

# Influence of processing conditions on the stability of poly(3-hexylthiophene)-based field-effect transistors

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Bottom-contact organic field-effect transistors (OFETs) based on poly(3-hexylthiophene)-2,5-diyl were fabricated under different process conditions. The devices displayed drastic differences in their ambient-air stability. Whereas it took only about 10 min in air for the off current to increase by one order of magnitude in OFETs prepared with chloroform and hexamethyldisilazane, a 120 min exposure to air caused only a slight degradation of OFETs prepared using 1,2,4-trichlorobenzene, *n*-octadecyltrichlorosilane, and a heat treatment. The differences in the film surface morphology were analyzed and possible mechanisms for the enhanced stability are discussed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2208938]

For low-cost plastic electronics, soluble conjugated polymers are very attractive because they can be deposited and processed at low temperatures over a large substrate area. Among various types of polymeric semiconductors, regioregular poly(3-hexylthiophene)-2,5-diyl (P3HT) is the most explored due to its wide commercial availability and high carrier mobility.<sup>1,2</sup> However, it is still very challenging to fabricate and measure P3HT-based organic field-effect transistors (OFETs) in ambient conditions due to the rapid, undesirable interactions of P3HT with atmospheric oxygen<sup>3</sup> and moisture.<sup>4,5</sup> For instance, Hoshino *et al.*<sup>5</sup> reported a very unstable transistor operation, e.g., an increase of the off current by at least one order of magnitude in P3HT-based OFETs after a few minutes of exposure to a moisturized nitrogen gas. Such a poor stability clearly imposes serious limitations for material and device research in ordinary research laboratories as well as possible industrial applications. Recently, through different chemical structural designs, a few types of semiconducting polymers have been synthesized with increased ionization potentials, leading to a significantly improved air stability.<sup>6–8</sup>

The electrical properties of P3HT are well known to sensitively depend on detailed process conditions. It was discovered that using chloroform as the P3HT solvent could lead to a higher field-effect carrier mobility compared with the films processed from toluene, tetrahydrofuran, 1,1,2,2-tetrachloroethylene, and other organic solvents.<sup>9,10</sup> Recently, high boiling-point solvents such as chlorobenzene and 1,2,4-trichlorobenzene (TCB) have been found to lead to a high degree of crystallinity and enhanced mobility.<sup>10</sup> Furthermore, substrate surface/interface treatments using self-assembled monolayers (SAMs) have strong influence on the carrier transport. Among the most commonly used SAMs are siloxanes<sup>2</sup> (e.g., hexamethyldisilazane, HMDS) and silanes (e.g., *n*-octadecyltrichlorosilane, OTS).<sup>11</sup> Moreover, thermal treatments of P3HT films at suitable temperatures were also found to improve the crystallinity.<sup>12</sup> Although the described process optimizations have been shown to improve the carrier mobility from about 10<sup>−4</sup> to over 10<sup>−1</sup> cm<sup>2</sup>/V s, little

work has been reported on the influence of these process conditions on the air stability of P3HT OFETs.

In this work, we fabricated bottom-contact (BC) P3HT OFETs since they are generally more favorable in circuit manufacture. An improvement in ambient-air stability by at least a few orders of magnitude was achieved via a combination of a high boiling-point polymer solvent, a highly hydrophobic SAM for dielectric surface treatment, and thermal annealing in a nitrogen gas. We analyzed the surface roughness and crystallinity of the P3HT films, which enabled us to discuss possible mechanisms for the improved stability.

For convenience and a direct comparison with most previous studies, highly doped silicon wafers with a thermally grown SiO<sub>2</sub> (200 nm) were used as substrates. Self-assembled monolayers, HMDS or OTS, were employed for SiO<sub>2</sub> surface modification. Gold source and drain electrodes were evaporated through a shadow mask, defining 40 μm long and 2 mm wide OFET channels. About 20 devices with other channel lengths were tested and similar results were obtained. P3HT (regioregular ratio >98.5%, molecular weight 87 k, Aldrich) was reduced with hydrazine<sup>13</sup> and spun at 2000 rpm from 1% solutions in chloroform or TCB. Since the polymer was processed in ambient conditions, samples were left in vacuum (<10<sup>−6</sup> Torr) for about 12 h before measurements to reverse the effect of oxygen doping. To minimize leakage currents, small trenches in the P3HT film around the electrodes were created with a needle. All devices were stored and measured in ambient air with a humidity level between 40% and 50% in the dark.

Typical OFET transfer characteristics were measured in the saturation regime with a source-drain voltage of  $V_{SD} = -80$  V. Figure 1 shows the results of OFETs prepared using different P3HT solvents (chloroform or TCB) and SAMs (HMDS or OTS). The transfer curves of the as-prepared devices in Figs. 1(a)–1(c) show that the OFET with the HMDS-modified dielectric had a much larger positive threshold voltage,  $V_T > 30$  V, and a much larger subthreshold swing,  $S = 11$  V/decade, than the OFETs with the OTS-treated insulator, regardless of the solvent (also including xylene, the results not shown here) used for the polymer deposition. The mobility in the saturation regime<sup>14</sup> was 0.0013 cm<sup>2</sup>/V s, which is typical for devices produced in ambient air. From

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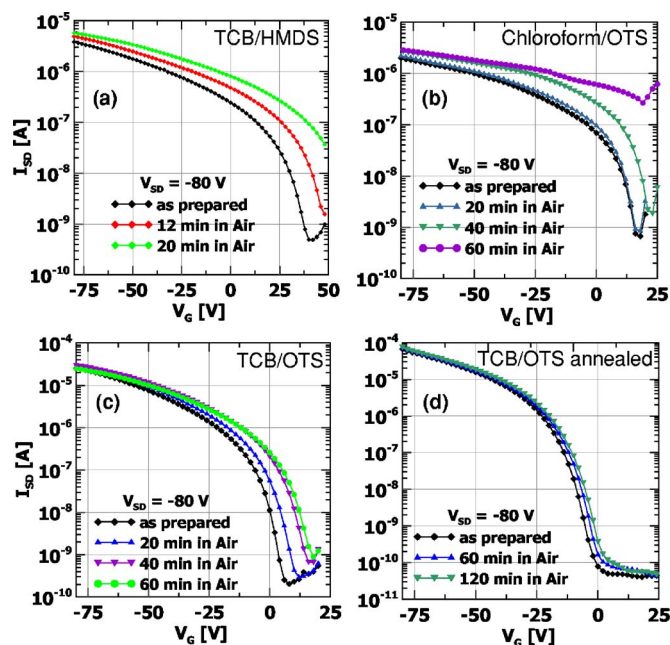


FIG. 1. (Color online) Ambient-air stability of the P3HT-based bottom-contact OFETs prepared using (a) TCB and HMDS, (b) chloroform and OTS, (c) TCB and OTS without annealing, and (d) TCB and OTS after annealing at 100 °C for 90 min. Note the different storage times and gate voltage ranges.

the transfer curves measured after different storage times, it is clear that the device was quickly doped in minutes, in agreement with the previous reports.<sup>4,5</sup> Since it took about 10 min to transfer the device from the vacuum chamber to the measurement setup, the initial doping certainly had affected the “as-prepared” device, as expected from the dramatic change of the transfer characteristics with time shown in Fig. 1(a). The result illustrates how difficult it is to perform controlled, reproducible experiments for material and device research on P3HT in ordinary research laboratories, given such a poor stability.

The stability was found to be dramatically improved in OFETs processed from chloroform on OTS-treated substrates as shown in Fig. 1(b) [note the different storage times and gate voltage range from those in Fig. 1(a)]. Virtually no degradation in device performance was observed during the first 20 min, in strong contrast to the rapid changes in Fig. 1(a). The enhanced stability resulted in much less doping in the as-prepared devices before they were transferred to the measurement setup, and hence a much reduced  $V_T$ , down to 14.6 V, was observed. Furthermore, the subthreshold swing,  $S=4.2$  V/decade, was significantly improved, indicating that there were much fewer carrier traps at the interface when OTS was used.<sup>15</sup> Both the field-effect mobility,  $0.00035\text{ cm}^2/\text{V s}$ , in the as-prepared device and the on/off ratio were reduced, which were expected because the fast evaporation rate of chloroform allowed only a short time for the P3HT molecules to self-organize compared to TCB.<sup>10</sup> The results suggest that whereas a high boiling-point solvent is more important for the carrier mobility, the surface treatment with a proper SAM can be more crucial for the air stability.

Given the above results, we fabricated OFETs using both TCB and OTS. Indeed, the mobility in the as-prepared device was improved to  $0.019\text{ cm}^2/\text{V s}$  and the on/off ratio was over  $10^5$ . Most strikingly, the stability was significantly im-

proved as shown in Fig. 1(c). After 60 min in air, the off current increased only by a factor of 5, in contrast to over two orders of magnitude increase in the device shown in Fig. 1(b). The threshold voltage was closer to 0 V, indicating that the device was much less doped, whereas  $S$  was reduced to 3.4 V/decade.

We further performed thermal annealing of the P3HT films spun from TCB onto OTS-treated  $\text{SiO}_2$  at 100 °C for 90 min in a slightly overpressured nitrogen gas, and found that the air stability increased by about another order of magnitude. Little change in the transfer characteristics was observed after 120 min, as shown in Fig. 1(d). The mobility also reached  $0.08\text{ cm}^2/\text{V s}$ , a factor of 4 increase from that of the devices that were not annealed. The on/off ratio was well above  $10^6$ . The device nicely switched on around 0 V, showing that the influence of doping and humidity on the performance of the devices was minimal. Additionally,  $S$  was reduced down to 2.9 V/decade. Although it is difficult to quantify, the overall stability improvement from the OFET shown in Fig. 1(a) to the annealed OFET in Fig. 1(d) is a few orders of magnitude. The stable performance in air for 2 h makes it much easier for P3HT-based devices to be processed and measured in ordinary research laboratories, and allows protective encapsulation to be implemented in air for long-term operational stability if so desired.

The different on currents in Figs. 1(a)–1(d) correlate with the carrier mobilities in the corresponding OFETs. For off currents the amount of doping is crucial.<sup>3–5</sup> In addition, it was reported that increased levels of doping dramatically enhanced gate leakage currents that affected off currents.<sup>16</sup> In our experiments, the amount of doping that the as-prepared OFETs received during the 10 min transfer to the measurement setup was determined by the level of their off currents and unambiguously reflected the differences in the devices air stability.

To gain an insight into the stability differences, the P3HT films were imaged using an atomic force microscope (AFM). A high degree of regioregularity was demonstrated to allow P3HT molecules to self-orient into a well-ordered lamellar structure with an “edge-on” orientation of the thiophene rings relative to the substrate.<sup>2</sup> Due to the better overlap of the  $\pi$  orbitals, a high mobility was achieved. Recently, it was also found that different P3HT solvents resulted in distinct differences in grain boundaries, branching of nanofibrillar crystalline domains, and interconnectivity.<sup>17</sup> For the air stability, the mechanism is more complex. First of all, crystallization is also crucial. A tight and ordered packing of P3HT molecules would provide effective resistance to atmospheric oxygen and water molecules penetrating the film and doping the P3HT at the semiconductor-insulator interface, where the hole transport takes place when an OFET is in action. Different solvents and SAMs may lead to different molecular packing and interface dipoles, which might also affect the highest occupied molecular orbital (HOMO) and influence the stability. In addition, the P3HT film should have as few pinholes as possible. The pinholes are not necessarily through the whole film, since shallow pinholes (or valleys) on the top surface, generally shown as fluctuations, may be interconnected with pinholes at different depths. Moreover, when the P3HT film is highly crystalline with deep and wide gaps at the boundaries between large grains, the boundaries may also be vulnerable locations for oxygen and water molecules to penetrate through the film.

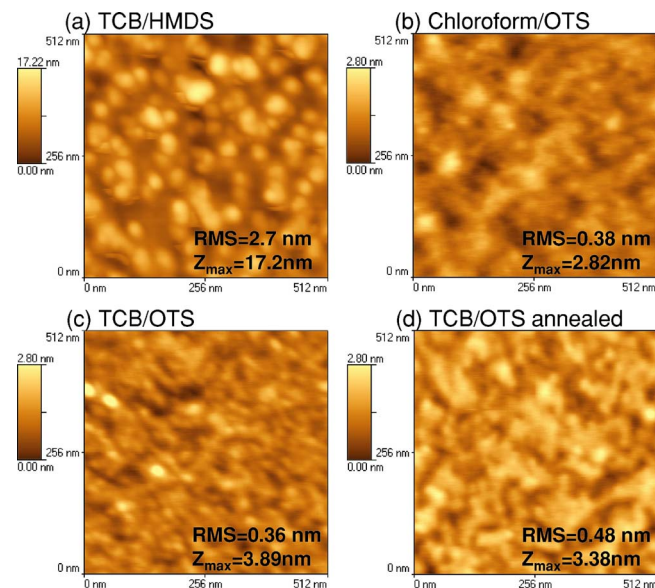


FIG. 2. (Color online) Atomic force micrographs of P3HT films processed under different conditions. Note the different height scales. The thicknesses of the P3HT films were 20, 45, 15, and 15 nm, respectively.

From the micrograph of the P3HT film processed using TCB and HMDS shown in Fig. 2(a), the surface was clearly very rough. The area fluctuation rms was 2.7 nm and the maximum peak-to-valley fluctuation was  $Z_{\max}=17.2$  nm, which were far greater than those of the surfaces shown in the other three micrographs. Oxygen and water molecules could hence easily find paths to penetrate the film, rapidly degrading the device performance. For the film processed from chloroform and OTS in Fig. 2(b), the surface roughness was significantly reduced (rms is 0.38 nm), which explains why the stability was much improved. The reduced fluctuation was most likely because the fast evaporation of chloroform resulted in a less crystalline film and hence relatively more amorphous or “featureless” morphology.<sup>10</sup> Although the degree of crystallization cannot be unambiguously determined by the AFM images and experiments such as x-ray diffraction are needed for quantitative studies, the lower carrier mobility in the film processed from chloroform and OTS suggests weaker crystallinity than in the film processed from TCB and HMDS. With the use of TCB and OTS, the micrograph in Fig. 2(c) yields a slightly reduced roughness rms of 0.36 nm and a larger  $Z_{\max}$  of 3.89 nm than in Fig. 2(b). This and the higher mobility suggest a higher degree of crystallization. Comparing the OFETs in Figs. 1(b) and 1(c), the device prepared using chloroform and OTS was more stable in the first 20 min. This was most likely because fewer deep pinholes were formed by the weaker crystallization, and it hence took time for oxygen to penetrate the film. For the OFET prepared using TCB and OTS, however, deep pinholes could arise at the boundaries of the formed crystalline domains, allowing a quicker doping in the first 20 min. Afterwards, however, it was very difficult for oxygen and water molecules to further penetrate through the domains because of the tightly packed ordered P3HT molecules, thereby resulting in a more sustained stability. Comparing the micrographs in Figs. 2(a) and 2(c), OTS was shown to lead to a

much more uniform P3HT film than HMDS. This is most likely because the long OTS molecules (2.8 nm) can effectively bend and stretch to accommodate the substrate surface fluctuations. The better film uniformity certainly led to a mobility increase by a factor of 15, but also more dramatically enhanced the air stability. Moreover, we note that previous studies revealed that P3HT-based OFETs were affected much more significantly in an inert gas that was humidified with water than in a pure oxygen gas.<sup>4,5</sup> Because OTS-treated surfaces exhibit a much greater hydrophobicity than HMDS-treated surfaces, indicated by the larger contact angle of water droplets, it would be more difficult for the penetrated water molecules to reside and affect the P3HT at the interface with the substrate. Visibly, the annealed film shown in Fig. 2(d), consists of domains of a larger size than in Fig. 2(c). The improved P3HT film morphology not only led to increased hole mobility from 0.019 before annealing to 0.08  $\text{cm}^2/\text{Vs}$ , but also enabled a significant increase of stability.

To gain further insight into the enhanced stability, investigations including x-ray diffraction and optical experiments and choosing more hydrophobic, longer-chain SAMs and higher boiling-point solvents may be carried out, which could similarly improve the stability of other polymers that exhibit a polycrystalline structure.

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