



# An Investigation of Transient Effects in Poly(3-hexylthiophenes) Based Thin Film Transistors Caused by Oxygen and Water Molecules

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In this article, we investigate hysteresis behavior observed in the current-voltage transfer curve of regioregular poly(3-hexylthiophene)(P3HT) based thin film transistors (PTFTs) using bi-directional voltage sweeping. According to the results of our experiments, the hysteresis effects were closely related to oxygen (O<sub>2</sub>) and water (H<sub>2</sub>O) molecules residing in the P3HT active layer. As a result, we hypothesized that O<sub>2</sub> and H<sub>2</sub>O in the P3HT could form two kinds of dopants, i.e., stable and transient states. Stable state dopants, which are commonly thought to be of the acceptor-type dopants, could induce holes in the channel region contributing to better on-current. On the contrary, transient state dopants were found to be unable to induce holes, however could enable the formation of polarization agents and create hysteresis. These two types of dopants seem have a common origin, thus they could be converted into each other through the combination of specific processes and applied external bias. From the viewpoint of device operation stability, except on-current level and characteristics including threshold voltage, off-current magnitude and on/off ratio, the impact of hysteresis should garner the attention of those pursuing high performance PTFTs.

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Manuscript submitted April 12, 2011; revised manuscript received May 26, 2011. Published July 8, 2011

Semiconducting organic materials have attracted much attention because of their great potential in applications ranging from light emitting diodes, solar cells, electronic papers, and radio frequency identification tags,<sup>1-4</sup> all of which can be easily processed on large area, flexible substrates at a relatively low process temperature and at very low cost. Recently, conjugated semiconducting polymers with high field-effect carrier mobility and solution processability characteristics (e.g., regioregular polythiophene) have been introduced into the fabrication process of organic thin film transistors (OTFTs). Since the performance of OTFTs strongly depends on the structural arrangement of the polymer thin film, solution processable self-organized regioregular poly(3-hexylthiophene) (P3HT) is then one of the most promising materials for its remarkably ordered structure that has a preferential orientation of  $\pi$ -conjugated planes parallel to the substrate surface, which seems to be very helpful in carrier transport. Therefore, the OTFTs with a P3HT active layer (i.e., PTFTs) have demonstrated high hole mobility (0.01–0.3 cm<sup>2</sup>/Vs) with a reasonable on/off ratio (more than 100 in air and 10<sup>6</sup> in an inert atmosphere).<sup>5-8</sup>

There are still many issues affecting PTFTs that need to be addressed in current research. First is the crystallinity of the P3HT layer. Many research studies have been devoted to enhancing the crystallinity of the P3HT layer via different approaches, such as changing the solvent, modifying coating methods, and/or adding annealing.<sup>7-10</sup> Although the crystallinity of the P3HT thin film formed by traditional spin coating is relatively poor compared to coating added by other means, it can be significantly improved with appropriate thermal annealing.<sup>7-9</sup> Secondly, the influence of air exposure on the operation of OTFTs based on thiophene polymers and oligomers has been studied extensively.<sup>11</sup> Air exposure usually results in a poor on/off ratio due to a significant increase in off-state conduction and an absence of saturation behavior in the current. Molecular oxygen (O<sub>2</sub>) and/or water have often been cited as the likely cause of these results.<sup>11-17</sup> It has been reported that the relatively low ionization potential of the conjugated molecular backbones of these thiophene derivatives allows O<sub>2</sub> to act as an acceptor-type dopant generating holes in the active layer. Furthermore, several unfavorable features observed in devices fabricated while exposed to the air have been explained by an increase in the conductivity of the P3HT active layer through p-type doping of O<sub>2</sub>.<sup>12,13,15</sup> It has been demonstrated that the oxygen doping effect observed with air exposure could be eradicated by situating the devices in a vacuum.<sup>12-14</sup>

Moreover, moisture has been illustrated to have a more significant impact on the performance of OTFTs than oxygen,<sup>15</sup> and a poor sub-threshold swing and on/off ratio were observed after devices were immersed in water.<sup>14-16</sup>

However, many studies of the post thermal annealing and doping effects of oxygen and/or moisture are published individually; that is, there has not been reporting about the doping effect after thermal annealing. In this article, we investigate transient effects in PTFTs using bi-directional voltage sweeping. We found that this effect intimately correlated to the presence of O<sub>2</sub> and H<sub>2</sub>O molecules embedded in the P3HT active layer. With some elaborate experiments, we demonstrate that O<sub>2</sub> and H<sub>2</sub>O in the P3HT could form two sorts of dopants, i.e., stable and transient states. Stable state dopants could induce holes in the channel region contributing to the better on-current. On the contrary, transient state dopants were not able to induce holes but could trigger the formation of polarization agents and produce the hysteresis. With the help of physical analyses, including x-ray photon electron spectroscopy (XPS), we further confirmed our speculation. From the viewpoint of operation stability, we cannot only evaluate on-current level, threshold voltage, off-current magnitude and on/off ratio, but also have to take the hysteresis width into account while pursuing high performance PTFTs.

## Experimental

The regioregular P3HT used in this study was purchased from FEM, Inc. (Mw = 50000), and the provided coupling ratio of head-tail to head-head and tail-tail was approximately 90%. The substrates of heavily phosphorous doped n-type silicon (100) wafers with resistivity of 0.001  $\Omega$ -cm, and SiO<sub>2</sub> with a thickness of 200 nm grew by thermal oxidation after RCA cleaning was used as the gate and gate dielectric of PTFTs. Next, Ti (2.5 nm)/Au (50 nm) and Ti (50 nm) for the source and drain (S/D) and backside contacts were deposited subsequently by an E-gun evaporator. The S/D was patterned by a lift-off process. Prior to the deposition of the P3HT channel, the substrate was treated by hexamethyl disilazane (HMDS) passivation in a vacuum oven at 150°C for a hydrophobic surface. Then, a P3HT active layer was spun on with a two step process—500 rpm for 10 s in the first step and 1500 rpm for 25 s in the second step, followed by baking at 150°C for 3 min. Chloroform was used as the solvent of P3HT, and the weight percentage of solutions of P3HT in chloroform were 0.05–0.2 wt %. All of the P3HT solutions were treated with ultrasonic vibration for 5 min and were percolated by a PTFE membrane syringe filter with a pore size of

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0.2  $\mu\text{m}$ . The thicknesses of the ratios P3HT, 0.05, 0.1 and 0.2, were around 30, 60 and 100 nm, respectively, which were confirmed by scanning electron microscope (SEM). The schematic structure of PTFTs is accordingly shown in Fig. 1a.

Different post treatments of PTFTs were carried out in order to study their impacts on the properties of PTFTs, such as thermal annealing and/or absorbance of oxygen and water molecules. We annealed the samples in a furnace with nitrogen or oxygen ambient for 30 min at 160°C with a gas flux of 10 L/min. Also, room temperature post treatments for the PTFTs with or without  $\text{N}_2$  annealing were executed by dropping D. I. water ( $\text{H}_2\text{O}$ ) or 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) water upon the P3HT layer, as shown in Fig. 1b, for 10 min, and then blown dry by nitrogen. On the other hand, in order to observe the reversibility of the doping effect, we performed an additional  $\text{N}_2$  annealing on the PTFTs, which were subjected only to water treatment previously. Moreover, we also fabricated devices in the photo bay, a region illuminated with long wavelength light, to investigate the influences of light on the characteristics of PTFTs. All the processes of the devices and post treatments were implemented under atmospheric conditions. The process flow and spreading conditions in this work were illustrated in Fig. 2.

The electrical properties of PTFTs were measured by a Hewlett-Packard 4156C semiconductor parameter analyzer. All the samples were characterized in the ambient air, except those studying the transient doping effect, which were measured with an accompanying nitrogen blow. The devices were evaluated at their saturation region. Furthermore, residual water and oxygen molecules in the P3HT active layer, were analyzed from the results of XPS by observing the intensity of binding energy of O1s. The X-ray source for XPS was a twin anode x-ray, which were Mg  $\text{K}\alpha$  and Al  $\text{K}\alpha$ .

### Results and Discussion

As reported by Wang et al., the PTFTs subjected to post thermal annealing depicted lower on-current, smaller threshold voltages, higher on/off ratios and lower off-current compared with the as-prepared ones.<sup>7</sup> Recently, they continued to show that post annealing

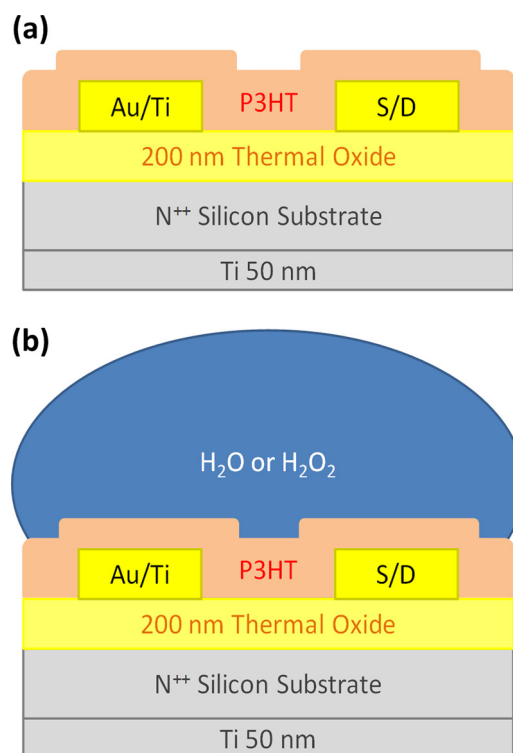


**Figure 1.** (Color online) (a) Schematic device structure and (b) illustration of  $\text{H}_2\text{O}$  or  $\text{H}_2\text{O}_2$  post treatments on the bottom contact P3HT TFTs.

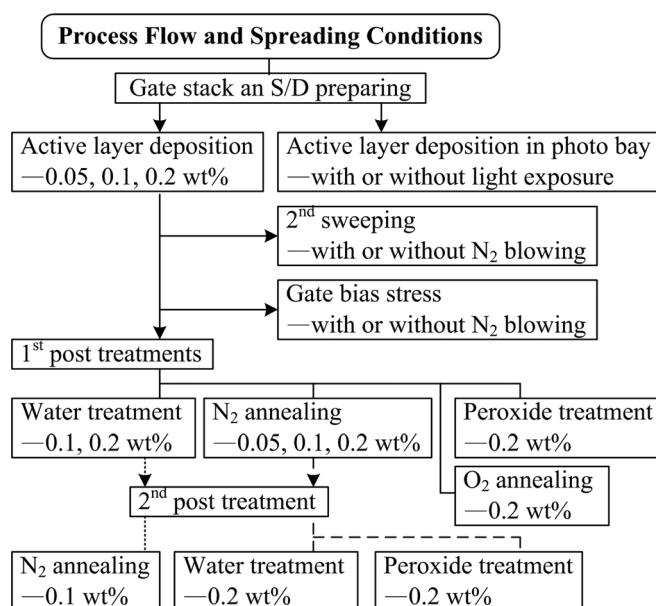


**Figure 2.** Process flow and spreading conditions in this work.

was also very helpful in improving the carrier mobility properties and contact resistance.<sup>8</sup> Consistent with their results, as shown in Fig. 3, we did observe a similar effect of thermal annealing on the electrical properties of PTFTs. It is worth mention that the degradation of on-current after annealing in our PTFTs was negligible since we used optimized conditions. However, we noticed that PTFTs with post annealing had larger hysteresis width than the as-prepared one when the bi-directional measurement was performed, a phenomenon which has seldom been discussed until now. By changing the weight percentages of P3HT solutions, we prepared PTFTs with different active layers of P3HT thicknesses. It was found that PTFTs with thinner active layer thickness displayed wider hysteresis width. Although annealing lead to improvements in mobility, subthreshold swing and a high on/off current ratio, could all be ascribed to the better crystallinity of P3HT layer, this feature, however, failed to satisfactorily explain the behavior in hysteresis. In order to further study the origin of the present hysteresis as well as its correlation

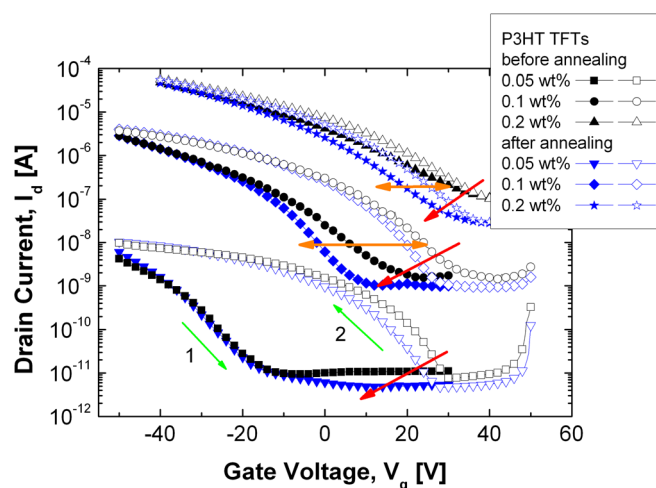


**Figure 3.** (Color online) Current-voltage transfer curves of P3HT TFTs with different active layer thicknesses with/without  $\text{N}_2$  annealing. Thickness was controlled by changing the weight percentage of solutions of P3HT in chloroform. They were 0.05–0.2 wt %. The measurements were performed in atmosphere. The channel width over length was 26,400/50  $\mu\text{m}/\mu\text{m}$ .

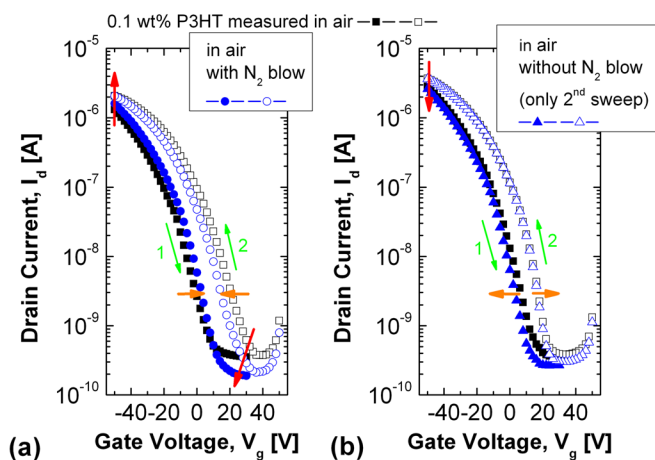


**Figure 4.** (Color online) Current-voltage transfer curves of P3HT TFTs. The used weight percentage of solution of P3HT in chloroform was 0.1%. The measurements were performed in atmosphere. The channel width over length was 26,400/50  $\mu\text{m}/\mu\text{m}$ . When the second sweep, they were measured in atmosphere (a) with and (b) without  $\text{N}_2$  blow, i.e., only second sweep.

with the active layer thickness, we performed another two additional subsequent measurements; one was measured in the atmosphere concomitant with  $\text{N}_2$  blow, and the other was another bi-directional measurement in the air without  $\text{N}_2$  blow. It should be noted that the results shown in Figs. 4a and 4b came from two distinct devices. The results of  $I_d$ - $V_g$  characteristic are shown in Figs. 4a and 4b, respectively. Obviously, accompanying the  $\text{N}_2$  blow with measurement reduced both the hysteresis width and the magnitude of off-current, but it also slightly increased the on-current level. A second bi-directional sweep without an  $\text{N}_2$  blow, on the contrary, led to more severe hysteresis, lower on-current with negligible off-current change. This implied that the narrowed hysteresis width arising from  $\text{N}_2$  blowing was not caused primarily by the applied external voltage. As a result, we conceived a hypothesis that the observed tendency might be closely related to moisture and/or oxygen molecules.

According to the literatures,<sup>12–15,17</sup> if we fabricate devices and measure in air, the presence of stable state of dopants, also named charge transfer complexes (CTC),<sup>12,13</sup> seems unavoidable in the P3HT layer, which would in turn induce holes in the channel region, contributing to the better on-current observation, but also causing a reduction in mobility to some extent due to more frequent impurity scattering. The existence of induced holes can be firmly evidenced by the more positive threshold voltage value and the higher initial off-current (smaller on/off current ratio) in the as-prepared samples. Moreover, these dopants might also induce energy states in the band gap of P3HT, and then lead to an inferior subthreshold swing. With post  $\text{N}_2$  thermal annealing, we supposed that some portions of these dopants in the P3HT layer could be eliminated due to the fact that high temperature  $\text{N}_2$  annealing could drive  $\text{O}_2$  and  $\text{H}_2\text{O}$  away from the P3HT layer, and thus reducing the likelihood of CTC formation. So, we hypothesized that as the samples are exposed to an environment containing  $\text{O}_2$  and  $\text{H}_2\text{O}$  molecules, diffusion most likely takes place, followed by the formation of some complexes. We presumed

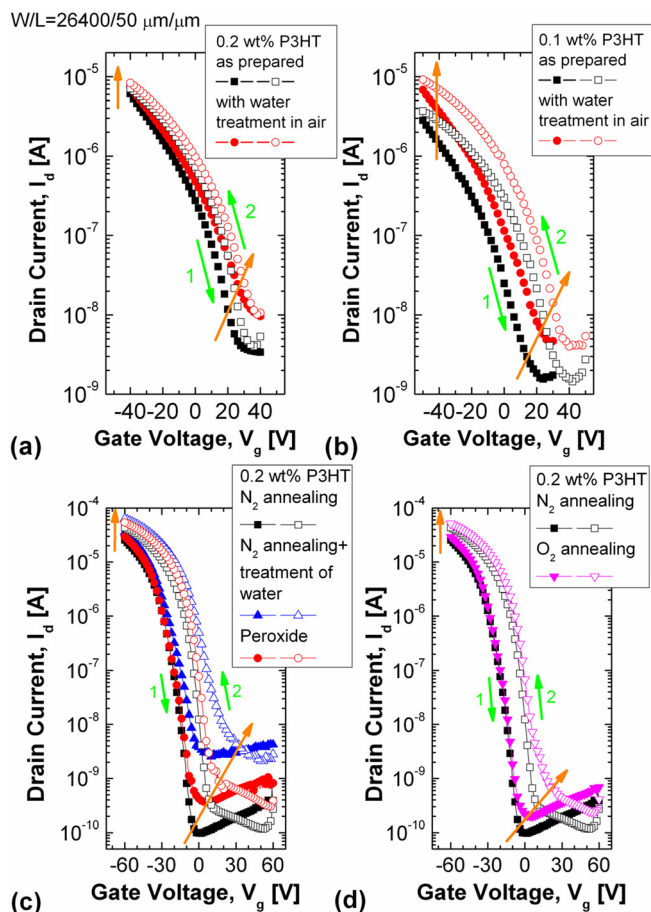


**Figure 5.** (Color online) Current-voltage transfer curves of P3HT TFTs subject to water treatment. The used weight percentages of solution of P3HT in chloroform were (a) 0.2% and (b) 0.1%, respectively. The measurements were performed in atmosphere. (c) Current-voltage transfer curves of P3HT TFTs (0.2 wt %) with  $\text{N}_2$  annealing or  $\text{N}_2$  annealing followed by water and peroxide treatments. (d) Current-voltage transfer curves of P3HT TFTs (0.2 wt %) with the  $\text{N}_2$  annealing or  $\text{O}_2$  annealing. All the devices had channel width over length of 26400/50  $\mu\text{m}/\mu\text{m}$ .

these complexes acted as a sort of transient state dopant since they possessed faster response rates as compared with the stable state dopants.<sup>14</sup> We thought the extent of charge transfer in these kinds of complexes were less than CTC, so that the presence of these complexes would probably contribute to significant polarization effects inside the P3HT layer and result in more severe hysteresis concomitant with additional impurity scattering as well as lower hole concentration. Even though we did not know the detailed structure of these complexes, this speculation can explain the observed phenomena well.<sup>17,18</sup> For example, the greater hysteresis width in PTFTs with thinner P3HT channels can be ascribed to the easier diffusion of moisture and oxygen into the channels. Blowing  $\text{N}_2$  led to a pronounced narrowing of hysteresis since it could effectively reduce the rate of moisture and oxygen absorption. In addition, the second

**Table I.** Summation of the impact of stable state and transient state dopants on the electrical properties.

| Dopant    | On-current             | Off-current | Subthreshold swing | Threshold voltage    | Hysteresis |
|-----------|------------------------|-------------|--------------------|----------------------|------------|
| Stable    | Increased              | Increased   | Increased          | Positive shift       | Decreased  |
| Transient | Decreased <sup>a</sup> | Increased   | Lessened           | Changed <sup>b</sup> | Increased  |

<sup>a</sup>On-current level decreased because the impurity scattering was much more severe.

<sup>b</sup>Threshold voltage had shifted in different ways for the two sweeping cases. Negative and positive voltage shifts were observed as sweeping from accumulation to inversion and from inversion to accumulation, respectively.

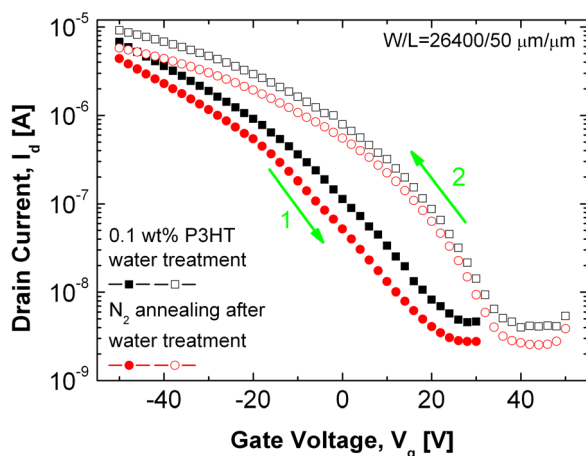


**Figure 6.** (Color online) Transfer current-voltage characteristics of P3HT TFTs with water treatment with or without subsequent  $N_2$  annealing. The used weight percentage of solution of P3HT in chloroform was 0.1%.

bi-directional measurement showed that stable state dopants would be partially removed by applying external bias and lead to enlarged hysteresis width. For clarity, the resultant characteristics are summarized in Table I.

In order to further confirm our inference, different post treatments were employed, as described in the experimental section. Please notice that all samples were blown dry after treatments. PTFTs with different active layer thicknesses were fabricated by using 0.2 and 0.1 wt % P3HT solutions. As shown in Figs. 5a and 5b, we clearly observed that the as-prepared samples showed increased on-current, similar hysteresis and more apparent increases in off-current and sub-threshold swing after water treatment. Moreover, PTFTs with a thinner P3HT layer suffered more severe degradation from treatment with  $H_2O$ . These outcomes suggest that stable state dopants and transient state dopants are convertible, which will be further discussed later. The transfer current characteristics of  $N_2$ -annealed PTFTs with water and peroxide treatments are also shown in Fig. 5c. The increase in on-current, off-current, hysteresis width, and subthreshold swings could be easily observed after treatments. However, the peroxide-treated sample exhibited more significant changes than the water-treated one. Figure 5d displays the effect of  $O_2$  annealing on the transfer curve of PTFTs. Obviously,  $O_2$  annealing had a similar influence on PTFTs as water and peroxide treatments. Therefore, we conclude that both  $O_2$  and  $H_2O$  contribute to the stable and transient state dopants, depending on the extent of charge transfer.<sup>15,16</sup> All of

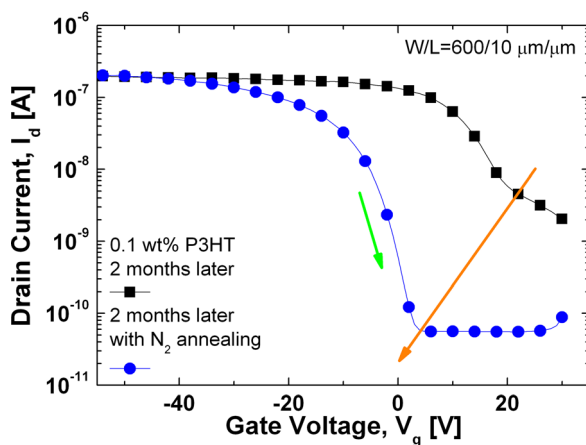


**Figure 7.** (Color online) Transfer current-voltage characteristics of 0.1 wt % P3HT TFTs, stored in air for 2 months and annealed with  $N_2$  after 2 months storage.

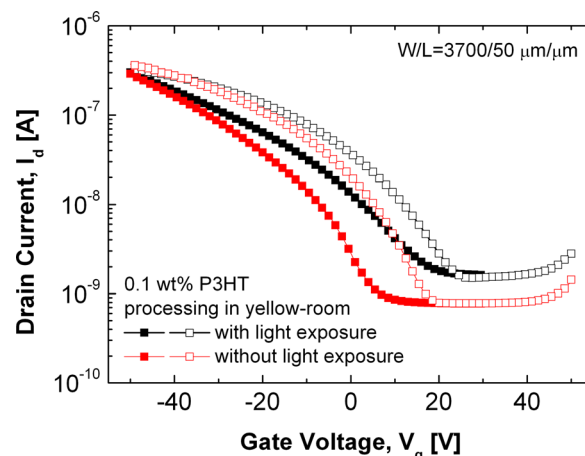


**Figure 8.** (Color online) Transfer current-voltage characteristics of 0.1 wt % P3HT TFTs, processed in an environment of long wavelength light with or without white light exposure.

these treatments increased the probability of stable and transient state dopant formation, since more dopants diffused into P3HT. Hence, we did observe a positive shift on threshold voltage, a more broad

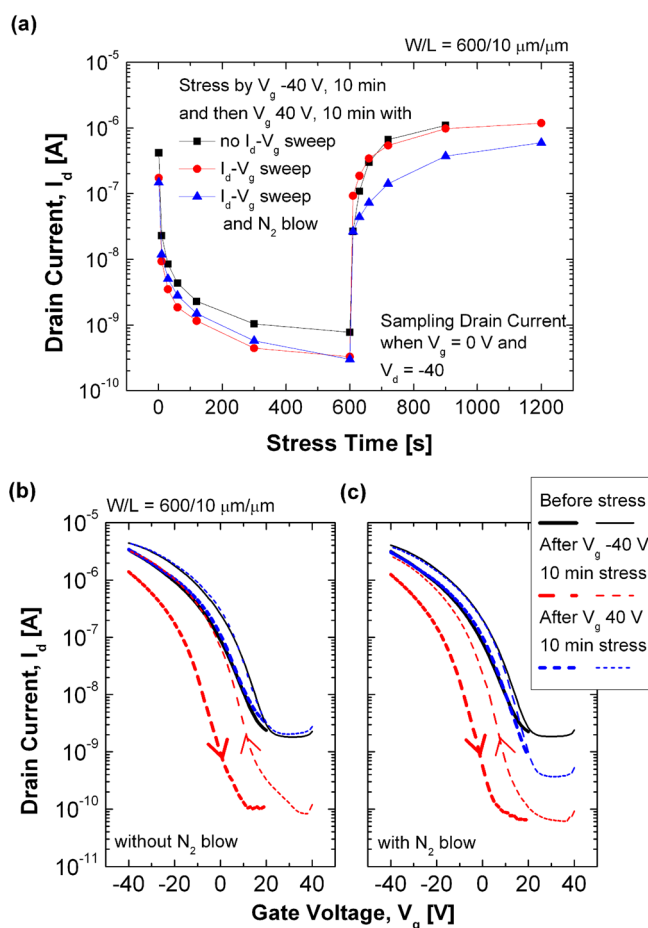


**Figure 9.** (Color online) (a) Drain current of PTFTs as a function of time under dynamic constant voltage stress— $-40$  V for 10 min followed by  $40$  V for another 10 min, with or without  $N_2$  blow. The drain currents recorded at a gate voltage of  $0$  V and a drain voltage of  $-40$  V during stressing. The  $I_d$ - $V_g$  curves of P3HT TFTs with bi-directional measurement before stress, after gate voltage stress of  $-40$  V,  $10$  min and  $40$  V,  $10$  min, (b) without and (c) with  $N_2$  blow.

hysteresis width, and increases in on-current, off-current and sub-threshold swings even with treatments at room temperature during a short time period. Moreover, Abdou et al. and Meijer et al. had pointed out that the doping effect was reversible in a vacuum chamber whenever the dopants are exposed to oxygen or air.<sup>12-14</sup>

Figure 6 depicts the transfer curves for the samples that were subjected to water treatment both with and without subsequent N<sub>2</sub> annealing. It was seen that N<sub>2</sub> annealing removed some stable state dopants in P3HT that resulted from the water treatment, i.e., on-current decreased, as that shown in Fig. 3. Figure 7 shows the reversibility of N<sub>2</sub> annealing on the stable state dopants. We successfully recovered the sample stored in air for 2 months, which was expected to absorb a lot of water and oxygen molecules from the air, with N<sub>2</sub> annealing. Moreover, inspired by the results of FTIR analyses presented by Zhuo and his colleagues,<sup>18</sup> we also fabricated PTFTs in the photo bay with or without intentional white-light exposure in order to further investigate the causes of the formation between stable dopants or transient dopants in P3HT. As the shown in Fig. 8, an enlarged hysteresis width of the devices without the white-light exposure was observed as compared to that with the white-light exposure. This result forwardly confirms that our previous inference is reasonable. Our argument is as follows: since processed in atmosphere, oxygen and water molecules would be highly likely to diffuse into P3HT. When an energy source was provided such as white-light source during processing, a charge interaction between P3HT molecules and oxygen/water molecules would have a good chance to be triggered and then followed by the formation of stable dopants. On the contrary, when processed in yellow bay without exposure to white light, the oxygen and water molecules could only diffuse and form the transient dopants which in turn led to the enlarged hysteresis width. We found this outcome seems consistent with their FTIR observation. As a result, we believe that our proposed model of forming stable dopants and transient dopants is convincing and able to well explain the hysteresis effect.

In order to further verify our speculation of a transient doping effect, dynamic constant gate voltage stress—40 V for 10 min followed by 40 V for another 10 min, performed twice to test the conditions of with and without N<sub>2</sub> blow on the PTFTs. The drain currents were recorded at a bias condition using a gate voltage of 0

V and a drain voltage of -40 V during the stressing, and are shown in Fig. 9a. We clearly saw that the drain current during the two individual periods of stressing decreased and increased drastically at the initial stages, respectively, and both became gradually saturated as the time evolved. Similar observations and mechanisms were discussed by many groups, but the mechanism was still not clear.<sup>19,20</sup> However, based on our inferences, we also found that the stable state dopants were driven out from their original stable positions and converted into transient dopants after negative gate voltage stress was applied. Thus, the decreased drain current, increased hysteresis width and higher on/off current ratio, as well as a negative shift on the transfer curve were observed as shown in Figs. 9b and 9c for the samples without/with N<sub>2</sub> blow, respectively. During positive gate stressing, there were large amounts of electrons existing in the inversion layer of P3HT. These induced electrons might attract transient state oxygen and water molecules to return to the stable state and contribute to the formation of extra holes. Noteworthy, we could see that the on-current after positive voltage stressing for the sample exposed to N<sub>2</sub> blow was much lower than that without N<sub>2</sub> blow accompanied by smaller hysteresis. This implies that the transient dopants of residual oxygen and water molecules can be reduced by N<sub>2</sub> blow, and decreased hysteresis width and on current were observed after the residual transient dopants converted into stable dopants. All the parameters, such as mobility, on/off current ratio and hysteresis width, of the devices in this paper were summarized in Table II. The hysteresis width was defined as the difference between the threshold voltages in the bi-directional C-V curves, and the mobility was evaluated by the classical saturation equation.<sup>21</sup>

Hysteresis in PTFTs was recently reported by Cheng and colleagues who suggest that it is mainly caused by existing vacancies acting like charge traps. These vacancies are hypothesized to appear as the solvent is slowly evaporated.<sup>22</sup> Unfortunately, this mechanism seems not able to explain the observations from our experiments. First, the vacancies tended to be erased after thermal N<sub>2</sub> annealing. If the hysteresis did correlate to the vacancies, a smaller hysteresis width should be observed. However, our results indicate that hysteresis becomes more severe after N<sub>2</sub> annealing. Second, the possibility of the number of vacancies changing seems very low with room temperature H<sub>2</sub>O or peroxide treatment, and yet we still observe

**Table II. Summary of the mobility, on/off current ratio and hysteresis width of different samples.**

| Samples                                          |                             | Mobility (cm <sup>2</sup> /Vs) | On/off current ratio | Hysteresis width (V) | References        |
|--------------------------------------------------|-----------------------------|--------------------------------|----------------------|----------------------|-------------------|
| As prepared                                      | 0.05 wt %                   | $2.5 \times 10^{-6}$           | $1.29 \times 10^3$   | 49                   | Figure 3          |
|                                                  | 0.1 wt %                    | $6.9 \times 10^{-4}$           | $2.55 \times 10^3$   | 26                   |                   |
|                                                  | 0.2 wt %                    | $6.7 \times 10^{-3}$           | $5.55 \times 10^2$   | 4                    |                   |
| After annealing                                  | 0.05 wt %                   | $5 \times 10^{-6}$             | $2.21 \times 10^3$   | 47                   |                   |
|                                                  | 0.1 wt %                    | $8.1 \times 10^{-4}$           | $4.29 \times 10^3$   | 31                   |                   |
|                                                  | 0.2 wt %                    | $7.7 \times 10^{-3}$           | $1.85 \times 10^3$   | 10                   |                   |
| With N <sub>2</sub> blow                         | 1st sweep                   | $2.8 \times 10^{-4}$           | $5.63 \times 10^3$   | 24                   | Figure 4          |
|                                                  | 2nd sweep                   | $2.8 \times 10^{-4}$           | $9.79 \times 10^3$   | 14                   |                   |
| Without N <sub>2</sub> blow                      | 1st sweep                   | $5.1 \times 10^{-4}$           | $9.67 \times 10^3$   | 19                   |                   |
|                                                  | 2nd sweep                   | $5.1 \times 10^{-4}$           | $1.22 \times 10^4$   | 21                   |                   |
| As prepared                                      | 0.2 wt %                    | $1.7 \times 10^{-3}$           | $1.79 \times 10^3$   | 21                   | Figures 5a and 5b |
|                                                  | 0.1 wt %                    | $7.3 \times 10^{-4}$           | $2.55 \times 10^3$   | 29                   |                   |
| Water treated                                    | 0.2 wt %                    | $1.7 \times 10^{-3}$           | $8.38 \times 10^2$   | 20                   |                   |
|                                                  | 0.1 wt %                    | $1.5 \times 10^{-3}$           | $2.28 \times 10^3$   | 28                   |                   |
| N <sub>2</sub> annealed followed by treatment of | water                       | $4.6 \times 10^{-3}$           | $2.26 \times 10^5$   | 19                   | 5c and 5d         |
|                                                  | peroxide                    | $4.5 \times 10^{-3}$           | $8.23 \times 10^4$   | 24                   |                   |
|                                                  |                             | $5.5 \times 10^{-3}$           | $1.41 \times 10^4$   | 27                   |                   |
| O <sub>2</sub> annealed                          |                             | $4.2 \times 10^{-3}$           | $1.47 \times 10^4$   | 24                   |                   |
| Before negative gate bias stress                 | With N <sub>2</sub> blow    | $4.0 \times 10^{-3}$           | $2.17 \times 10^3$   | 8                    | Figure 9          |
|                                                  | Without N <sub>2</sub> blow | $4.1 \times 10^{-3}$           | $2.43 \times 10^3$   | 7                    |                   |
| After negative gate bias stress                  | With N <sub>2</sub> blow    | $3.6 \times 10^{-3}$           | $4.31 \times 10^4$   | 12                   |                   |
|                                                  | Without N <sub>2</sub> blow | $3.6 \times 10^{-3}$           | $3.93 \times 10^4$   | 15                   |                   |
| After positive gate bias stress                  | With N <sub>2</sub> blow    | $3.8 \times 10^{-3}$           | $1.04 \times 10^4$   | 6                    |                   |
|                                                  | Without N <sub>2</sub> blow | $3.9 \times 10^{-3}$           | $2.14 \times 10^3$   | 7                    |                   |

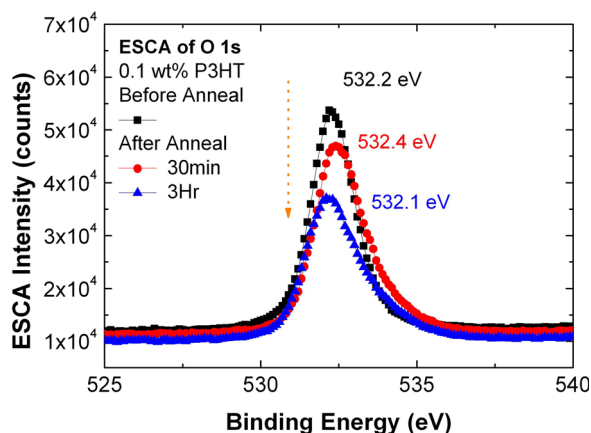


**Figure 10.** (Color online) XPS spectra for the active layer of 0.1 wt % P3HT TFTs, which P3HT were with or without N<sub>2</sub> annealing.

variation in hysteresis width after treatment with either. On the contrary, the speculation we propose here could explain why more serious hysteresis is observed when the P3HT film contains more vacancies. In short, more vacancies in the P3HT film could lead to easier diffusion of H<sub>2</sub>O or O<sub>2</sub> and in turn can affect hysteresis behavior. Gu et al. have ever tried to address the hysteresis effect observed in the pentacene-based TFTs from the electrical viewpoint.<sup>23</sup> They attributed the hysteresis effect to the electron trapping. However, their conclusion obviously conflicted with our result that the more severe hysteresis was presented after negative gate bias stress. According to their analyses, the states trapping electron would be partially detrapped to some extent or even become empty without inducing extra hole population after being stressed by the negative gate voltage. However, the hysteresis effect obviously could not be satisfactorily explained by the filled trapping states. In contrast, our inference could well explain both the observed phenomena after gate bias stressing and the presented hysteresis effect. More detail of the microscopic structures of complex of transient and stable dopants might be explained by the formation of different electronegative molecules in P3HT layer, which Zhuo et al. had studied by results of FTIR spectrums.<sup>18</sup>

The incorporation of oxygen and water molecules in the P3HT layer was one of the major issues responsible for the hysteresis effect. To avoid them, e.g., via N<sub>2</sub> annealing, from forming whatever stable or transient dopants inside P3HT would be helpful for the fabrication of high-performance and reliable PTFTs. In addition to the evidences from the electrical measurements, we found that the recovery of stable dopants after N<sub>2</sub> annealing could directly confirmed by XPS. Worth mention was that the analyses were carried out in vacuum and only those transient dopants could be removed but the stable dopants were not. Figure 10 shows the XPS spectra of O1s of P3HT layers with and without N<sub>2</sub> annealing. Spectra were calibrated by aligning the binding energy of C1s to the value of 284.6 eV, which corresponded to the major bonds of C-C and C-H in P3HT. The peak position for the binding energy was around 532.2 eV, which had been earlier indicated as the peak position of water.<sup>24</sup> The result seemingly supports our previous arguments because we clearly observed that the peak area decreased as the

annealing time increased. As a result, we are confident that our inference regarding the effect of N<sub>2</sub> thermal annealing is reasonable and deserving of further study. To further make a passivation layer in vacuum environment, such as coating a parylene layer on P3HT after annealing might be one of the possible methods to completely isolate the influences from air environment.

## Conclusion

In this article, we investigated transient effects in regioregular P3HT-based PTFTs with bi-directional voltage sweeping. With the results of our several elaborated experiments, we demonstrated that there were stable state and transient state doping effects caused by O<sub>2</sub> and H<sub>2</sub>O molecules residing inside the P3HT layer. We also employed physical analyses, such as XPS, to collect supporting data for our speculation. From the point of view of operation stability, we can not only evaluate on-current level, threshold voltage, off-current magnitude and the on/off ratio but also have to take the hysteresis width into account in pursuing high performance PTFTs. The implication of this study is to point out the importance of effectively eliminating O<sub>2</sub> and H<sub>2</sub>O molecules from being incorporated into the P3HT layer during fabrication as the negative effects may have consequential effects in future applications.

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