



## Enhanced Performance of Poly(3-hexylthiophenes) Based Thin Film Transistors Using Double-Coated Active Layer

Chia-Hao Chang<sup>a</sup> and Chao-Hsin Chien<sup>b,c,z</sup>

<sup>a</sup>Department of Electronics Engineering and Institute of Electronics, National Chiao Tung University, Hsinchu, Taiwan

<sup>b</sup>Department of Electronics Engineering and Institute of Electronics, National Chiao Tung University, Hsinchu, Taiwan

<sup>c</sup>National Nano Device Laboratories, Hsinchu, Taiwan

This study demonstrates that thin-film transistors with double-coated poly(3-hexylthiophene) (P3HT) channel layers (DPTFTs), which are formed by coating a second P3HT layer on top of the N<sub>2</sub>-annealed first P3HT layer, show a higher on/off current ratio and better subthreshold swing, compared to single-layer P3HT transistors (PTFTs). Characteristics of DPTFTs were investigated by varying the thicknesses of the first P3HT layer and the second P3HT layer. Moreover, DPTFTs with an as-prepared first layer, i.e., without N<sub>2</sub> annealing, were also prepared for comparison. A thin gate oxide was incorporated into the DPTFTs, which resulted in an impressive subthreshold swing (smaller than 1 V/decade). Furthermore, the study proposes new DPTFTs with an N<sub>2</sub>-annealed first layer and a functionalized single-wall carbon nanotube (F-SWCNT)-doped P3HT second layer. Significant improvements are observed not only in subthreshold swing and on/off current ratio but also in mobility induced by the innovative channel structure and doping of F-SWCNTs, respectively.

© 2012 The Electrochemical Society. [DOI: 10.1149/2.012206jss] All rights reserved.

Manuscript submitted April 23, 2012; revised manuscript received August 17, 2012. Published October 2, 2012.

Semiconducting polymers are attractive because they can be processed easily on a large-scale flexible substrate at a low processing temperature and at low cost. Solution-processable, self-organized, regioregular poly(3-hexylthiophene) (P3HT) is suitable for fabricating organic thin-film transistors (OTFTs) because of their high carrier mobility. OTFTs with a P3HT active layer (i.e., PTFTs) have demonstrated high hole mobility (0.01–0.3 cm<sup>2</sup>/V s), with a reasonable on/off ratio (more than 100 in air and 10<sup>6</sup> in an inert atmosphere).<sup>1–3</sup> Studies have attempted to improve their performance by enhancing the crystallinity of the P3HT layer through various techniques, such as changing solvents, modifying coating methods, and/or incorporating thermal annealing.<sup>3–6</sup> Other than improving crystallinity, the dopant concentration in the P3HT and the injection barrier between P3HT and the electrodes can also be modified by thermal annealing.<sup>3,7–10</sup> Recent studies have proposed a correlation between the characteristics of PTFTs and the thickness of the active layer.<sup>11–13</sup> This correlation was attributed to the existence of bulk current in the active layer before the formation of the accumulation layer, and a higher bulk current is usually conducting in a thicker active layer.<sup>11,12</sup> Moreover, poor off-current and subthreshold swing were observed when the thickness of the active layer was increased.<sup>11,12</sup> Therefore, based on this knowledge, this study developed an innovative technique that can dramatically improve the performances.

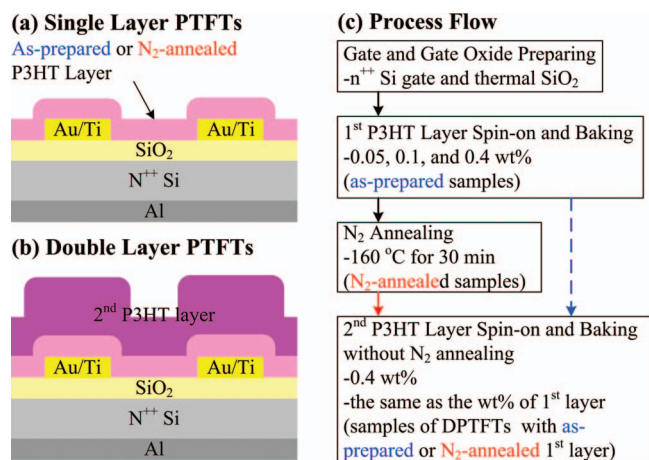
In this study, a systematic investigation was conducted on new devices with double-coated channel layers (DPTFTs). The DPTFTs were formed by coating a second P3HT layer on top of the N<sub>2</sub>-annealed first P3HT layer, which showed superior characteristics to conventional PTFTs (i.e., channels composed of a single P3HT layer). More than two orders of magnitude of improvement were observed for the on/off current ratio, as well as a significantly lower subthreshold swing. To explain such extraordinary improvements, different thicknesses of the first and second active layers were used to study the mechanism. Evident correlation between the improvement and the thickness of the N<sub>2</sub>-annealed first layer and second layer were observed. We also extracted the contact resistance of the as-prepared and N<sub>2</sub>-annealed PTFTs. The results were interpreted by evaluating the different levels of dopant concentration present in the channels. A lower dopant concentration in the N<sub>2</sub>-annealed P3HT resulting in higher injection barrier can reduce leakage current and improve subthreshold swing because of suppression of bulk current. Lowered on-current accompanying with the reduction of bulk current can be overcome by using the double-coated channel structure. There is on-current as high as that of devices with conventional, thick and/or as-prepared single channel. A simple equivalent circuit and a speculated band structure show that

the enhancements of the DPTFTs resulted from the carriers conducting away from the interface between the first channel layer and the SiO<sub>2</sub> gate oxide before the formation of accumulation layer. Moreover, the study demonstrates that the operational voltage of fabricated DPTFTs with a thin first N<sub>2</sub>-annealed active layer and gate dielectric can be lowered to operate under less than 10 V, with a minimized subthreshold swing value of <1 V/decade. The DPTFTs with an N<sub>2</sub>-annealed P3HT first layer and second layer composed of F-SWCNTs and P3HT exhibit improvements in mobility, on/off current ratio, and subthreshold swing.

### Experimental

A schematic cross section of PTFTs and DPTFTs is shown in Figs. 1a and 1b. An N<sup>++</sup>-doped silicon substrate and thermally grown oxides of 200 nm in thickness were used as gate electrodes and insulators, and a lift-off process-patterned Au/Ti (50 nm/2.5 nm) was deposited by electron beam thermal evaporation as the source/drain (S/D). Prior to deposition of the P3HT channel, the substrate was cleaned individually by acetone, isopropyl alcohol, and deionized (DI) water in an ultrasonic cleaner for 5 min, and treated by hexamethyl disilazane (HMDS) passivation in a vacuum oven at 150°C to create a hydrophobic surface. The P3HT active layer was then spun at 500 rpm for 10 s, and at 1500 rpm for 25 s, followed by baking at 150°C for 3 min on a hot plane. For the N<sub>2</sub>-annealed PTFTs, annealing in a furnace with N<sub>2</sub> for 30 min at 160°C was sequentially executed after formation of the P3HT layer. For the DPTFTs with the N<sub>2</sub>-annealed first layer, the first layer was also annealed with the same process as that of the N<sub>2</sub>-annealed PTFTs, immediately followed by the formation of the second P3HT layer without additional N<sub>2</sub> annealing. For comparison, DPTFTs with the first layer without N<sub>2</sub> annealing, referred to as the as-prepared first layer, were also prepared. The second P3HT layers were coated using the same spin coating and baking processes. To systematically investigate the mechanism, three weight percentages of P3HT solution were used (0.05, 0.1, 0.4 wt%) to obtain different thicknesses for the first P3HT layer of DPTFTs. Moreover, to further study the influences induced by the thicknesses of the second P3HT layers of DPTFTs, we designed two situations. In the first situation, the thickness of the second layer of DPTFTs was fixed by using the 0.4 wt% P3HT solution. In the second situation, the thicknesses of the second layer were varied to match the same thicknesses of the first layer of DPTFTs. The active layers of PTFTs, i.e., devices with single-channel layers, were also coated with the 0.05, 0.1, 0.4 wt% P3HT solutions to act as the control. The process flow of this work is shown in Fig. 1c. Additionally, thin thermal oxide (25 nm) was used as the gate dielectric for the DTFTs.

<sup>z</sup>E-mail: [chchien@faculty.nctu.edu.tw](mailto:chchien@faculty.nctu.edu.tw)

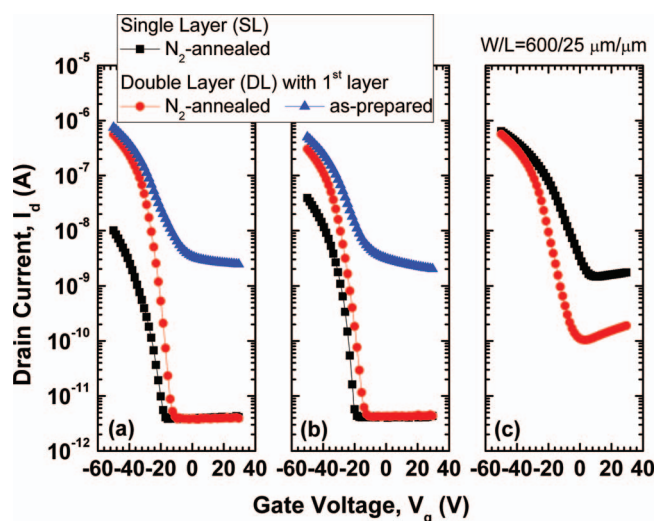


**Figure 1.** Scheme of the device structure of (a) PTFTs and (b) DPTFTs, and (c) the process flow. The first P3HT layer of DPTFTs are either as-prepared or  $N_2$ -annealed.

This study also proposes DPTFTs with the  $N_2$ -annealed first layer and the functionalized single-wall carbon nanotube (F-SWCNT)-doped P3HT second layer. The  $N_2$ -annealed first layer was coated with the 0.05 wt% P3HT solution, and the second layer was coated with a solution blend of F-SWCNTs and P3HT (1:5) in chloroform (0.2 wt%). The PTFTs with  $N_2$ -annealed P3HT, 0.05 wt%, channel layer, or with as-prepared F-SWCNT-doped P3HT channel layer, of which the component was the same as the second layer of DPTFTs, and DPTFTs with  $N_2$ -annealed, 0.05 wt%, first layer and as-prepared, 0.2 wt%, second layer are employed for a comparison. Chloroform, which evaporates easily after baking, was used as the solvent for P3HT, so that the effects of a residual solvent in the P3HT film can be excluded. All of the P3HT solutions were treated with ultrasonic vibration for 5 min and percolated by a PTFE membrane syringe filter with a pore size of 0.2  $\mu\text{m}$ . The regioregular P3HT used in this study was purchased from FEM, Inc. ( $M_w = 50\,000$ ), and the given coupling ratio of head-tail to head-head and tail-tail was approximately 90%. The thicknesses of PTFTs and DPTFTs were confirmed by scanning electron microscopy (SEM). P3HT thin films were not uniform, which might have been due to the fast evaporating of the solvent. The average thicknesses of PTFTs, with 0.05, 0.1, and 0.4 wt% solutions, were approximately 50, 90, and 200 nm, respectively. Moreover, the thicknesses of DPTFTs with the second layer coated with the 0.4 wt% P3HT solution and the  $N_2$ -annealed first layers, which were coated with 0.05 and 0.4 wt% solutions, were approximately 250 nm and 470 nm, respectively. The electrical properties of P3HT TFTs were measured by a Hewlett-Packard 4156C semiconductor parameter analyzer, and the devices were evaluated at their saturation region with a drain voltage of  $-40$  V. Mobility was extracted by maximum transconductance in the saturation region. All of the devices were processed and characterized in air atmosphere.

## Results and Discussion

The drain current-gate voltage ( $I_d$ - $V_g$ ) properties of the fabricated PTFTs and DPTFTs are shown in Fig. 2. The weight percentages of solutions of P3HT in chloroform for the PTFTs and the first layer of DPTFTs were (a) 0.05, (b) 0.1, and (c) 0.4 wt%. The thickness of the second layer of the DPTFTs was fixed by coating it with the 0.4 wt% P3HT solution. As expected, the electrical characteristics were improved for on-current level, on/off current ratio, and subthreshold swing for single-layer PTFTs with  $N_2$  post-annealing.<sup>3,4</sup> Characteristics of the as-prepared PTFTs are not shown, for the sake of simplicity. However, significant enhancements were observed in the proposed DPTFTs with the  $N_2$ -annealed first layer. An enhancement of greater than one order of magnitude on the on-current level, greater



**Figure 2.** Transfer current characteristics of PTFTs and DPTFTs that PTFT channels or the first layers of DPTFTs use (a) 0.05, (b) 0.1 and (c) 0.4 wt% P3HT solutions. PTFTs are  $N_2$ -annealed, and the first P3HT layers of DPTFTs are either with or without  $N_2$  annealing. The second layer of DPTFTs use 0.4 wt% P3HT channel without annealing.

than two orders of magnitude in the on/off current ratio, and a steeper subthreshold swing for the DPTFTs with the 0.05 wt% P3HT first layer were observed. Slightly less significant improvements were observed for those with the 0.1 wt% P3HT first layer. To exclude the possibility that the improvements resulted from the thicker active layer, characteristics of the DPTFTs with the as-prepared first layer were also observed. An increased on-current level, but an inferior on/off current ratio and subthreshold swing were observed. The result was expected when the active layer in the PTFTs thickened. To further understand the primary cause of the tremendous improvements observed in the DPTFTs, PTFTs with a thicker P3HT channel formed by the 0.4 wt% solution were also fabricated. The  $I_d$ - $V_g$  characteristics of the PTFTs with a thicker P3HT layer are shown in Fig. 2c. DPTFTs with a thicker  $N_2$ -annealed first P3HT layer show a better subthreshold swing and on/off current ratio, but no gain on the on-current level compared to the PTFTs with a  $N_2$ -annealed thicker channel. This result implies that the on-current, which is increased by using the double-coated structure, decreases with the thicker  $N_2$ -annealed P3HT first layer. The properties of DPTFTs with the as-prepared first layer (Figs. 2a and 2b) were similar to those of PTFTs with a thick single-channel layer, (Fig. 2c). However, the DPTFTs with the  $N_2$ -annealed first layer showed properties that were superior to those of the DPTFTs with the as-prepared first layer, or PTFTs with a thick channel. The extracted values of the saturation field effect mobility, on/off current ratio, and subthreshold swing for these samples are shown in summary form in Table I.

To gain insight on the enhanced performance induced by incorporating a double-coated channel layer, we further investigated the characteristics of DPTFTs with different thicknesses in the second layer. We found that their properties were different from those shown in Fig. 2. Thus, we extracted the contact resistances of PTFTs by using the transmission line method (TLM). The drain current-gate voltage ( $I_d$ - $V_g$ ) characteristics of the fabricated PTFTs and DPTFTs are shown in Fig. 3. The weight percentages of the solutions of P3HT in chloroform for PTFTs and the first layer of DPTFTs were 0.05 and 0.1, respectively. The thicknesses of the second layer of DPTFTs were controlled to be the same as that of the first layer. Comparing DPTFTs with PTFTs shows improvements in the on-current level, in the on/off current ratio, and the subthreshold swing in the proposed DPTFTs with the  $N_2$ -annealed first layer, particularly for the DPTFTs with the 0.05 wt% P3HT first layer. However, slightly less significant improvements were observed for those with the 0.1 wt% P3HT first

**Table I. Summary of the extracted values of field effect mobility, on/off current ratio, and subthreshold swing for the devices presented in Fig. 2. The devices are biased at saturation region.**

Samples			$\mu_{\text{FET}}$ (cm <sup>2</sup> /V s)	S.S. (V/dec.)	$I_{\text{ON}}/I_{\text{OFF}}$
First layer	Second layer				
0.05 wt%	N <sub>2</sub> -annealed	n/a <sup>a</sup>	0.00016	5.07	$2.67 \times 10^3$
		0.4 wt% <sup>b</sup>	0.00397	2.97	$1.49 \times 10^5$
0.1 wt%	As-prepared	0.4 wt% <sup>b</sup>	0.00332	13.1	$3.05 \times 10^2$
		N <sub>2</sub> -annealed	n/a <sup>a</sup>	0.00048	2.76
0.4 wt%	As-prepared	0.4 wt% <sup>b</sup>	0.00242	3.6	$7.36 \times 10^4$
		N <sub>2</sub> -annealed	0.00237	12.7	$2.5 \times 10^2$
0.4 wt%	N <sub>2</sub> -annealed	n/a <sup>a</sup>	0.00166	12.9	$4.34 \times 10^2$
		0.4 wt% <sup>b</sup>	0.00249	7.24	$5.43 \times 10^3$

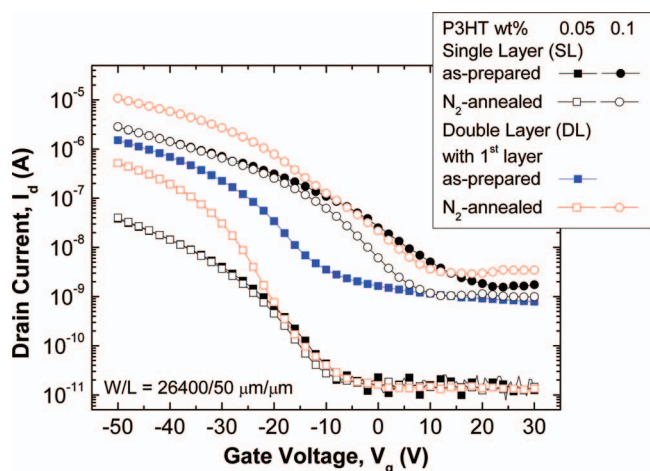
<sup>a</sup>Samples with the second layer labeled n/a denote PTFTs. In other words, they are P3HT based TFTs with a single channel layer.

<sup>b</sup>Samples with the second layer labeled a weight percentage of P3HT solution, which is 0.4 wt% in this table, denote DPTFTs, i.e. P3HT based TFTs with double channel layers.

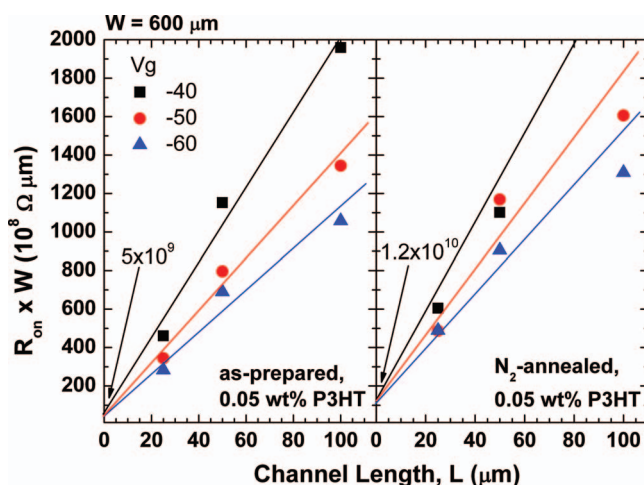
layer. Characteristics of DPTFTs with the as-prepared first layer, in which both the first and second layers were coated with the 0.05 wt% P3HT solution, were similar to those of PTFTs with a thicker channel layer, i.e., using the 0.1 wt% solution. These results demonstrate that the improvement in performance induced by using DPTFTs with an N<sub>2</sub>-annealed first layer is still effective when the thickness of the second layer is reduced. Furthermore, by comparing the results of the DPTFTs with the N<sub>2</sub>-annealed first layer in Fig. 3 with those in Fig. 2, the correlation between the improved performance in the on-current and the thickness of the second layer can be observed. The DPTFTs with an N<sub>2</sub>-annealed first layer and thicker second layer exhibit more significant on/off current ratio enhancements. However, the subthreshold swing and off-current exhibited no correlations with the thickness of the second layer. The contact resistances between PTFTs with the as-prepared or N<sub>2</sub>-annealed channel layer coated with the 0.05 wt% P3HT solution were extracted (Fig. 4). For N<sub>2</sub>-annealed PTFTs (Fig. 4, right), the data point of the device with a channel length of 100  $\mu\text{m}$  under a gate voltage of  $-40$  V is over the scale of the y-axis and higher than the position of the fitting line. For the sake of simplicity, this data point is not shown in the figure because we employed the same y-axis scale for both sides. The values of contact resistance are  $5 \times 10^{-9}$  and  $1.2 \times 10^{-10}$  for PTFTs with the as-prepared and N<sub>2</sub>-annealed channel layer, respectively. The channel resistances of as-prepared PTFTs were observed to be smaller

than those of N<sub>2</sub>-annealed PTFTs. This result can be interpreted by the change in dopant concentration.<sup>7-10,14</sup> The effects of annealing on the performances of P3HT TFTs in an N<sub>2</sub> environment are similar to those observed in the annealed organic devices in an inert environment, such as in glove box full of Ar, N<sub>2</sub>, or vacuum chamber. With N<sub>2</sub> annealing, the dopant concentration in the P3HT decreases, so that the channel resistance and carrier injection barrier increase.<sup>9,10</sup> Moreover, thin active layer also contributes to reduce bulk current.<sup>15</sup> Therefore, leakage current, i.e., off-current, and poor subthreshold swing induced by the bulk current should be suppressed. Nevertheless, the on-current will decrease with bulk current suppression.<sup>15</sup> Lower on-current induced by thinner channel layer was also observable as shown in Figs. 2 and 3. Less difference between on-current of the devices with as-prepared and N<sub>2</sub>-annealed, single layer channels, as shown in Fig. 3, might be due to improvement in crystallinity of P3HT. Fortunately, the on-current of DPTFTs (N<sub>2</sub>-annealed first layer and thick second layer) is as high as that of PTFTs with thick channel layer as shown in Fig. 2.

However, there might be issue on the viability of double-coated channel structure. The performance enhancements might be suggested to have resulted from a specific action on the N<sub>2</sub>-annealed first layer while coating the second layer. For example, the solvent in the solution for second layer coating might have redissolved the first layer, and thus, a new single P3HT layer was formed, instead of the structure that was proposed. This hypothesis contradicts that the extent of the performance enhancement correlates with the thickness of the second layer. If there was only a residual layer, the on/off current ratio would



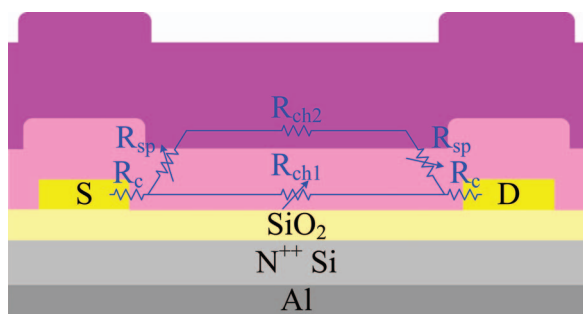
**Figure 3.** Transfer current characteristics of PTFTs and DPTFTs. PTFT channels, or the first P3HT layers of DPTFTs, were coated with (a) 0.05 and (b) 0.1 wt% P3HT solutions. PTFTs and the first P3HT layers of DPTFTs are either with or without N<sub>2</sub> annealing. The second layer of DPTFTs were used as the same as the first layer without annealing.



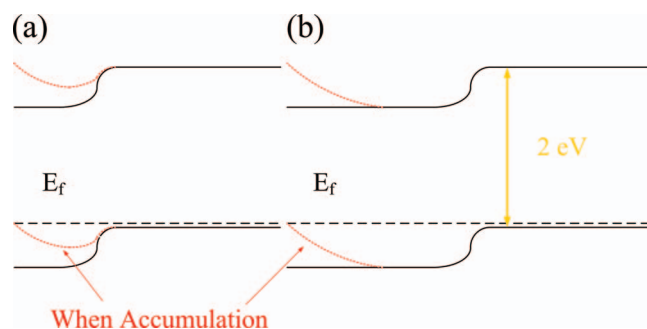
**Figure 4.** Contact resistances of PTFTs with as-prepared or N<sub>2</sub>-annealed channel layer coated by 0.05 wt% P3HT solution.

decrease with increased thickness of channel layer. But, in contrast, on/off current ratio was increased. Moreover, if the effect of redissolving was critical, the properties of the devices would be related to the thickness of the first P3HT layer. In other words, the thinner  $N_2$ -annealed first layer would undergo a more significant impact from redissolution because the thin  $N_2$ -annealed first layer might be fully redissolved. Furthermore, the dopant concentration of a new single P3HT layer should not be as low as that of the  $N_2$ -annealed P3HT layer, i.e., the dopant concentration should be similar to that of the as-prepared P3HT layer. Accordingly, the characteristics of the device with the new single P3HT layer, which was formed by a second coating of P3HT on a thin  $N_2$ -annealed first layer, should be similar to those of PTFTs with the as-prepared channel layer. If devices with the new single P3HT layer formed by second coating P3HT on a thick  $N_2$ -annealed first layer, the characteristics of the device should be similar to those of the PTFTs with the  $N_2$ -annealed channel layer. However, this argument conflicts with the results shown in Figs. 2 and 3. Instead, the situation is contrary, i.e., DPTFTs with the thin  $N_2$ -annealed first layer exhibit conspicuous performance improvements. Furthermore, in some articles, the authors formed the bilayer structure by using the same solvent or solvents applicable to both layers.<sup>16–19</sup> In their works, performance difference between the devices with bilayer and bulk-heterojunction active layers could still be observed.<sup>16,17</sup> The device with the bulk-heterojunction structure was used as a comparison and formed by blending the same two materials as in the bilayer formation. The results showed different device performances in their bilayer structure deposition performed with different sequences.<sup>19</sup> Thus, fabricating the bilayer structural active layer by using the same solvent was feasible. Furthermore, an intermixed zone between the upper and under layers was observed after formation of the bilayer structure.<sup>17</sup> The under layer survived after spin coating the upper layer, despite the under layer not being annealed. Therefore, the re-dissolution effect is considered minor in this study, so that we could neglect it. Moreover, PTFT and DPTFT thicknesses described in the experiment can be considered evidence.

To better understand DPTFT properties with the  $N_2$ -annealed first layer, specifically for on-current and threshold voltage shift, a simplified equivalent circuit is proposed and shown in Fig. 5. The circuit is lumped into the cross-sectional structure of a DPTFT. For DPTFTs with the  $N_2$ -annealed first P3HT layer,  $R_{ch1}$  is larger than  $R_{ch2}$ .  $R_{ch1}$  and  $R_{sp}$  can be varied by the gate bias. They decrease or increase depending on whether the gate is biased at a negative voltage or positive voltage, respectively. Before formation of the accumulation layer,  $R_{sp}$  is smaller than  $R_{ch1}$  because the channel length is considerably larger than the thickness of the first layer. There is a possibility that the carrier will conduct through the sidewall path and the second layer if the sum of  $2R_{sp}$  and  $R_{ch2}$  is smaller than  $R_{ch1}$ . For the results shown in Fig. 2,  $R_{ch2}$  of the second P3HT layer coated using the 0.4 wt% solution is substantially smaller than  $R_{ch1}$  of the  $N_2$ -annealed first P3HT



**Figure 5.** Schematic cross section of a DPTFT incorporating the simplified equivalent circuit. The circuit includes the contact resistance between the electrodes and the semiconductor,  $R_c$ , and channel resistances of first and second P3HT layer,  $R_{ch1}$  and  $R_{ch2}$ , respectively, and resistance of sidewall path through the first layer to the second layer,  $R_{sp}$ .

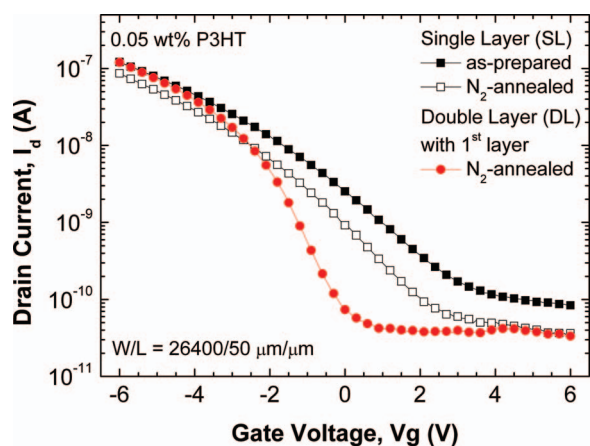


**Figure 6.** Band structures of DPTFTs with (a) thin and (b) thick first P3HT layers. For the sake of simplicity, we illustrate only the band structure of DPTFTs that are biased at flatband or accumulation mode.

layer, which was coated by the 0.05 or 0.1 wt% solution. Therefore, a substantially larger on-current is observed, the earlier conduction, i.e., prior to the conduction in the accumulation layer, is also found to be relative to the positive-shifted threshold voltage, as shown in Figs. 2a and 2b. Additionally, if the thickness of the second layer is fixed similarly to the first layer, the difference between  $R_{ch2}$  and  $R_{ch1}$  is reduced, although  $R_{ch2}$  is still smaller than  $R_{ch1}$ . Therefore, the improvement in on/off current ratio resulted from the enlarged on-current by the presence of second layer was lowered. Moreover, when the first layer is grown,  $R_{sp}$  and  $R_{ch1}$  tend to increase and decrease, respectively. The sum of  $R_{sp}$  and  $R_{ch2}$  might only be less small than, or equal to,  $R_{ch1}$ , thus leading to the results shown in Fig. 3.

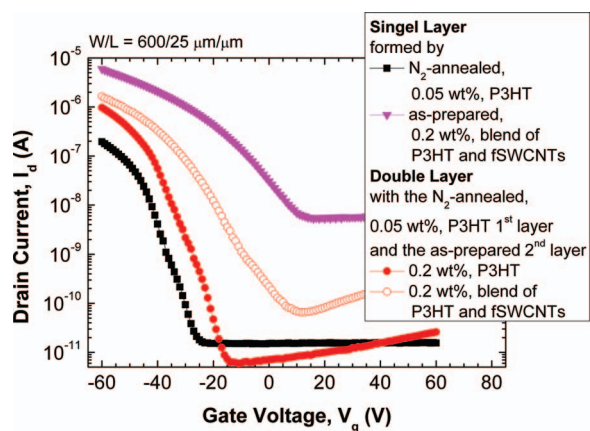
In addition to the simplified equivalent circuit, the illustrative band structure can be used to explain the improvements. Fig. 6 shows the illustrative band structures of DPTFTs with (a) thin and (b) thick  $N_2$ -annealed first P3HT layers hypothesized in this study after applying external bias. The DPTFTs are biased at a flatband or accumulation mode. As discussed, for the results of Fig. 4, the number of holes, which are induced by species in an air atmosphere in the first  $N_2$ -annealed P3HT layer, should be less, compared to that in the second P3HT layer, which was not subjected to  $N_2$  annealing during fabrication.<sup>7,8</sup> The effect of dopant concentration in P3HT before and after  $N_2$  annealing can be also correlated to the different threshold voltages, which resulted in different Fermi levels.<sup>3,9</sup> The results of UV-Vis spectroscopy by Zen et al. showed that the band gaps of P3HT before and after  $N_2$  annealing were almost the same.<sup>10</sup> Consequently, a built-in potential presented because of the energy difference of the Fermi level at the interface of these two stacked layers. For DPTFTs using a sufficiently thin first layer, the entire band bending of the first layer that occurred when DPTFTs were biased at a negative gate voltage permitted barrier lowering and facilitated hole population in the second P3HT layer. These holes in the second channel are beneficial for transportation because they are separate from the interface between the gate oxide and P3HT layer and certainly experience less scattering, which consequently result in an improved on-current level and subthreshold swing.

Fig. 7 shows the  $I_d$ - $V_g$  characteristics of DPTFTs with a thinner gate dielectric and  $N_2$ -annealed first active layer accomplished by the solution of 0.05 wt%. The second P3HT layer of DPTFTs was coated using the same solution of the first layer. The PTFTs with the as-prepared or  $N_2$ -annealed channel are used as the control. The DPTFTs using a thin gate oxide and first active layer exhibit not only tremendously scaled down operation voltage, but also these improvements. The subthreshold swing can be reduced to less than 1 V/decade, which is an impressive value for PTFTs. Moreover, the improvements of the on/off current ratio and subthreshold swing of DPTFTs are still observable when the material of the second layer is changed. Fig. 8 shows the  $I_d$ - $V_g$  characteristics of DPTFTs with the  $N_2$ -annealed first layer coated by the 0.05 wt% solution and the F-SWCNT-blended P3HT second layer. The characteristics of PTFTs with the  $N_2$ -annealed, 0.05 wt%, P3HT channel, or with the F-SWCNT-blended P3HT



**Figure 7.**  $I_d$ - $V_g$  characteristics of DPTFTs with thinner gate dielectric and  $N_2$ -annealed first active layer. Both channel layers were coated with a solution of 0.05 wt%. PTFTs with as-prepared or  $N_2$ -annealed P3HT channel used as the control.

channel, and DPTFTs with the  $N_2$ -annealed, 0.05 wt%, first layer and the conventional, 0.2 wt%, second layer are included in Fig. 8 for a comparison. After doping by F-SWCNTs, the on-current improved, and the poor on/off current ratio and subthreshold swing were observed to be similar to the results of our earlier study.<sup>20</sup> These might be due to the poor interface between the blended channel and gate oxide, or the increased bulk current that can act as a reference to the lower contact resistance.<sup>20</sup> In addition, compared with the PTFTs with the  $N_2$ -annealed channel, the DPTFTs with the  $N_2$ -annealed, 0.05 wt%, first layer and the conventional, 0.2 wt%, second layer exhibit similar improvements as those shown in Fig. 2. However, the improvements can still be observed for the DPTFTs with the  $N_2$ -annealed, 0.05 wt%, first layer and the F-SWCNT-blended P3HT second layer. Compared with PTFTs with the blend channel, over 20-fold and twofold of improvements on the on/off current ratio and subthreshold swing, respectively, were obtained. The on-current decreased, possibly because of the difference in contact resistance; that



**Figure 8.**  $I_d$ - $V_g$  characteristics of DPTFTs with  $N_2$ -annealed, which was coated with 0.05 wt% P3HT solution, first layer and F-SWCNTs blended P3HT second layer. The performance of PTFTs with the F-SWCNTs blended P3HT channel is included for comparison. PTFTs, the channel of which was formed by 0.05 wt% P3HT solution, and DPTFTs with an  $N_2$ -annealed first layer, the first layer and second layer of which were coated by 0.05 and 0.2 wt% P3HT solutions, respectively, were also used as the control. The drain voltage is  $-60$  V.

is, the contact resistance of DPTFTs is larger than that of PTFTs in a similar manner of the difference in contact resistance between P3HT on Au and the blended channel on Au.<sup>20</sup> However, the on-current of DPTFTs with the blended second layer is still larger than that of DPTFTs with the conventional P3HT second layer. In other words, the improvements induced by double coated channel and doping of F-SWCNTs were observed in subthreshold swing, on/off current ratio, and mobility, and these results also confirm the mechanisms proposed in this article.

## Conclusions

In summary, P3HT TFTs with double-coated active layers were fabricated. The resultant DPTFTs showed more than two orders of magnitude of improvement in the on/off current ratio and demonstrated an improved subthreshold swing. The improvements can be due to the following: i) the  $N_2$ -annealed P3HT first layer possessed a higher injection barrier between Au and P3HT and also greater film resistance than the as-prepared P3HT layer because of the reduced dopant concentration. Both result in the reduced bulk current that benefits the subthreshold current and off-current as the DPTFTs are turned off; and ii) The equivalent circuit and illustrative band structure of DPTFTs show that the carriers could conduct in the second layer as the devices are biased at the mode before formation of the accumulation layer, thus leading to the positive-shifted threshold voltage and the dependence of performance upon the thickness of the second layer.

Both the improvements in subthreshold performances and on-current due to the reduced bulk current and high conductivity of second layer can be obtained by using double-coated channel layer structure. Furthermore, this study also demonstrated that improvements induced by the double-coated channel layer can still be observed as the thin gate oxide and the F-SWCNT-blended P3HT second layer were used for the DPTFTs.

## References

- H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, and D. M. de Leeuw, *Nature*, **401**, 685 (1999).
- H. Sirringhaus, N. Tessler, and R. H. Friend, *Science*, **280**, 1741 (1998).
- G. Wang, J. Swensen, D. Moses, and A. J. Heeger, *J. Appl. Phys.*, **93**, 6137 (2003).
- S. Cho, K. Lee, J. Yuen, G. Wang, D. Moses, A. J. Heeger, M. Surin, and R. Lazzaroni, *J. Appl. Phys.*, **100**, 114503 (2006).
- H. Yang, T. J. Shin, Z. Bao, and C. Y. Ryu, *J. Polym. Sci. Part B: Polym. Phys.*, **45**, 1303 (2007).
- Y. D. Park, H. S. Lee, Y. J. Choi, D. Kwak, J. H. Cho, S. Lee, and K. Cho, *Adv. Funct. Mater.*, **19**, 1200 (2009).
- M. S. A. Abdou, F. P. Orfino, Z. W. Xie, M. J. Deen, and S. Holdcroft, *Adv. Mater.*, **6**, 838 (1994).
- S. Hoshino, M. Yoshida, S. Uemura, T. Kodzasa, N. Takada, T. Kamata, and K. Yase, *J. Appl. Phys.*, **95**, 5088 (2004).
- B. H. Hamadani, H. Ding, Y. Gao, and D. Natelson, *Phys. Rev. B*, **72**, 235302 (2005).
- A. Zen, J. Pflaum, S. Hirschmann, W. Zhuang, F. Jaiser, U. Asawapirom, J. P. Rabe, U. Scherf, and D. Neher, *Adv. Funct. Mater.*, **14**, 757 (2004).
- M. J. Deen, M. H. Kazemeini, Y. M. Haddara, J. Yu, G. Vamvounis, S. Holdcroft, and W. Woods, *IEEE Trans. Electron Devices*, **51**, 1892 (2004).
- E. von Hauff, F. Johnen, A. V. Tunc, L. Govor, and J. Parisi, *J. Appl. Phys.*, **108**, 063709 (2010).
- L. Reséndiz, M. Estrada, A. Cerdeira, B. Iñiguez, and M. J. Deen, *Org. Electron.*, **11**, 1920 (2010).
- C. H. Chang, M. F. Chen, and C. H. Chien, *J. Electrochem. Soc.*, **158**, H854 (2011).
- C.-H. Chang and C.-H. Chien, *Org. Electron.*, **13**, 2620 (2012).
- R. A. Marsh, C. R. McNeill, A. Abrusci, A. R. Campbell, and R. H. Friend, *Nano Lett.*, **8**, 1393 (2008).
- D. H. Wang, H. K. Lee, D. G. Choi, J. H. Park, and O. O. Park, *Appl. Phys. Lett.*, **95**, 043505 (2009).
- E. Kymakis, E. Koudoumas, and I. Frangiadakis, *Sol. Energy Mater. Sol. Cell*, **90**, 1705 (2006).
- K. Kaneto, M. Yano, M. Shibao, T. Morita, and W. Takashima, *Jpn. J. Appl. Phys.*, **46**, 1736 (2007).
- C. H. Chang and C. H. Chien, *IEEE Electron Device Lett.*, **32**, 1457 (2011).