

# Doping level and work function control in oxidative chemical vapor deposited poly (3,4-ethylenedioxythiophene)

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Control over doping level and work function is achieved for poly(3,4-ethylenedioxythiophene) (PEDOT) films deposited by oxidative chemical vapor deposition (oCVD). Surface analysis reveals the equivalence of the surface and bulk compositions for the oCVD films. The oCVD PEDOT polymer chains doped solely with Cl<sup>-</sup> ions. By increasing the substrate temperature used for deposition, the doping level was monotonically increased from 17 to 33 at. %, resulting in a corresponding ability to tune the work function from 5.1 to 5.4 eV. The controllability of doping level and work function of oCVD PEDOT offers great potential advantages for organic devices.

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Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most promising conjugated polymers, possessing high electrical conductivity, good optical transparency, and chemical stability.<sup>1</sup> PEDOT films can be applied by a variety of methods, and the aqueous suspension of PEDOT with poly(styrenesulfonate) (PSS) makes solution processing possible.<sup>1</sup> Indeed most organic device applications have been fabricated with PEDOT:PSS. Some limitations of the solution processing are that (a) hydrophilic surface treatment of substrate is critical to obtain uniform films,<sup>2</sup> (b) metallic ionic impurities are detrimental to device performance,<sup>3</sup> and (c) the excess PSS in PEDOT:PSS system leads to corrosion.<sup>4,5</sup> Indeed, x-ray photoelectron spectroscopy (XPS) studies show that PSS segregates to the surface which may induce interfacial degradation in devices.<sup>6</sup> Low conductivity also limits the PEDOT:PSS film from practical applications, such as conducting electrodes.<sup>7,8</sup> The conductivity of PEDOT:PSS film can be increased by treating with ethylene glycol or sorbitol, but still the mechanism of conductivity enhancement is controversial.<sup>7,8</sup>

PEDOT:PSS has been widely used as a hole injecting layer (HIL) in organic light emitting diodes.<sup>3</sup> The efficiency of hole injection depends critically on the work function of the HIL layer.<sup>9</sup> Numerous empirical methods have been developed for altering work function. Dedoping treatments (electrochemical doping) have achieved modulation of the work function in both PEDOT:PSS<sup>10</sup> and in electrochemically deposited PEDOT.<sup>11</sup> Chemical acid and/or base treatment also produce changes in the work function of PEDOT:PSS.<sup>3</sup> Metal ion concentration, pH,<sup>12</sup> and post-heat-treatment<sup>9</sup> have also been shown to influence work function.

Recently, the formation of PEDOT films via oxidative chemical vapor deposition (oCVD) technology was reported. The oCVD vacuum process formed highly conductive and optically transparent PEDOT films.<sup>13</sup> The inherently confor-

mal nature of coating makes oCVD PEDOT suitable for substrates with high surface area without damaging the substrate structure. Moreover, by controlling the substrate temperature of the oCVD process, the electrical conductivity and conjugation length of the resultant PEDOT film were systemically controlled with ease.<sup>13</sup> The systematic variation in chemical structure of the oCVD films presents an opportunity to perform research that will enhance the fundamental understanding of structure-property relationships in conducting polymers.

In this study, XPS, scanning transmission electron microscopy (STEM) with energy dispersive x-ray analysis (EDX), and photoelectron spectroscopy were used to determine the chemical and electrical properties of a series PEDOT films systematically prepared by varying only the substrate temperature of the oCVD process.

The oCVD reactor for PEDOT has been described in detail elsewhere.<sup>13</sup> All the chemicals were purchased from Sigma-Aldrich and used without further purification. To create a series of samples, the substrate temperature was systematically incremented over the range from 15 to 100 °C. For all depositions, the vacuum level was controlled at 150 mTorr and 3,4-ethylenedioxythiophene was introduced into the chamber at 3 SCCM (SCCM denotes cubic centimeter per minute at STP), sublimated Fe(III)Cl<sub>3</sub> was used as oxidizing agent, the process time was 30 min. The as-deposited film was subsequently annealed in dry oven at 70 °C for 2 h and rinsed with copious methanol to remove any unreacted oxidant and oxidation by-products. XPS was done on a Kratos Axis Ultra spectrometer equipped with a monochromatized Al K $\alpha$  source. STEM (VGHB603 STEM) was performed on cryomicrotomed samples, using an Oxford EDX detector and Inca VISION SOFTWARE for elemental analysis. The work function of oCVD PEDOT was also monitored with a surface analyzer using Riken-Keiki AC-2.<sup>14</sup> The measurements were performed at room temperature with nitrogen purge. The measured work function was calibrated by measuring the ionization potential of N,N'-(dinaphthalene-1-yl)-N,N'-diphenyl-benzidine (NPB)

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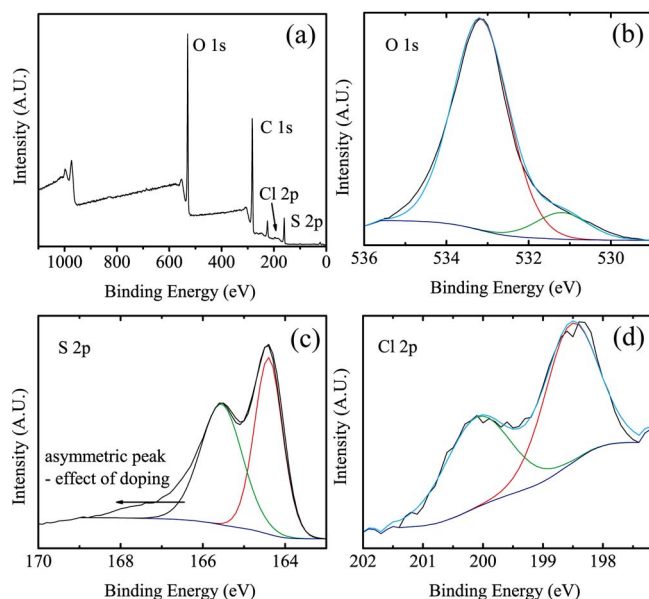


FIG. 1. (Color online) (a) XPS survey scan of oCVD PEDOT deposited at a substrate temperature of 15 °C; high resolution XPS spectrum of (b) O 1s; (c) S 2p; and (d) Cl 2p of oCVD PEDOT deposited at a substrate temperature of 100 °C.

and compared with the reference value of 5.4 eV.<sup>15</sup>

Figure 1(a) shows the XPS survey scan of oCVD PEDOT deposited at substrate temperature of 15 °C. The C, O, and S are the characteristic elements of the PEDOT polymer while Cl represents the dopant ions. Significantly, Fe was not detected at the surface indicating that reaction by-products from Fe(III)Cl<sub>3</sub> oxidant were completely removed by the rinsing step, allowing a pure PEDOT:Cl surface to be obtained. XPS survey scans of the samples deposited at higher temperature (not shown) also detected only C, S, and O and no Fe. The XPS clearly shows that surface consists of pure, conductive PEDOT doped with Cl<sup>-</sup> ions without any phase segregation. In contrast, in PEDOT:PSS, the phase segregation occurs between PEDOT and PSS phases and corrosive PSS-rich (78 at. %) phase is dominant at the surface of PEDOT:PSS.<sup>6</sup>

The O 1s (b), S 2p (c), and Cl 2p (d) core-level high resolution XPS spectra of oCVD PEDOT deposited at the substrate temperature of 100 °C are also shown in Fig. 1. The XPS spectra of PEDOT deposited at the other substrate temperatures (not shown) showed all of the same major peaks. In O 1s core-level XPS spectrum [Fig. 1(b)], the dominant peak at 533.2 eV corresponds to the sole oxygen bonding environment in PEDOT, while a small broad shoulder most likely results from residual rinsing solvent (methanol) or moisture adsorption.<sup>6</sup> The S 2p core-level high resolution XPS spectrum [Fig. 1(c)] corresponds to single sulfur bonding environment in PEDOT with a spin-split doublet, S 2p<sub>1/2</sub> and S 2p<sub>3/2</sub> with a 1.18 eV energy splitting.<sup>6,16</sup> The asymmetric tail to higher binding energy is related with the doping process,<sup>6</sup> in which the delocalized  $\pi$  electrons in thiophene ring broaden the binding energy spectrum of the S atom. The Cl 2p core-level high resolution XPS spectrum [Fig. 1(d)] also reveals a single chemical species of Cl, which has a spin-split doublet, Cl 2p<sub>1/2</sub> and Cl 2p<sub>3/2</sub> having a 1.60 eV energy splitting.<sup>16</sup> Previous study of oxidatively synthesized PEDOT film with Fe(III)Cl<sub>3</sub> oxidizing agent has reported that the possible dopants of PEDOT are FeCl<sub>4</sub><sup>-</sup> or

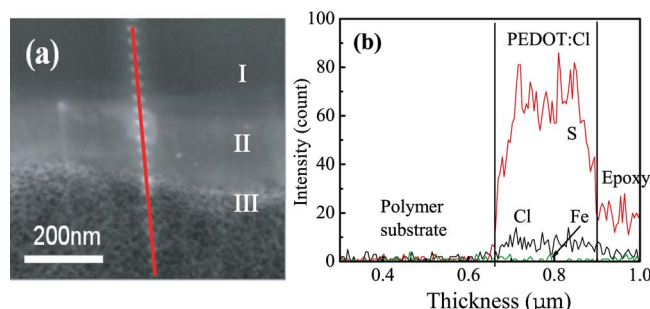


FIG. 2. (Color online) (a) STEM cross-sectional image; (b) EDX data obtained by scanning along the red line in (a). The lateral resolution of EDX measurement was 5 nm.

simple Cl<sup>-</sup> ion.<sup>17</sup> From both wide scan and Cl 2p core-level XPS spectrum, the possibility of FeCl<sub>4</sub><sup>-</sup> dopants can be clearly excluded. Therefore it can be concluded that the surface consists only of PEDOT chains doped solely with Cl<sup>-</sup> ion.

The cross-sectional STEM image in Fig. 2(a) shows a 200 nm thick oCVD PEDOT film (deposited on a rubbery block copolymer) having a conductivity of  $\sim 300$  S/cm. An EDX scan of the red line in Fig. 2(a) is given as chemical profile information in Fig. 2(b). This line scan, performed after rinsing, shows a sharp decrease of S and Cl at the interface between the PEDOT film and polymer substrate. The observation of Cl in the postrinsed films indicates that it is mostly likely present in the form of Cl<sup>-</sup> ions with strong electrostatic attraction to the PEDOT polymer. Additionally, the level of Fe detected in the PEDOT layer was negligible ( $<4$  counts) and indistinguishable from the level detected in the substrate, confirming that the majority of Fe from oxidizing agent is removed. Thus, the cross-sectional STEM analyses are fully consistent with the surface analysis observation. From the combined result of STEM and XPS, we can conclude that the oCVD PEDOT film is uniform throughout its thickness and doped solely with Cl<sup>-</sup> ions.

The doping level of oCVD PEDOT is equal to the atomic ratio of [Cl] to [S] and thus can be directly calculated from XPS survey scan [Fig. 3(a)]. As the substrate temperature increase from 15 to 100 °C, the doping level changed from 17 to 33 at. %, and the corresponding conductivity of oCVD PEDOT increases from a low of  $9.1 \times 10^{-4}$  S/cm to a high of 348 S/cm. Interestingly, the maximum doping level observed here for the oCVD films of 33 at. % is identical to the theoretical maximum doping level for PEDOT:PSS.<sup>1</sup>

The measured work function of oCVD PEDOT [Fig. 3(b)] decreases monotonically with increasing oCVD deposition temperature. Previously, increasing substrate tempera-

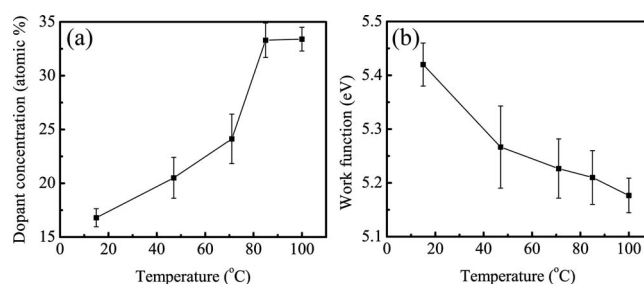


FIG. 3. Effect of the oCVD PEDOT deposition temperature on (a) doping level and (b) work function.

ture was demonstrated to result in the longer conjugation length and higher dopant concentrations in oCVD PEDOT.<sup>13</sup> Figure 3 demonstrates that higher dopant concentration produced at higher substrate temperatures introduces new electronic states in the otherwise forbidden energy gap which induce the movement of Fermi energy level,<sup>18</sup> leading to a decrease in work function. This observation is in good agreement with previous reports that increasing of doping level decreases work function.<sup>3,9</sup> From oCVD process, the systematic control over the work function is obtained without the need for postprocessing. While doping by electrochemical and chemical methods is reversible,<sup>10,11</sup> the control achieved by oCVD has a permanent upper bound imposed by the maximum achievable conjugation length. The ability to tune the work function of PEDOT over the range from 5.1 to 5.4 eV has technological importance for achieving balanced charge injection into organic devices.<sup>3</sup> In particular, the ionization potential of NPB is estimated to be 5.4 eV, and thus giving a very small barrier height between oCVD PEDOT and NPB which is desired for an Ohmic contact.

In summary, we have demonstrated with XPS that the surface of oCVD PEDOT consists purely of PEDOT doped with Cl<sup>-</sup> ions. Uniform composition was maintained uniformly throughout the entire thickness of bulk film and its surface. The EDX demonstrates that the oCVD film forms an abrupt interface with the substrate. Unlike PEDOT:PSS where excess dopant is observed to segregate to the surface, dopant segregation was not observed in the oCVD PEDOT films, creating an enormous potential benefit for producing organic device with superior interfaces. The elimination of the PSS dopant enhances conductivity. Indeed, the maximum conductivity for current series of oCVD was 348 S/cm. In addition, the dopant concentration of oCVD films can be systemically controlled from 16 to 33 at. % by changing only the substrate temperature employed for film growth, and thus the work function of the final material can also be precisely tuned over the range of 5.1–5.4 eV. Tuning the work

function over this range is anticipated to facilitate the formation of Ohmic contacts in organic devices.

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<sup>1</sup>S. Kirchmeyer and K. Reuter, *J. Mater. Chem.* **15**, 2077 (2005).

<sup>2</sup>T. Kawase, H. Sirringhaus, R. H. Friend, and T. Shimoda, *Adv. Mater.* (Weinheim, Ger.) **13**, 1601 (2001).

<sup>3</sup>P. K. H. Ho, J. S. Kim, J. H. Burroughes, H. Becker, S. F. Y. Li, T. M. Brown, F. Cacialli, and R. H. Friend, *Nature (London)* **404**, 481 (2000).

<sup>4</sup>M. P. de Jong, L. J. van Ijzendoorn, and M. J. A. de Voigt, *Appl. Phys. Lett.* **77**, 2255 (2000).

<sup>5</sup>W. H. Kim, A. J. Makinen, N. Nikolov, R. Shashidhar, H. Kim, and Z. H. Kafafi, *Appl. Phys. Lett.* **80**, 3844 (2002).

<sup>6</sup>G. Greczynski, T. Kugler, M. Keil, W. Osikowicz, M. Fahlman, and W. R. Salaneck, *J. Electron Spectrosc. Relat. Phenom.* **121**, 1 (2001).

<sup>7</sup>J. Ouyang, Q. F. Xu, C. W. Chu, Y. Yang, G. Li, and J. Shinar, *Polymer* **45**, 8443 (2004).

<sup>8</sup>J. Y. Kim, J. H. Jung, D. E. Lee, and J. Joo, *Synth. Met.* **126**, 311 (2002).

<sup>9</sup>J. S. Huang, P. F. Miller, J. S. Wilson, A. J. de Mello, J. C. de Mello, and D. D. C. Bradley, *Adv. Funct. Mater.* **15**, 290 (2005).

<sup>10</sup>F. Zhang, A. Petr, H. Peisert, M. Knupfer, and L. Dunsch, *J. Phys. Chem. B* **108**, 17301 (2004).

<sup>11</sup>H. Frohne, S. E. Shaheen, C. J. Brabec, D. C. Muller, N. S. Sariciftci, and K. Meerholz, *ChemPhysChem* **3**, 795 (2002).

<sup>12</sup>M. M. de Kok, M. Buechel, S. I. E. Vulto, P. van de Weijer, E. A. Meulenlamp, S. de Winter, A. J. G. Mank, H. J. M. Vorstenbosch, C. H. L. Weijtens, and V. van Elsbergen, *Phys. Status Solidi A* **201**, 1342 (2004).

<sup>13</sup>J. P. Lock, S. G. Im, and K. K. Gleason, *Macromolecules* **39**, 5326 (2006).

<sup>14</sup>D. H. Hwang, J. I. Lee, N. S. Cho, and H. K. Shim, *J. Mater. Chem.* **14**, 1026 (2004).

<sup>15</sup>S. T. Lee, Y. M. Wang, X. Y. Hou, and C. W. Tang, *Appl. Phys. Lett.* **74**, 670 (1999).

<sup>16</sup>J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy* (Physical Electronics, Eden Prairie, MN, 1995), Chap. 2, p. 44.

<sup>17</sup>T. Yamamoto and M. Abila, *Synth. Met.* **100**, 237 (1999).

<sup>18</sup>M. Logdlund, R. Lazzaroni, S. Stafstrom, W. R. Salaneck, and J. L. Bredas, *Phys. Rev. Lett.* **63**, 1841 (1989).