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## Bilayer heterojunction polymer solar cells using unsubstituted polythiophene via oxidative chemical vapor deposition

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### ABSTRACT

We demonstrate the use of a vacuum-based, vapor phase technique for the deposition of a donor polymer for use in polymer solar cells. Unsubstituted polythiophene (PT), which is insoluble and infusible and thus typically difficult to process, is easily prepared by oxidative chemical vapor deposition (oCVD). The oCVD process results in a conductive PT film that is heavily doped with FeCl<sub>3</sub>, which is used as the oxidizing agent. A post-deposition methanol rinse sufficiently dedopes the film and removes spent oxidant, leaving semiconducting PT with an optical bandgap close to 2 eV. Drastic changes in the film color, absorption spectra, and film composition confirm the dedoping process. The resulting semiconducting PT is then applied as an electron donor in bilayer heterojunction solar cells with a thermally evaporated C<sub>60</sub> electron acceptor layer, resulting in power conversion efficiencies up to 0.8%. The absorption edge of the PT at ~620 nm closely matches the edge present in the external quantum efficiency spectra, indicating that the oCVD PT contributes to the photocurrent of the devices. This demonstrates that the oCVD technique can be used in the processing and design of polymer active layers for polymer solar cells and hybrid small molecular organic solar cells without solubility, temperature, or substrate considerations.

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### 1. Introduction

Semiconducting polymers and low molecular weight organic molecules have received significant attention for their application as active layers in organic solar cells, due to their potential low cost, high mechanical flexibility, wide array of functionalities, and well-understood structure–composition–property relationships [1–4]. In fact, both solution-printed polymer solar cells and vacuum-deposited small molecule organic solar cells have independently reached record certified efficiencies of 8.3% [5], through careful materials selection and device architecture engineering.

Vapor-deposited polymer solar cells would enhance the ability to integrate attractive materials into organic solar cells. For example, unsubstituted polymers, which are reported to be more stable because their highly compact structures prevent oxygen permeation into the polymer bulk [6,7], are also insoluble and infusible because of their compact structures. Furthermore, the vacuum fabrication of multilayered devices is not constrained by the requirement of finding solvents that will not dissolve the underlying layers to prevent mixing between layers during deposition. However, the high temperatures necessary to physically deposit polymers by vacuum thermal

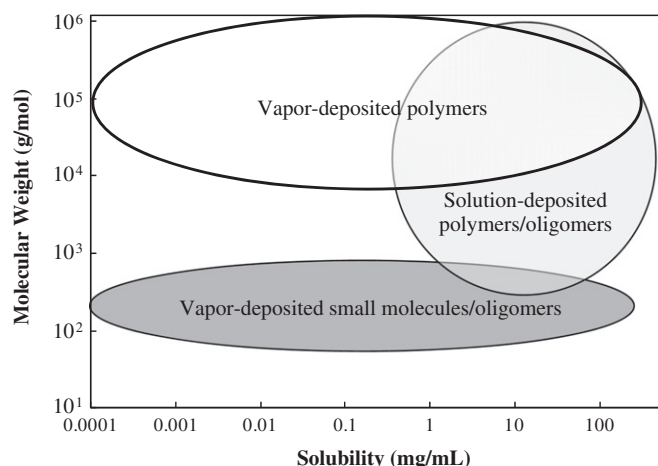
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evaporation leads to polymer degradation [8], limiting materials to low-molecular-weight organics. The few reports in the literature of the use of a vapor deposition technique (such as physical deposition [9], plasma polymerization [10], and thermal chemical vapor deposition [11]) to deposit a polymer photoactive layer resulted in low corresponding device efficiencies (<0.3%). Thus a soluble derivative (e.g. poly(3-hexylthiophene)) or an oligomeric version are typically used to facilitate processing by standard solution printing or vacuum thermal evaporation. This leaves a largely unexplored domain of materials for use in organic solar cells (Fig. 1). This work demonstrates an alternative vacuum fabrication method for the utilization of this region of polymers that is independent of solubility properties.

Oxidative chemical vapor deposition (oCVD) offers a facile route to processing conjugated polymers (including insoluble polymers) via vacuum deposition, offering a potential link between many of the above considerations. In oCVD, conjugated polymers are simultaneously synthesized from vapor phase precursors (monomer and oxidant) and deposited on the substrate at low temperature (25–100 °C) and moderate vacuum (~0.1 Torr) [12,13]. Thus, oCVD offers the well-cited processing benefits of vacuum processing, including parallel and sequential deposition, well-defined thickness control and uniformity, and inline integration with other standard vacuum processes (e.g. vacuum thermal evaporation). Moreover, oCVD is conformal over nonplanar substrates, enabling compatibility with substrates such as paper and textiles [13]. In contrast, vacuum thermal evaporation is generally subject to line-of-sight deposition, while conformal deposition of liquid-phase systems is



**Fig. 1.** Properties of materials deposited by various techniques for use in organic solar cells. Traditionally, the use of polymer is limited to those that can be dissolved so that it can be deposited by some solution-based technique. Vapor deposition is usually limited to molecules with low enough molecular weight to be thermally evaporated. This leaves a region of vapor-deposited polymers that is difficult to access by traditional methods.

complicated by surface tension effects around micro- and nano-scale features [14]. oCVD has previously been used to conformally deposit thin films of doped conducting polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT) [12], which have recently been incorporated as transparent electrodes in small molecule organic solar cells on a variety of substrates, including unmodified paper [13].

Unsubstituted polythiophene (PT) has been prepared by several techniques in the literature, including electropolymerization [15,16], chemical polymerization [17,18], thermo-cleavage of solubilizing side chains [7,19], and various types of vapor deposition techniques such as plasma polymerization [20,21] and others [22–25]. However, largely because of difficulties in processing PT due to its insolubility or harsh deposition conditions, PT has only been reported in polymer solar cells via electropolymerization [26,27] and thermo-cleavage of a solution-processable alkylated polymer precursor [7,28–30].

Here we report the preparation, characterization, and application of unsubstituted PT by oCVD for use as a photoactive semiconductor in organic solar cells. We characterize as-deposited and methanol-rinsed oCVD PT films to confirm polymer dedoping upon post-processing with methanol. The resulting semiconducting PT is then applied as an electron donor in bilayer heterojunction solar cells with a thermally evaporated  $C_{60}$  electron acceptor layer, resulting in power conversion efficiencies up to 0.8%. This demonstrates that the oCVD technique can be used in the processing and design of polymer active layers for polymer solar cells and hybrid small molecule organic solar cells without solubility, temperature, or substrate considerations.

## 2. Experimental

### 2.1. Polythiophene depositions

The polymer deposition procedure using the oCVD process and the custom-built reactor configuration are described in detail elsewhere [31,32]. Briefly, the oCVD reactor consists of a vacuum chamber with monomer inlet ports and an exhaust to a pump. A heated crucible holding the oxidizing agent is in the bottom of the chamber, and directly above it is an inverted stage for the substrate. The stage and reactor body were maintained at 30 °C and 45 °C, respectively. The chamber pressure was held constant at 150 mTorr using a butterfly valve. Iron(III) chloride ( $FeCl_3$ , 97%,

Sigma–Aldrich) and thiophene ( $\geq 99\%$ , Sigma–Aldrich) were used as purchased. Quartz slides, silicon wafers, and ITO-coated glass were used as substrates.  $FeCl_3$  was used as the oxidizing agent and it was sublimed at 340 °C. Polymer film thickness was controlled by varying the amount of  $FeCl_3$  loaded in the crucible. Vapor phase thiophene monomer was introduced into the reactor from a side port on the reactor. The thiophene monomer jar was maintained at a temperature of 25 °C and a needle valve was used to limit the flow rate to about 1 sccm. A deposition time of 20 min was used for all films. After deposition, the films were rinsed in methanol ( $\geq 99.9\%$ , Sigma–Aldrich) for 2 min to remove reacted oxidant.

### 2.2. Polymer characterization

UV–vis spectra of the studied films on quartz substrates were measured with a Varian Cary 5000 UV–vis spectrophotometer. Transmission and reflection spectra were measured. The reflection spectra were obtained using a specular reflectance accessory and an Al standard reference mirror (ThorLabs). Fourier transform infrared (FTIR) measurements of PT films on silicon wafers were performed on a Nexus 870, Thermo Electron Corp. spectrometer. Film compositions were estimated by XPS using a Surface Science Instruments (SSI) model SSX-100 with operating pressure  $< 2 \times 10^{-9}$  Torr utilizing monochromatic  $AlK\alpha$  X-rays at 1486.6 eV. Photoelectrons were collected at an angle of 55° from the surface normal. Film thicknesses were measured using a Veeco Dektak 150 surface profilometer. PT film thicknesses used for devices were approximated by measuring the thickness of PT on glass slides placed close to the ITO substrates from the same deposition. The sheet resistance of the as-deposited PT films were measured with a Jandel four-point probe in air. Conductivity values were calculated using the measured sheet resistivity and thickness measured with the profilometer. Cyclic voltammetry measurements were conducted using a 660D potentiostat (CH Instruments) with a standard three-electrode configuration under a nitrogen atmosphere. The oCVD PT film on ITO/glass was the working electrode,  $Ag/AgNO_3$  (0.01 M in acetonitrile) was the reference electrode, and a platinum mesh attached to a platinum wire was used as the counter electrode. The measurements were performed in acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte at a scan rate of 100  $mV s^{-1}$ . The  $Fc/Fc^+$  redox couple was used to calibrate the  $Ag/Ag^+$  reference electrode.

### 2.3. Device fabrication and characterization

The OPVs were fabricated on glass substrates that were pre-coated with a 150 nm thick, patterned indium-tin oxide (ITO) transparent anode with 15  $\Omega/sq$  sheet resistance (Kintec Co.). Prior to use, the substrates were successively cleaned by ultrasonic treatment in detergent solution (Micro 90),  $2 \times$  de-ionized water,  $2 \times$  acetone and  $2 \times$  isopropanol for 5 min each. The substrates were then treated with  $O_2$  plasma for 30 s. A PT film of varying thickness was deposited onto the cleaned ITO via oCVD as described above. Samples were exposed to air for approximately 10 min in transferring them to a glovebox.  $C_{60}$  (99.9%, sublimed, Sigma–Aldrich) was purified once by vacuum train sublimation prior to loading, while bathocuproine (BCP, from Luminescence Technology Corp.) and Ag (Alfa Aesar, 1–3 mm shot, 99.9999%) were used as purchased.  $C_{60}$ , BCP (8 nm), and a 100 nm thick Ag cathode were sequentially deposited via thermal evaporation at a rate of 0.1 nm/s. The cathode films were deposited through a shadow mask for single devices, defining a 1 mm  $\times$  1.2 mm active device area, and there were 10 devices per substrate. The current–density–voltage ( $J$ – $V$ ) measurements were recorded by a Keithley 6487 picoammeter and

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