Nanostructured Unsubstituted Polythiophene Films Deposited Using Oxidative Chemical Vapor Deposition: Hopping Conduction and Thermal Stability

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Unsubstituted polythiophene (PT), a promising material that is challenging to process into thin films due to its intrinsic insolubility, can be synthesized and deposited using unique oxidative chemical vapor deposition (oCVD) at room temperature. The conduction mechanism of nanostructured oCVD PT thin films is illuminated through the investigation of in situ conductivity measurements. It is identified that the 3D variable range hopping process governs the transport of charge carriers in oCVD PT thin films with an activation energy of \( \approx 48 \text{ meV} \) regardless of doping concentrations. It is also reported that the thermal stability of oCVD PT largely relies on the doping concentration of the material; oCVD PT demonstrates excellent thermal stability at temperatures up to 160 °C with carrier density values lower than \( 1 \times 10^{17} \text{ cm}^{-3} \), while higher doping leads to a reduction in conductivity at \( T \geq 100 \text{ °C} \) due to electron–hole recombination. X-ray photoelectron spectroscopy analyses on the change in the concentrations of dopant anions (Cl\(^-\) and FeCl\(_4\)\(^-\)) support the suggested mechanisms.

1. Introduction

Polythiophenes and their functional derivatives have been extensively investigated as an important class of conjugated polymers for various applications in organic and hybrid optoelectronics, including photovoltaics,[1,2] photodetectors,[3] thin film transistors (TFT),[4,5] and electroluminescent devices.[6] Among thiophene-based polymers, the majority of work in the literature has focused on substituted polythiophenes due to monomer solubility in solvents, which is essential for the conventional solution process techniques. Poly(3,4-ethylenedioxythiophene) (PEDOT), which shows high conductivity and excellent optical transmittance in the visible, has been implemented as transparent electrode or hole transport layer or buffer layer for application in organic photovoltaics (OPVs). Poly(3-hexylthiophene-2,5-diyl) is a widely studied polymer used as an electron donor in OPVs since this material has shown its favorable absorption and charge-transport properties.[7] Unlike substituted thiophenes that feature side chains, increasing solubility by separating the backbones and reducing the backbone rigidity,[8] unsubstituted polythiophene (PT) has been challenging to synthesize, mainly attributed to its insolubility in spite of promising properties of good environmental and thermal stability as well as high electrical conductivity.[2,9]

Oxidative chemical vapor deposition (oCVD) has uniquely demonstrated a simple and easy synthesis and deposition of conjugated polymers at low temperatures (20–150 °C).[10,11] Unlike conventional solution-based techniques, the oCVD method does not require polymer solubility or solvent compatibility with the substrate and underlying materials, which leads to greater film uniformity over the large areas,[11,12] electrical properties (e.g., conductivity[11] and mobility[13]), and conformality for nonplanar[14,15] and patterned[10,16] structures. In addition, the doping level of the resulting polymers can be altered in situ during oCVD deposition by controlling substrate temperature[17] and ex situ by post process acid treatments.[12,13] The oCVD films find many promising applications, including transparent conductors for electrodes[14] and hole transport layers[18] in OPVs, sensors,[19] and electrochromic devices.[20] Moreover, oCVD offers the various processing benefits, including parallel and sequential deposition, excellent large-area homogeneity, and inline integration with other standard vacuum processes.

Particularly, among the advantages of oCVD technique, the ability to synthesize, technically, any polymers irrespective of monomer solubility has broadened the selection of promising materials. The oCVD platform has been demonstrated for the dedoped semiconducting homopolymers such as unsubstituted PT,[21,22] polyisothianaphthene,[23] and polyselephenephen,[24] which have been challenging to process through conventional solution-based techniques.

In spite of difficulties in processing PT due to its insolubility or harsh process conditions, there have been several attempts to realize unsubstituted PT. Electrochemical polymerization...
was reduced to $10^{-6}$ in the oCVD chamber during depositions. Previously, we depend on deposition parameters such as working pressure reported PT, and the low threshold voltage of 1 to 0.3 V. For the electronic transport analysis, temperature-dependent in situ conductivity measurements along with microstructure analysis. In addition, we also report on the thermal stability of the PT films that depend on the doping concentrations. Relevant mechanisms are suggested to account for the thermal stability, and X-ray photoelectron spectroscopy (XPS) investigations support the mechanisms.

2. Results and Discussion

Unsubstituted PT films were deposited using oCVD with a rotating stage and the resulting PT films presented great uniformity (±5% deviation in thickness) over the area of 12.7 × 12.7 cm² glass substrates. A photograph of the typical oCVD PT films, which presents the characteristic red color of dedoped unsubstituted PT, and the thickness uniformity are shown in Figure S1 in the Supporting Information. In order to investigate the conduction mechanisms and the thermal stability of oCVD PT films, the temperature-dependent conductivity measurements were made in situ from Ag-electrode devices. Figure 1a shows the typical structure of the device and the scanning electron microscopy (SEM) micrograph of the devices used to measure the conductivity is presented in Figure 1b. A red square in Figure 1b was further investigated at higher magnification and its SEM image is shown in Figure 1c, presenting uniform distribution of poly-crystalline Ag electrode and well-defined oCVD PT thin film.

Unsubstituted PT has been synthesized using oCVD. Then, postdeposition rinse in methanol was used to make the semi-conducting form and remove residual oxidant, by which the postdeposition rinse in methanol was used to make the semi-conducting form and remove residual oxidant, by which the dedoped conductivities depend on deposition parameters such as working pressure in the oCVD chamber during depositions. Previously, we reported the first demonstration of organic solar cells implementing oCVD PT as an electron donor, resulting in power conversion efficiencies of up to 0.8%. More recently, organic field-effect transistors (OFETs) based upon oCVD PT for p-type channel application have been reported with the field-effect mobility up to 0.02 cm² V⁻¹ s⁻¹, which is the highest value for reported PT, and the low threshold voltage of ~1 to 0.3 V. Further, these oCVD PT-based OFETs presented excellent performance stability over time in air.

In order to understand the role of PT in electronic and optoelectronic device applications and to ensure high and stable device performance, the fundamental understandings of carrier transport and thermal behavior need to be preceded since these properties determine the electrical conduction and the stability, which is significant for potential real-world device applications such as solar cells and OFETs. Conducting polymers are known to behave like disordered semiconductors, where the charge carriers are located at localized energy states within the gap, rather than move in bands which is more dominant in ordered semiconductors. Therefore, the relevant carrier transport mechanism is generally termed hopping conduction. This mechanism has been well described as the cause for the low conductivity of organic/polymeric materials, particularly for the low- to modest-doped materials such as polypyrrole, poly(3n-decylpyrrole), and some other substituted thiophene derivatives, including poly(3-alkylthiophene). In this paper, we deal with, for the first time, the electrical transport properties of unsubstituted PT films processed using oCVD, which are governed by a 3D variable range hopping (VRH) conduction mechanism. The mechanism was identified through the temperature-dependent conductivity measurements along with microstructure analysis. In addition, we also report on the thermal stability of the PT films that depend on the doping concentrations. Relevant mechanisms are suggested to account for the thermal stability, and X-ray photoelectron spectroscopy (XPS) investigations support the mechanisms.
increased carrier density was also correlated with increased conjugation length and few defects. Our previous Raman measurements\cite{22} revealed that PT films deposited at the lower pressure demonstrated lower absorption and a lower degree of conjugation, and a higher amount of polymer chain distortions than films deposited at the higher pressure conditions. Since conjugation length is directly related to the carrier density and conductivity of conjugated polymers including PT, the Raman measurements well support the change in carrier density as a function of a chamber pressure. Typical plots of the conductivity measured in situ for the sample whose carrier density of $0.9 \times 10^{17}$ cm$^{-3}$ are shown in Figure 2a. These conductivities are the equilibrium conductivity at each temperature, which is achieved in ~5 min after varying temperature. The room temperature (20 °C) conductivity was measured to be $2.77 \times 10^{-5}$ S cm$^{-1}$ and the conductivity kept increasing to reach $4.36 \times 10^{-4}$ S cm$^{-1}$ at 160 °C, increased more than an order of magnitude compared with the room temperature conductivity. During the in situ measurements, the conductivity measured at each temperature remained nearly constant, which indicates that no structure evolutions were made during the measurements and the origin of the conductivity increase is intrinsic and no dopant-related carrier generation/annihilation is involved during the thermally activated process. Further, the constant conductivity at each temperature during the 2 h measurements in air indicates the excellent thermal stability of oCVD PT films up to 160 °C investigated in the present study compared with other conjugated polymers such as PEDOT\cite{13} and/or PEDOT:PSS,\cite{32} which show significant thermal degradation in conductivity during air-annealing at temperatures lower than 80 °C in less than 2 h. This is in good agreement with the recent report\cite{5} addressing persistent air stability of PT over periods longer than three months in ambient conditions. The stability of oCVD PT is likely attributed to the rigid nature of the backbone that prevents oxygen and water permeation into the polymer bulk and hinders the rotation of unsubstituted monomers.\cite{5}

In Figure 2b, representative double-swept (forward and reverse) current–voltage (I–V) curves scanned at 20, 40, and 160 °C in the bias range of ~0.5 to 0.5 V are presented, from which the conductivity results shown in Figure 2a were extracted using the transmission line model (TLM) series resistance model ($R_{\text{Total}} = 2R_C + (R_L/L)/W$) and the dimensions (PT thickness = 40 nm, length ($L$) = 60 μm, and width ($W$) = 1000 μm) of the two-terminal device used in the measurements. The linear behavior of the I–V curves in Figure 2a accounts for Ohmic contacts between the oCVD PT and Ag electrodes, indicating that the measurement was performed in a field-independent conductivity regime. No prominent hysteresis behavior (or very weak for 140 °C) of the I–V curves is observed during the forward and reverse scans, indicating that no significant trap- or defect-based conduction is involved during the measurements which is in a good agreement with the discussion above in Figure 2a (i.e., no dopant-related carrier generation/recombination involved).

Figure 2a–c shows the atomic force microscopy (AFM) images obtained from a 1 μm × 1 μm area by tapping mode AFM measurements that describe the microstructure of oCVD PT films deposited at varied working pressures, which yields PT films with different carrier concentrations. The PT nanostructure presented in this study is typical morphology with the FeCl$_3$ oxidant, and similar nanostructures were observed in various deposition conditions. However, the morphological structure of oCVD polymers was found to be significantly dependent on oxidizing agents,\cite{16} the morphology of PT would vary with other oxidants used in oCVD process. From the AFM topographic images, the root-mean-square roughness for the films is ~10–20 nm depending on deposition conditions. Entangled nanostructures of 3D networked PT films result from the intermolecular overlap of neighboring molecules. These conjugated molecules are typically longer than polymer chain length and therefore charge carriers need to hop to neighbors to travel the full length of a molecule.\cite{8} A schematic of PT nanostructured network is shown in Figure 3d, where entangled PT molecules are 3D networked.

The in situ conductivity measurements were repeated for the oCVD PT films with different doping concentrations and temperatures ($T$). Plots of conductivity versus $1/T^{1/4}$ in Kelvin are shown in Figure 3e as a function of the carrier concentrations. For the conduction mechanisms for disordered materials, including a majority of organic/polymeric semiconductors, previous theoretical and experimental studies\cite{27,28,30} reported that the conductivity is governed by VRH conduction, where the average hopping distance varies with temperature ($T$) and consequently, the DC conductivity. This temperature-dependent behavior is described by the Mott law\cite{29}

$$\sigma = \sigma_0 \exp \left( \frac{T_0}{T} \right)^\gamma $$

(1)

where $\sigma_0$ is the preexponential factor pertaining to the rate of conductivity change with $T$, $T_0$ is the characteristic temperature that
determines the thermally activated hopping between localized states and the exponent, $\gamma$ is the factor relating dimensionality of the transport process via the equation $\gamma = 1/(1 + d)$. The dimension factor, $d$, can be 1, 2, 3 depending on the structure of conduction path for VRH.[28] Although both the prefactor $\sigma_0$ and the characteristic temperature $T_0$ depend on the density and distance of the localized states, $\sigma_0$ is considered, in most cases, as constant due to its very weak dependence.[28] The parameter $T_0$ is defined as$^{[28,34]}
\begin{equation}
T_0 = \frac{3\pi\hbar}{2q^2k_F^2}\left(\frac{3\pi}{\pi}\right)^{\frac{1}{3}}\sqrt{\frac{\hbar}{\sigma_0}}
\end{equation}

where $\hbar$ is the Planck constant, $k_F$ is the Fermi wave-vector which is defined as $k_F = (3\pi n)^{1/3}$, $q$ is the unit charge of electron, and $\mu$ is the carrier mobility. For the evaluation of the mean free path, the field-effect mobility measured using PT-based TFTs was used for the values of mobility and these values are summarized in Table 1. The calculated mean free path values of the oCVD PT films are as small as $\approx 10^{-5}$–$10^{-4}$ nm, which is much shorter than the dimensions of the PT AFM micrographs in Figure 3a–c. Therefore, this discussion on the mean free path of the oCVD PT is in good agreement with that the charge transport for the conduction is clearly prevailing through VRH hopping process. Further, the investigation on the mean free path of charge carriers also supports that the oCVD PT structure is 3D networked. The mean free path ($L$) of the charge carrier is determined by the equation

$$L = \frac{3\pi\hbar}{2q^2k_F^2}\left(\frac{3\pi}{\pi}\right)^{\frac{1}{3}}\sqrt{\frac{\hbar}{\sigma_0}}$$

Table 1. Mean free path ($L$) of the oCVD PT thin films determined from the carrier density and carrier mobility using Equation (4).

| Carrier density [cm$^{-3}$] | Carrier mobility [cm$^2$ V$^{-1}$ s$^{-1}$] | $L$ [nm] |
|-----------------------------|------------------------------------------|--------|
| $3.38 \times 10^{17}$       | $1.90 \times 10^{-3}$                   | $4.79 \times 10^{-5}$ |
| $1.65 \times 10^{17}$       | $3.74 \times 10^{-3}$                   | $8.35 \times 10^{-5}$ |
| $0.89 \times 10^{17}$       | $2.42 \times 10^{-3}$                   | $4.40 \times 10^{-5}$ |
| $0.63 \times 10^{17}$       | $1.08 \times 10^{-3}$                   | $1.75 \times 10^{-5}$ |
| $0.48 \times 10^{17}$       | $0.45 \times 10^{-3}$                   | $0.65 \times 10^{-5}$ |
three-dimensionally. The values of the mean free path are found to be significantly shorter than those (~1–50 nm) of conventional inorganic semiconductors in single- or poly-crystalline states such as Si[35] and transition metal oxides (e.g., ZnO).[36] These lower mean free path values of the oCVD PT are likely due to charge carriers that need to hop from energy states to adjacent available energy states for the conduction, like many other organic and polymeric semiconductors. Particularly for polymers, their chain length is known to dominate the hopping mechanism for the conduction.

In Figure 3e, the plots of conductivity versus \(\sqrt{1/T}\) as a function of carrier density show experimental results and their linear fits, satisfying the 3D VRH conduction behavior. It should be noted that the slope of the conductivity is identical for all the PT films regardless of the carrier concentration, which indicates that the required activation energy for the thermal process is identical. From the linear fit, the activation energy was determined to be 48 meV for the conductivity of oCVD PT films. Since, in general, hopping mechanism requires small activation energy one the order of ~10–100 meV, the value extracted for activation energy (i.e., 48 meV) supports that the hopping conduction is the dominant conduction mechanism in oCVD PT films.[37] The relevant literature to compare \(E_a\) of oCVD PT for the hopping conduction is not available, since unsubstituted PT has been challenged to process due to its insolubility in any solvents. If compared with its derivatives, the value 48 meV of oCVD PT is comparable to its derivatives and other conjugated polymers of poly(3-alkylthiophene), known as P3HT (~80–280 meV),[38] poly(3-alkylthiophene) (~42–83 meV),[39] and polyaniline (~22–29 meV).[40]

Figure 4 shows the in situ conductivity measurements as a function of temperature for the oCVD PT with the highest carrier density of \(3.4 \times 10^{17} \text{ cm}^{-3}\). Unlike other PT films with lower carrier density, the PT film with the highest carrier concentration of \(3.4 \times 10^{17} \text{ cm}^{-3}\) shows a different behavior. In Figure 4a, although the conductivity increases from \(2.84 \times 10^{-4} \text{ S cm}^{-1}\) to \(1.11 \times 10^{-3} \text{ S cm}^{-1}\) initially at lower temperatures from 20 to 80 °C, the trend reverses at higher \(T\) and the conductivity decreases to \(6.43 \times 10^{-4} \text{ S cm}^{-1}\). Since other lower-doped PT films present a continuous increase in conductivity with temperature in the same \(T\) regime, the behavior of the conductivity decrease shown in the highest doped PT is neither attributed to structure nor to hopping transport degradation. Instead, the resulting conductivity decrease is likely associated with the doping concentration in the film. During oxidative polymerization through oCVD process, FeCl₃ is utilized as doping agents, which accept delocalized electrons and leave dopant counterions, i.e., Cl⁻ and FeCl₄⁻. This process leads to p-type conductivity in PT. A large number of dopant counter ions and residual FeCl₃ likely react with water and oxygen in the air during the measurements at relatively high \(T\) above ~100 °C, which releases electrons back to the polymer backbone. These electrons recombine with positive hole carriers, which yields a reduction in carrier density and hence the conductivity.[33,41] Although previous studies on the conductivity degradation of unsubstituted PT are not available in the literature due to the novelty of the present study and partially to its process difficulties through conventional solution techniques, the effect of high doping concentration (i.e., high density of dopant counterions) and residual oxidizing agents on the conductivity of oxidative polymerized thiophene is possibly considered by other thiophene derivatives. We previously suggested the dedoping mechanisms that govern poly(3,4-ethylenedioxythiophene) (PEDOT) processed utilizing FeCl₃ as oxidants, where a similar conductivity decrease was observed in the presence of water and oxygen, reacting with FeCl₄⁻ and residual FeCl₃ according to reactions (5) and (6)

\[
\text{FeCl}_3^- + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 = \text{Fe(OH)}_2^- + 2\text{Cl}_2^- + \text{e}^- \quad (5)
\]

where Fe(OH)₂ and Cl₂ are the reaction products in gas phase. The formation of an Fe(OH)₂ liberates one electron, which was initially removed from the polymer backbone while leaving one p-type carrier (i.e., hole). The generated electrons reduce the hole carrier density in the polymer by recombining with the holes and, consequently, decrease the electrical conductivity.

Another dopant counterion, Cl⁻ also contributes to the degradation process via the reaction

\[
\text{Cl}^- + \text{FeCl}_3 = \text{FeCl}_4^- \quad (6)
\]

where Cl⁻ produces additional FeCl₄⁻ when residual FeCl₃ exists, this FeCl₄⁻ repeats reaction (5) and generates additional electrons, reducing the conductivity. Likewise, if there are excessive dopant counter ions and residual oxidizing agents in PT and high temperature that allows faster reaction and gas (e.g., \(\text{H}_2\text{O}\) and \(\text{O}_2\) in the present study) diffusion rates, the carrier density is facilitated to decrease and,
consequently, the overall conductivity of PT is reduced. The conductivity values that decrease at higher temperature are replotted on conventional Arrhenius plot in Figure 4b, where the activation energy for the conductivity reduction for oCVD PT is found to be \( \approx 180 \text{ meV} \). This \( E_g \) value is much smaller than that of oCVD PEDOT, a well-known thiophene derivative, \( E_g = 560–710 \text{ meV} \) for conductivity decrease in air.\(^{[13]}\) The smaller \( E_g \) value of PT can be understood by the acceptor level of FeCl\(_3\) dopants within the bandgap \( (E_g \text{PT} \approx 1.98 \text{ eV}) \) is located in a shallower energy level than that of PEDOT \( (E_g \text{PEDOT} \approx 1.80 \text{ eV}) \) since the conductivity change is associated with electron–hole recombination processes as discussed with reactions (5) and (6). Figure 4c shows the change in conductivity of PT with the highest carrier density whose conduction is governed by VRH hopping, at lower temperatures ranging from 20 to 80 °C (adapted from Figure 3e).

In order to investigate the chemical environment and the valence state of the oCVD PT films and also to evaluate the effect of annealing at relatively high T of 150 °C on the doping state, the binding energy of major elements was measured by XPS survey and core-level high-resolution scans before and after annealing in air. Figure 5a shows full survey scans (0–700 eV) of not-annealed and annealed oCVD PT and the spectra are similar to each other showing considerable peaks from O, C, S, and Cl with a substrate Si peak. Core-level high-resolution XPS spectra of Cl 2p are given in Figure 5b,c for the not-annealed and annealed PT. The Cl 2p spectrum in Figure 5b was best fitted into two spin–orbit splitting doublets of Cl 2p\(_{3/2}\) and Cl 2p\(_{1/2}\) with the binding energy difference of 1.6 eV, whose Cl 2p\(_{3/2}\) components are located at \( \approx 200.8 \) and 198.4 eV. The intensity ratio between doublets is conserved to 2:1 as typical Cl species. The strong peak components (91.55 at\% of total Cl species whose value was determined from the area of the Cl 2p spectra in (Figure 5b)) with Cl 2p\(_{3/2}\) at BE 200.8 eV and Cl 2p\(_{1/2}\) at 202.4 eV are attributed to the C–Cl species, resulting from the chlorination of the polymer backbone during doping.\(^{[42]}\) The components with Cl 2p\(_{3/2}\) at 198.4 eV and Cl 2p\(_{1/2}\) at 199.9 eV (8.45 at\% of total Cl species in (Figure 5b)) are associated with the formation of Cl\(^{−}\) and FeCl\(_4^{−}\).\(^{[42,43]}\) The existence of chlorine in Cl\(^{−}\) and FeCl\(_4^{−}\) species in the polymers suggests that the oCVD-processed PT is in the partially doped state even after postdeposition dedoping rinse in methanol, which is also expected from the carrier density \( (0.5–3.4 \times 10^{17} \text{ cm}^{-3}) \) of the films. Figure 5c shows the Cl 2p high-resolution spectra after annealing at 150 °C in air for 2 h. Two similar spin–orbit splitting doublets are seen at nearly the same binding energies. However, a significant intensity decrease is clearly observed in the doublet with Cl 2p\(_{3/2}\) at 198.4 eV (1.88 at\% of total Cl species in (c)) compared with that of the not-annealed PT in Figure 5b, which indicates that the FeCl\(_4^{−}\) concentration in the PT film is reduced after annealing process and hence the carrier density as well in the film. A similar trend was observed in the high-resolution XPS spectra of S 2p species before and after annealing (Figure S2, Supporting Information): the intensity of a spin–split double of S 2p\(_{3/2}\) at 168.37 eV and S2p\(_{1/2}\) at 169.57 eV, which results from the broadening due to the delocalized \( \pi \) electrons in thiophene ring (i.e., doping effect), decreased after annealing. This XPS analysis of oCVD PT which describes the reduced doping concentration is in good agreement with the discussion of the mechanism for the electron–hole recombination process that decreases hole density during annealing in the presence of water and oxygen.

3. Conclusion

Unsubstituted PT, which is promising but has been challenging to process, was synthesized and deposited using the oCVD technique in a relatively simple and easy way. We reported on the conduction mechanism of nanostructured oCVD PT thin films through the investigation of in situ conductivity measurements at temperatures ranging from 20 up to 160 °C. It was identified that 3D VRH process governs the transport of charge carriers in oCVD PT with an activation energy of \( \approx 48 \text{ meV} \) regardless of doping concentrations. oCVD PT films demonstrated excellent thermal stability at modest temperatures up to 160 °C used in this study. However, this thermal stability was found to be significantly related to the doping concentration of PT films: the thermal stability was degraded for the PT film with high carrier density \( (3.4 \times 10^{17} \text{ cm}^{-3}) \) in the present study), which led to the conductivity reduction at temperatures above 100 °C. XPS analysis accounted for the conductivity decrease resulting from the reduction in dopant FeCl\(_4^{−}\) concentration and carrier density, which was supported...
by the suggested chemical reactions describing electron–hole recombination.

4. Experimental Section

**oCVD PT Deposition**: PT films were deposited using oCVD in a custom-built reactor described in detail elsewhere. Briefly, monomer vapor flowed from a heated glass jar outside of the reactor and into the reactor chamber through an inlet port. A dry pump was used to achieve chamber pressures down to \(\approx 10\) mTorr, while a turbomolecular pump (Pfeiffer Vacuum, HiPace 300C) was used to maintain reactor pressures around 1 mTorr. A throttle valve (MKS Instruments, Model 628D), and an active pirani/cold cathode gauge (Pfeiffer Vacuum, PKR 261), respectively.

Glass slides and thermally oxidized (50 nm) silicon wafers (SiO\(_2\)/Si) were used as substrates and placed on the stage, which was rotated at about three rotations per minute. Iron(III) chloride (FeCl\(_3\), 97%, Sigma-Aldrich) oxidizing agent and thiophene (\(\approx 99\%\), Sigma-Aldrich) monomer were used as purchased. The thiophene monomer jar was maintained at a temperature of 20 °C and a needle valve was used to introduce the gas at a flow rate of \(\approx 31\) sccm into the reactor chamber. The chamber pressure during deposition impacted the flow rate of FeCl\(_3\) from the crucible and therefore the heating temperatures were adjusted to give similar deposition rates. For deposition pressures of 1, 75, 150, and 300 mTorr, the FeCl\(_3\) crucible was heated to 170, 190, 200, and 225 °C. 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, except for depositions run at 1 mTorr, which required 40 min. After deposition, the samples were removed from the chamber and rinsed in methanol (\(\approx 99.9\%\), Sigma-Aldrich) for 30 min, 0.2 \(\mu\)L HCl in methanol for 10 min, and then 1 min in methanol to remove reacted and excess oxidant and dedope the PT. Postdeposition rinsing has been shown to improve the electrical and physical properties of the vapor phase polymerized films, 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). However, the current rinsing process may be more effective in the near surface region than the region away from the surface. Longer rinsing times, higher rinsing temperatures, and the use of thinner films would all be expected to favor further removal of residual oxidant from the entire thickness of the films.

**Device Fabrication and the Conductivity Measurements**: The devices for the evaluation of the conductivity of oCVD PT were fabricated on SiO\(_2\)/Si substrates. The PT (\(\approx 40\) nm) was deposited on the substrates using oCVD in the conditions described in the previous section. As an electrode layer, patterned Ag was thermally evaporated on top of the oCVD PT films. The PT and Ag electrode regions were patterned by vapor-printing technique using in situ shadow masks. The sheet resistance (\(R_s\)) of samples was obtained from current–voltage (\(I-V\)) measurements through TFT/TLM analysis (see Figure S3 in the Supporting Information) using Agilent B1500 integrated with Materials Development Corporation temperature controllable probe station and hence, the conductivity was extracted from the measured sheet resistance and the geometric dimensions (width \(W\), length \(L\), and thickness \(t\)) of the sample. It should be noted that the resulting conductivity values obtained through the TFT/TLM measurements were independent of the contact resistance (\(R_c\)) between active layer (oCVD-processed unsubstituted PT film in the present study) and the metallization material (i.e., Ag) since, in principle, the conductivity (obtained from \(R (L \times t)\)) was separately determined using the equation, 

\[
R_{\text{total}} = R_{\text{c}} + (R(L)/W),
\]

where \(R_{\text{total}}\) is the total resistance extracted from the measured \(I-V\) plots. The carrier density (\(\rho\)) of the oCVD PT films was also evaluated through the TFT/TLM measurements. This TFT/TLM analysis allowed for the determination of the field-effect mobility (\(\mu_{\text{FE}}\)) and the conductivity (\(\sigma\)) of each PT film, and consequently the carrier density was estimated using the equation \(\sigma = \rho \mu_{\text{FE}} q\), where \(q\) is the unit charge of electron (i.e., \(1.6 \times 10^{-19}\) C). More detailed procedures to evaluate the conductivity, the carrier density and contact resistance through the TFT/TLM measurements can be found elsewhere.[5,22,44]

**Material Characterizations**: For chemical environments and valence states analysis for the major elements of the samples, XPS measurements were performed in a Thermo Scientific K-Alpha XPS spectrometer under high vacuum below \(2 \times 10^{-8}\) Torr using focused monochromatic Al K\(_\alpha\) X-ray radiation at 1486.6 eV and an electron flood gun that prevents charging. Photoelectrons were collected at an angle of 55° from the surface normal. Microstructures of the oCVD PT films and devices were analyzed using JEOL JSM-6610LV SEM. Film thicknesses were measured using a Veeco Dektak 150 surface profilometer and a J.A. Woollam M-2000 variable angle spectroscopic ellipsometer. Topographic images of the oCVD PT films were obtained using an Agilent Technologies AFM in noncontact tapping mode with a Bruker Si cantilever (tip frequency of 330 kHz).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

carrier transport, oxidative chemical vapor deposition (oCVD), thermal stability, unsubstituted polythiophene, variable range hopping

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