom of the chamber (off-centered and angled  $\sim 30^\circ$  from vertical) was used to heat the iron (III) chloride oxidizing agent. The substrate stage at the top of the reactor chamber was inverted to face down and about 20 cm from the iron (III) chloride source and was able to be rotated for improved uniformity. Pressures between 10 mTorr and 10 Torr were read with an absolute capacitance monometer (MKS Instruments, Model 628D), and an active pirani/cold cathode gauge (Pfeiffer Vacuum, PKR 261) was used to monitor lower pressures.

Glass slides and thermally oxidized (50 nm) silicon wafers ( $\text{SiO}_2/\text{Si}$ ) were used as substrates and placed on the stage, which was rotated at about 3 rotations per minute. Thiophene ( $\geq 99\%$ , Sigma-Aldrich) monomer and iron (III) chloride ( $\text{FeCl}_3$ , 97%, Sigma-Aldrich) oxidizing agent were used as purchased. The thiophene monomer jar was maintained at a temperature of  $20 \text{ }^\circ\text{C}$  and a needle valve was used to introduce the gas at a flow rate of  $\sim 31 \text{ sccm}$  into the reactor chamber and was directed toward the stage. The chamber pressure was maintained at 150 mTorr and the stage and reactor body were unheated for this study. The  $\text{FeCl}_3$  crucible was heated from room temperature to  $130 \text{ }^\circ\text{C}$  at  $8 \text{ }^\circ\text{C}/\text{min}$ , and  $130 \text{ }^\circ\text{C}\text{--}200 \text{ }^\circ\text{C}$  at  $4 \text{ }^\circ\text{C}/\text{min}$ . Thiophene monomer vapors reacted via oxidative polymerization with sublimated oxidizing agent (iron(III) chloride) to result in the deposition of solid, polymer films on the substrates. Total deposition time was 25 min. After deposition, the samples were removed from the chamber and rinsed in methanol ( $\geq 99.9\%$ , Sigma-Aldrich) for 30 min, 0.2 M HCl in methanol for 10 min, and then 1 min in methanol to remove unreacted monomers and excess oxidant on the surface and inside the films and therefore to ensure the stable device performance. Post-deposition rinsing has been shown to improve the electrical and physical properties of the vapor phase polymerized films [22,23], because as-processed conductive polymers are likely to contain a majority of residual oxidant and unreacted monomers that may cause instability in electrical properties (e.g., conductivity, carrier density and mobility). After post-rinsing, the resulting carrier density of oCVD PT films is in the  $\sim 10^{16}\text{--}10^{17}/\text{cm}^3$  range [32], which enables oCVD PT for active layer applications in OTFTs and organic photovoltaics unlike oCVD PEDOT leading to the carrier density of  $\sim 10^{20}\text{--}10^{21}/\text{cm}^3$  [23] that is suitable for electrode application.

To vary the carrier density of the oCVD PT films, several other

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