Chapter 7

Reliability Characteristics of P3HT-Based OTFTs

It has been reported that the device operation of TFTs based on thiophene polymers and oligomers is markedly influenced by air exposure. Operation in an ambient atmosphere usually results in a significant increase in off-state conduction, threshold voltage shift, and, to some extent, in a deficiency of the saturation behavior in the output current [7.3]. It has been suspected that molecular oxygen and/or water can influence the device operation. For example, it is well-documented that oxygen has a high diffusion coefficient of 1.2×10^{-8} cm^2/s in P3HT and would form a weakly bound donor-acceptor complex (charge transfer complex) with P3HT or localized states within the $\pi - \pi^*$ gap [7.1]. Since oxygen is an effective dopant for P3HT, the current increases by an order of magnitude and the output I_D - V_D curves take on considerable "Ohmic" behavior in the presence of oxygen. However, the oxygen atoms in P3HT can be partially removed to restore the initial I-V characteristics of OTFTs by vacuum storage or heat treatment [6.39], [7.1], [7.2].

In addition to oxygen, H_2O incorporation is another issue. It was reported by S. Hoshino et al. that the I_S - V_D curves of a TC-type OTFT exhibit an ohmic-like response to the V_D sweep, and the saturation behavior was scarcely observed; the output I_D could not be reduced even though applied positive V_G of more than 30 V to the gate electrode and made the OTFT operate in a hole-depletion mode. It required a long period of desiccation in a vacuum to restore the operation of a moisture-affected device, because the water molecules interacted exoergically with the surface of the P3HT layer and were bound very tightly [7.4]. Besides polymers, oligomers materials such as pentacene are more susceptible to moisture. By flooding the chamber with wet air, a positive threshold voltage shift for pentacene-based OTFTs can be seen [7.5]. H_2O molecules can easily diffuse into the crevices of the pentacene

thin film and interact with the trapped carriers by altering the electric field at the grain boundaries. H_2O might also be incorporated into the pentacene film and change their morphology, resulting in significant fluctuation of off-state leakage current and carrier mobility [7.6], and therefore pentacene-based OTFTs can even be utilized as a humidity sensor [7.7].

In this section, we will perform a systematic research about the P3HT OTFTs being exposed to air, O_2, N_2 and H_2O environments with time evolution. Furthermore, similar to the situation of inorganic poly-Si TFTs in chapter 3 or chapter 4, the electrical stability is also very important for circuits composed by OTFTs, but few investigations have been done about the electrical stability issues of OTFTs. Here, we will carry out several endurance tests such as gate bias stress or hot carrier stress to examine the reliability characteristics of P3HT based OTFTs.

7.1 Environmental Stability of P3HT-OTFTs

7.1.1 Experimental: Sample Preparation

The P3HT organic TFTs with bottom contact architecture were fabricated on a heavily doped n^+ silicon substrate with thermally grown gate insulator and thick field oxide. First, phosphorus atoms were diffused into an n-type Si wafer by $POCl_3$ to create a common gate electrode. A field SiO_2 layer with a thickness of 500 nm and a thin gate oxide layer with a thickness of 100 nm were subsequently grown in a furnace. Afterwards, source/drain regions were defined using photo lithography process followed by the thermal evaporation of a 20 nm-thick layer of Ti as an adhesion layer and a 100 nm-thick layer of Pt as a contact material. The wafer was then immersed in acetone to lift off the photo resist and form the source/drain regions. The samples, after S/D patterning, were treated with hexamethyldisilazane (HMDS) to improve adhesion and regioregularity between the polymer chain and the oxide surface.

Next, P3HT of 0.3 wt. % dissolved in chloroform was filtered through a 0.2-μm pore-size PTFE filter and then spun onto the wafer surface, which was then cured at 120℃.

To clarify the origin of electrical properties variation, the samples were first stored in a vacuum chamber with base pressure of 10^{-6} torr for at least two days to restore the initial electrical characteristics which probably have degraded during the fabrication process of OTFTs. Next, these samples were then treated with N_2/O_2 gas in a furnace at room temperature or immersed in D.I. water; some of the other samples were stored in the air by a moisture-proof cabinet with a relative humidity of 40% and their electrical properties were measured on the 1st, 2nd, 5th, 11th, 15th and 30th days to examine the evolution of electrical properties with time.

7.1.2 Results and Discussion

Comparing to inorganic transistor, the organic devices are quite susceptible to oxygen or moisture in the atmosphere. From either Fig. 6-8 or Fig. 6-9(a), it can be found that the threshold voltage of OTFTs is larger than 20 V, implicating that the devices are normally ON at zero gate bias. Since the spin coating and measurement processes were performed in the air, the electrical characteristics of OTFTs would be inevitably influenced by O_2, H_2O or N_2. Figure 7-1 compares the $I_S - V_G$ curves for two samples: one was measured immediately after fabrication while the other was stored in a vacuum chamber (<10^{-6} torr) for two days after fabrication and then measured immediately in the air. The threshold voltage was found to decrease from 28 V to 18 V and the mobility increased from 4×10^{-3} to 8×10^{-3} cm^2/Vs after vacuum treatment, so the influences of the ambient condition, presumably the oxygen auto-doping effect, can be partially reversed [7.9].

Figure 7-2 plots the threshold voltage of OTFTs versus time. Clearly, the oxygen treatment caused the threshold voltage to increase significantly from 26 V to 34 V within 8 hrs. As mentioned before, the oxygen atom is a kind of p-type dopant for P3HT. Therefore,

the conductivity increases with oxygen incorporation, and a large gate voltage must be applied to fully deplete the channel region and turn the device OFF. Furthermore, because of oxygen reaching its solid-state solubility in P3HT, the threshold voltage gradually saturates at 36 V; another two weeks of exposure time is required for oxygen to diffuse to the interior of P3HT film, resulting in V_{th} up to 46 V. We also found that the vacuum treatment is useless for samples exposing in the air over 24 hrs (V_{th} > 30 V) because the P3HT film had been doped seriously. Besides, when the V_{th} becomes too positive (>50 V), the operating voltage exceeds the breakdown field of gate insulator, so the electrical properties of the OTFTs could not be measured on the 30th day.

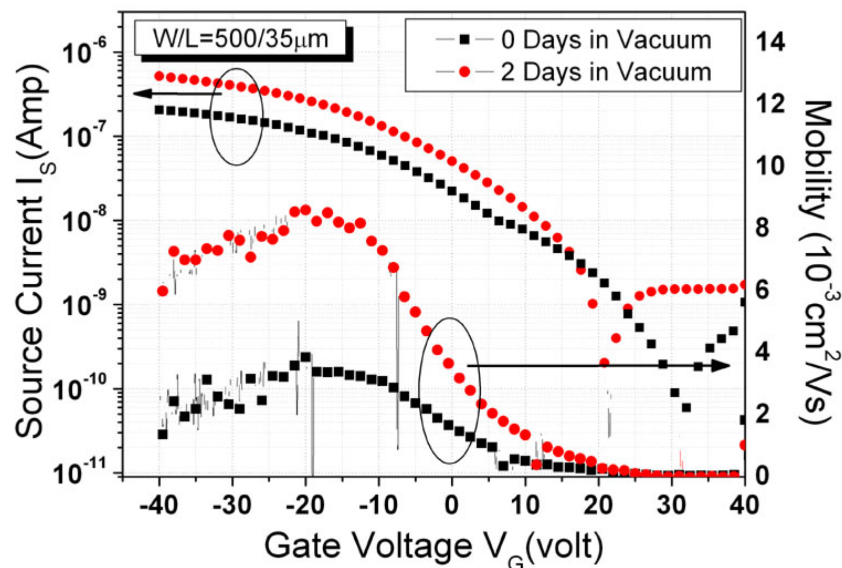


Figure 7-1 Electrical characteristics of an as fabricated OTFT and an OTFT after vacuum treatment for two days

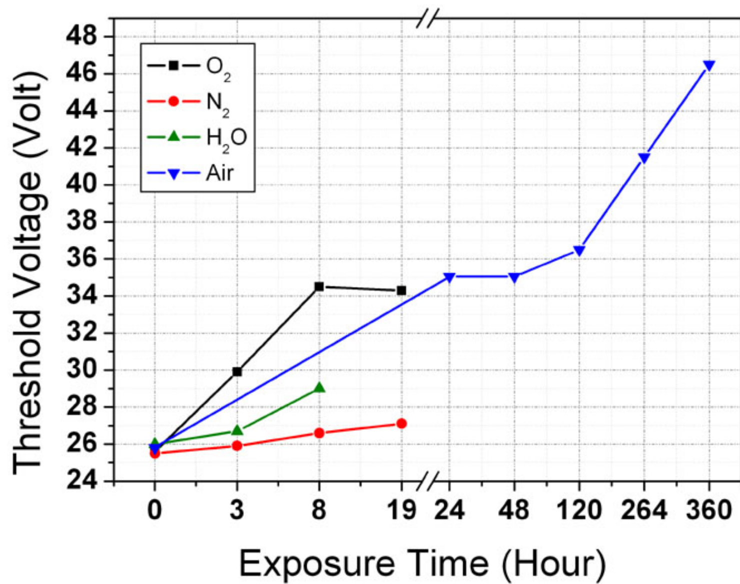


Figure 7-2 Threshold voltages vs. exposure time for OTFTs with O_2, N_2, H_2O or air treatments

In contrast to oxygen, both N_2 and H_2O treatments exhibit negligible influence to the V_{th} shift of OTFTs. Because P3HT film is highly hydrophobic, we infer that the threshold voltage shift from 26 to 29 V after immersing in H_2O is resulted from the dissolved O_2 in water and the device measurement processes.

The dependence of carrier mobility versus different treatment conditions are illustrated in Fig. 7-3. For first three hours, the mobility of OTFTs after O_2 treatment increased significantly since the conductivity and the associated parasitic source/drain series resistance decreased, contributing to an over estimation of mobility calculation. Meanwhile, the impurity scattering becomes more serious with increasing the oxygen doping concentration so that the carrier mobility declines continuously for a longer exposure time. For N_2 treatment, the mobility would also increase and then saturate owing to the out-diffusion of oxygen atoms, which is the case similar to the vacuum treatment. Moreover, although H_2O does not induce a significant shift of both threshold voltage and mobility, an abrupt yield loss was observed when the immersion time reaches 19 hrs. It may be attributed to the permeation of water through the pin holes of P3HT film and the creation of trap states at P3HT/SiO_2

interface. Consequently, the investigation to figure out the detailed failure mechanism is still in progress.

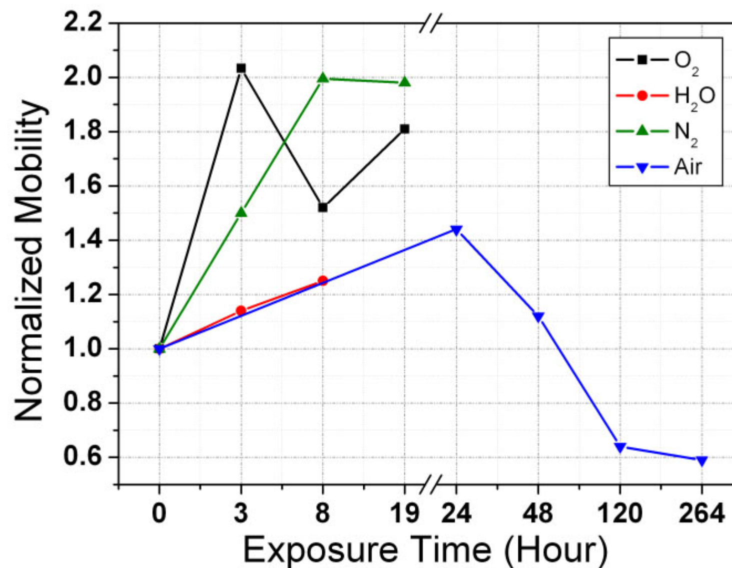


Figure 7-3 Normalized carrier mobility vs. exposure time for OTFTs with O_2, N_2, H_2O or air treatments

Several techniques have been proposed to prevent the degradation of OTFTs when exposing to the atmosphere. One of these methods is to encapsulate the organic devices with a water/gas barrier such as polyarylate based adhesive (~15 μm) after manufacturing. Life time of organic devices with passivation layer was over 200 hr compared to that without passivation layer of less than 50 hr [7.9]. Earlier on, passivation with photo resist had also been tested, but the authors found some solvents of P.R., primarily xylene, react with the P3HT layer and cause the mobility of OTFTs to decrease by 60% after encapsulation [7.10]. Besides, for a novel "top-gate" configuration similar to the conventional poly-Si TFTs, because the polymeric active layer is fully capped under the thick gate insulator and Au gate, the electrical characteristics of OTFTs are not altered for an astonishing 1400 hr (i.e. 2 years) even under extreme conditions of 85°C and 85% relative humidity [7.11]. For pentacene-OTFTs, a H_2 plasma treatment for a short period after deposition of pentacene is

reported to be effective to suppress the oxygen concentration in the active layer [7.12].

7.2 Electrical Stability of P3HT-OTFTs

7.2.1 Sample Preparation and Stress Conditions

Bottom-contacted OTFTs with Ti/Pt as the source/drain metals and thermally grown SiO_2 as the gate insulator were utilized in this experiment. Detailed process flow had been described in both *Section 6.3.1* and *Section 7.1.1*.

Two kinds of stress conditions were applied to examine the electrical reliability of OTFTs. First, a constant gate bias of +25 V or -25 V was applied while the source/drain electrodes were grounded for 0 – 2000 sec. Since the measurement process was conducted in the atmosphere and the electrical properties of OTFTs, especially the threshold voltages, would shift with the exposure time, a control sample was prepared to which no gate bias stress was applied, but the I_S - V_G curves (sweep V_G from +40 V to -40 V) were measured at the same time interval with those samples being stressed. Through this approach, we can differentiate the actual variations caused by stress measurements from those by oxygen auto doping.

The second stress condition was hot carrier stress. A constant gate bias of -10 V and a constant drain bias of -20 V were applied for 0 – 2000 sec while the source electrode was grounded. The electric field near the drain side should accelerate the free holes in the depletion region and cause some damages at the interface or the gate insulator.

7.2.2 Constant Gate-Bias Stress

As shown in Fig. 7-4, a positive V_{th} shift was observed after a +25 V gate bias stress and a negative V_{th} shift after a -25 V stress; for control sample, a slight positive V_{th} shift can be found due to the oxygen auto-doping effect during the measurement processes. Several

mechanisms are responsible for the above observation, such as charge trapping/relaxing near the semiconductor-insulator interface, mobile ions/trap-states in the high-k gate dielectric, or polarization effect. It was also reported that the electro-negativity of the molecule's functional group, such as self-assembly monolayer at the interface, influences the charge distribution within the organic active layer and can lead to the formation of an electric dipole [7.13]. However, if the interface states were the dominant mechanism, the trap states would fill with holes under negative bias stress (because many holes now accumulated in the channel region) and then these filled trap states would not deteriorate the ON current during the following I_S - V_G measurement, i.e. the V_{th} or current I_S should increase. But actually the V_{th} decreases under a negative bias stress. Similarly, a positive bias stress would deplete the trap states and then these empty states would trap the free holes during the following I-V measurement, causing a reduction of ON current, which also contradicts our observation. Besides, the gate insulator is a thermally grown SiO_2 and the I-V characteristics was measured at room temperature, so we can exclude the influence of mobile ions or oxide-trapped charges in the gate dielectric. Moreover, as shown in Fig. 7-5, the leakage current I_G did not change with the constant V_G stress for over 5000 sec, implying that the gate oxide was not damaged during the stress measurement. Finally, we examined the results of gate bias stress for OTFTs with or without HMDS treatment, and found in both cases the V_{th} shift phenomenon were the same, indicating that the electric dipoles created by those self-assembly monolayers were not responsible for the V_{th} shift of OTFTs.

Using the concept of polarization can satisfactorily explain the results of gate bias stress. When the gate electrode was applied a constant negative bias, the dipoles from the polar part of P3HT molecules would rearrange and induce a polarization electric field as shown in Fig. 7-6(a). The polarization electric field enhances the free holes to be depleted, and thus the device is easily turned off and the threshold voltage would decrease. Similarly, as shown in Fig. 7-6(b), the well-arranged dipoles and the induced polarization electric field

under positive gate bias would enhance the accumulation of free holes. Therefore, the OTFT is easily turned ON while the threshold voltage would increase. Additionally, we stressed the samples with alternative gate bias, e.g., V_G = 25 V for 10 sec and V_G = - 25 V for another 10 sec, then V_G = 25 V for 20 sec, - 25 V for another 20 sec, and so on. The results are shown in the embedded part of Fig. 7-4. The polarization phenomenon is fully reversible and not a degradation process. Accordingly, the hysteresis will not hinder use of the transistors in applications with a time scale of the order of seconds or tens of seconds, such as information recovery from a memory card or in applications with alternating polarity gate bias such as switches in active-matrix liquid-crystal displays [6.28].

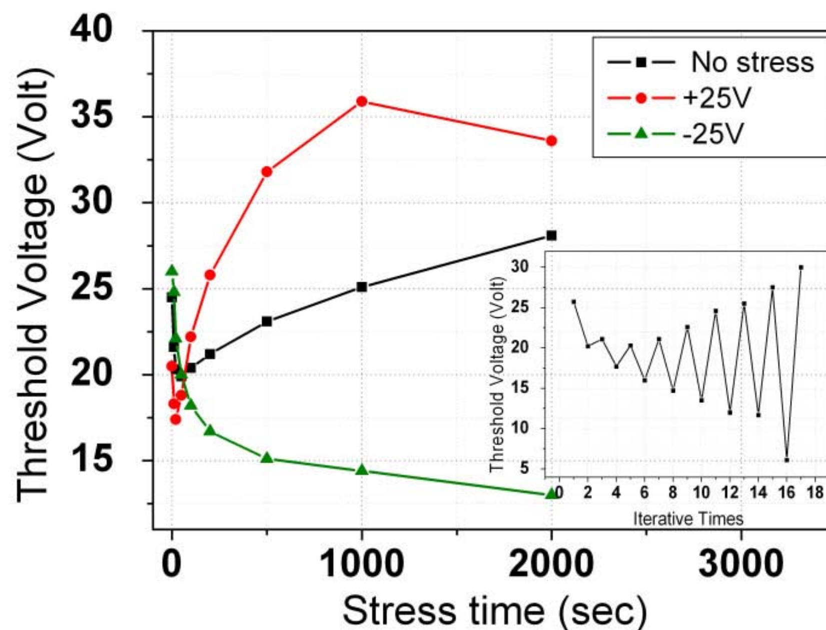


Figure 7-4 Threshold voltage shift of OTFTs with a constant +25 V/-25 V gate bias stresses and an alternative gate bias stress (insert)

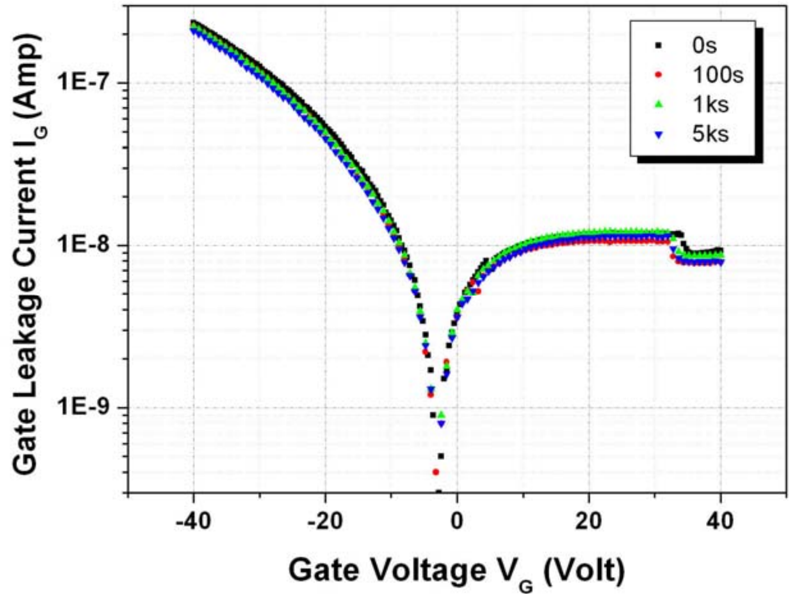


Figure 7-5 $I_G - V_G$ curves after OTFTs being stressed with a constant -10 V gate bias

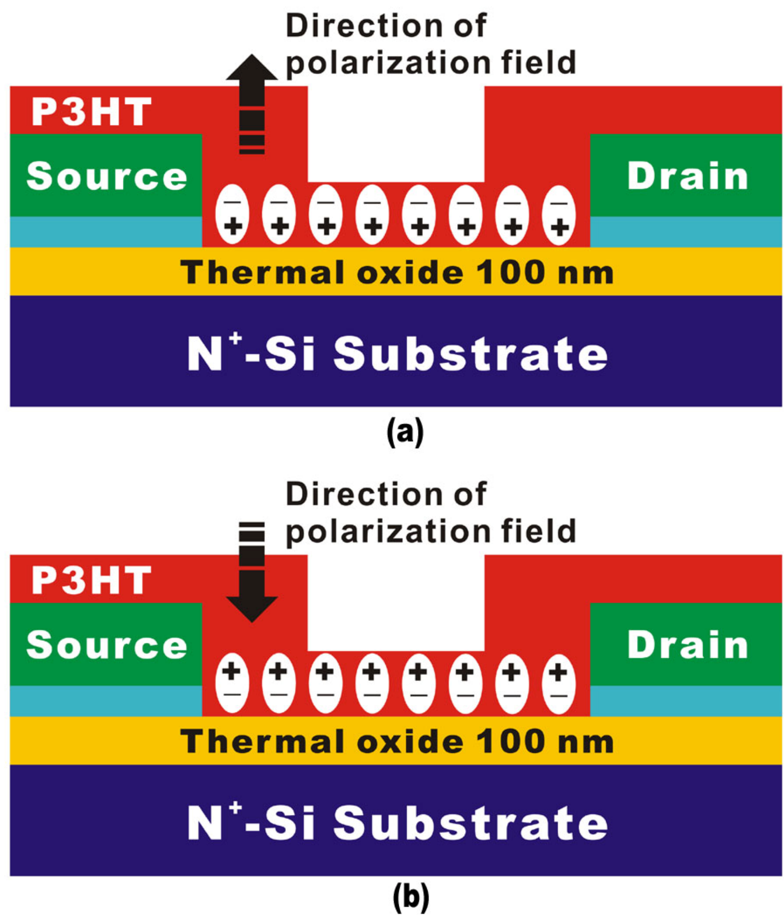
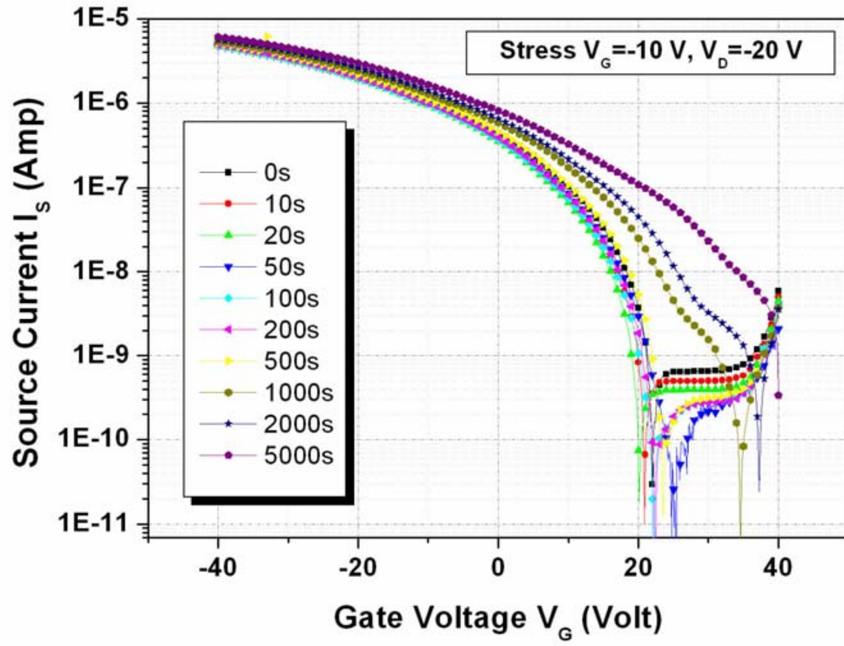


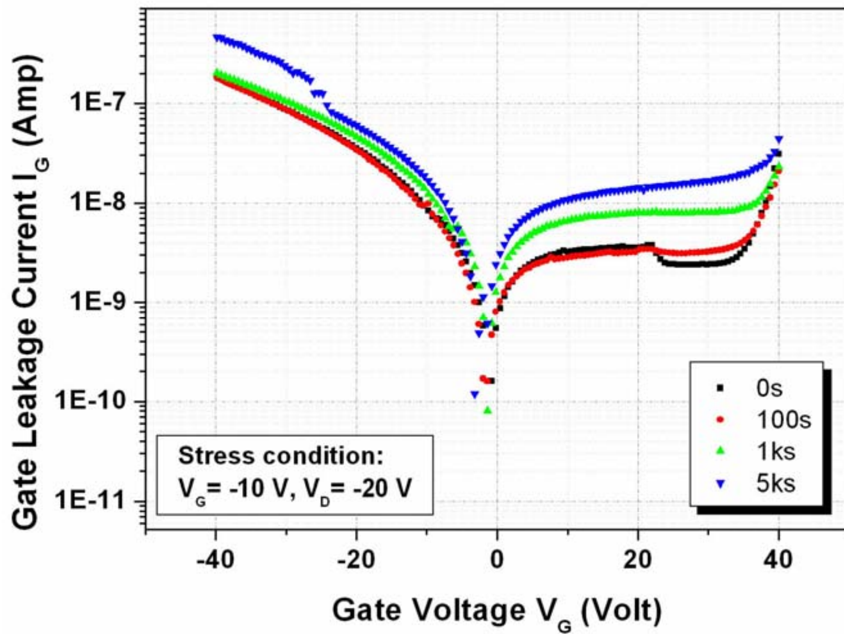
Figure 7-6 Direction of polarization electric field under a constant gate bias stress of (a) -25 V and (b) +25 V

7.2.3 Hot Carrier Stress

Figure 7-7(a) shows the I_S - V_G curves of OTFTs after hot carrier stress, and Fig. 7-7(b) illustrates the gate leakage current versus gate bias with increasing the stress time. From Fig. 7-7(a), we can find a slight decrease for the V_{th} when the stress time shorter than 500 sec and then a significant positive threshold voltage shift for over 20 volts was observed when the stress time larger than 500 sec; meanwhile, the ON current and the OFF state leakage current didn't change. Two mechanisms were responsible for the V_{th} shift. First, the negative gate bias could cause holes to inject into the gate oxide, forming positive trapped charges. These hole traps, however, did not deteriorate the gate oxide quality as shown in Fig. 7-7(b) but reduced the threshold voltage of OTFTs slightly. With increasing the stress time, the strong electric field established between the gate and the drain electrodes twirled the direction of dipoles in the organic active layer as illustrated in Fig. 7-8, contributing to V_{th} gradually shifted to more positive value. Moreover, the oxygen auto-doping during stress measurements further increased the V_{th} value, so that the effect of hole trapping was overwhelmed. The hot carrier degradation usually observed in the Si-based transistors is not significant here in this test, because both the large gate length (10 μm) and the nature of OTFTs with extremely low carrier mobility suppress the number and the associated damages of those hot carriers.



(a)



(b)

Figure 7-7 (a) I_S - V_G curves and (b) I_G - V_G curves of OTFTs after hot carrier stress; V_G = -10 V, V_D = -20 V, V_S = 0 V; W/L = 5000/10 μm

Figure 7-8 Directions of dipoles in the organic active layer when V_G = -10 V, V_D = -20 V and V_S = 0 V

To verify the hypothesis about the changes of dipole moment under specific stress conditions, it is straightforward to apply a reverse electric field for those samples after hot carrier stress and to see whether the direction of dipoles near the drain side could be reversed or not. Consequently, while always keeping source electrodes grounded, we applied a constant gate bias of -10 V and drain bias of -20 V for 10 sec, and then changed the drain bias to 0 V for another 10 sec, next, V_D = -20 V for 20 sec, then V_D = 0 V for another 20 sec, and so forth. In this way, the potential difference between the gate and the drain electrode was kept in 10 volts while the direction of the electric field changed alternatively. The result is shown in Fig. 7-9. As expected, the change of the electric field would cause the dipoles in the active area to vary their direction, and more dipoles reacted to the applied electric field with increasing the stress time, so that the curve of V_{th} versus iterative times oscillated.

Figure 7-10 summarized the variation of threshold voltage and field-effect mobility versus stress time under different bias conditions. In Fig. 7-10(a), we can find that the V_{th} of OTFTs keeps increasing with time (square symbol) when exposing to the atmosphere containing oxygen and moisture. This phenomenon can be suppressed by applying a negative gate bias of -10 V to alter the direction of dipoles as shown in Fig. 7-6(a), and if we further increased the negative gate bias to -25 V (as is the case in Fig. 7-4) or enlarged the drain voltage to +20 V (down-triangle symbol), the V_{th} would start to decrease. On the other hand,

a negative drain bias of -20 V (triangle symbol) would contribute to hole trapping in the gate oxide followed by the torsion of dipole moment, so the V_{th} first decreased slightly and then increased gradually with stress time. Besides, the field-effect mobility did not change with stress time except the case of V_G = -10 V, V_D = 20 V, implying that the OTFTs were quite stable under normal operation conditions. Nevertheless, as a p-type transistor, bias conditions such as V_G = -10 V and V_D = +20 V will not occur in the circuit design. The decrease of μ_{FE} under this stress condition was presumably attributed to the severe hole injection to the gate insulator and the associated trap-state creation near the P3HT/SiO_2 interface under large voltage difference of 30 volts between the gate and the drain electrodes.

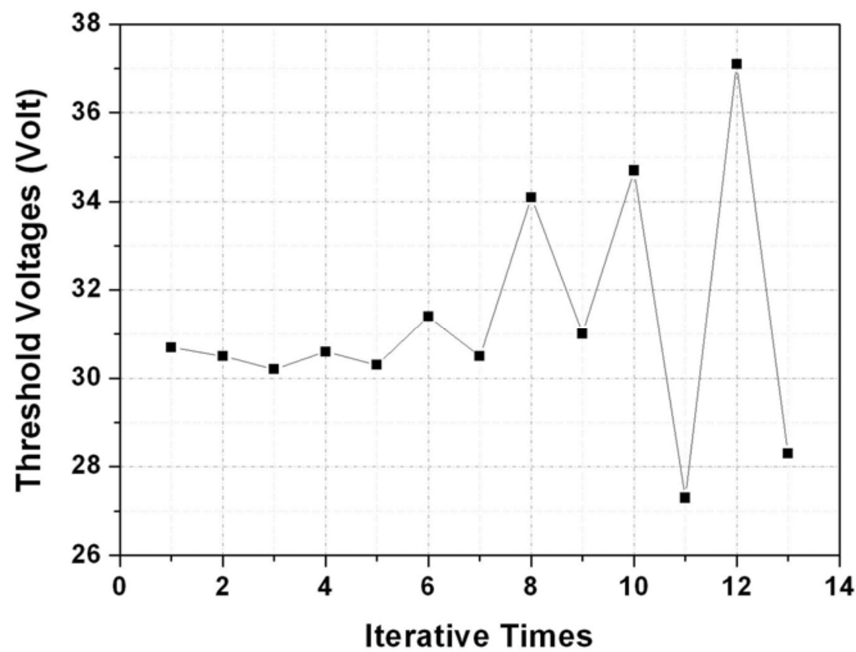
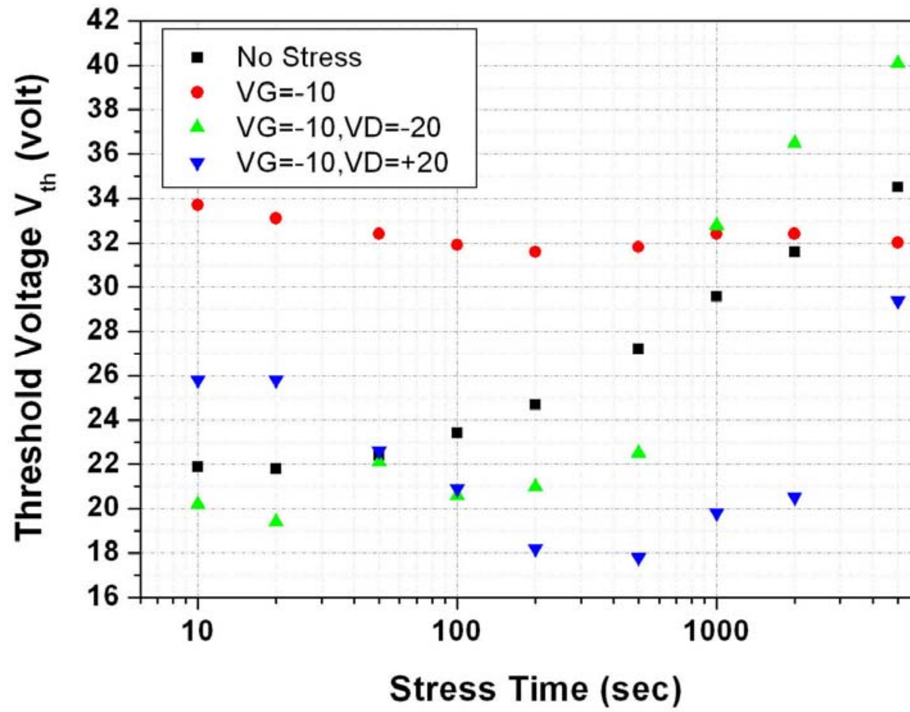
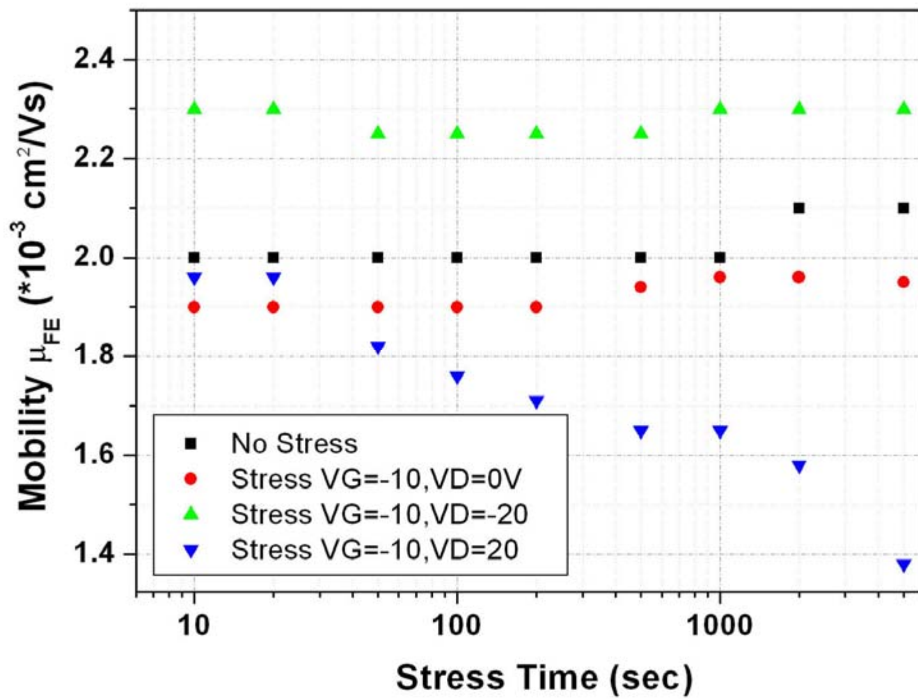


Figure 7-9 Variation of the threshold voltages versus iterative times



(a)



(b)

Figure 7-10 Variation of (a) the threshold and (b) the field-effect mobility versus stress time under different bias conditions

7.3 Summary

In this chapter, the impacts of oxygen and moisture on the electrical characteristics of OTFTs had been explored. It was found that the oxygen atoms act as the p-type dopant in the P3HT active area and caused the V_{th} shift to a more positive value significantly. By storing the samples in a vacuum chamber, the electrical characteristics of OTFTs can be effectively restored. Actually, it is obligated to control the fabrication and the measurement conditions of P3HT-based OTFTs properly; otherwise every electrical property such as ON current, transconductance or threshold voltages could be affected easily by the atmosphere and then the experimental results were misled. Throughout the experiments performed in chapter 6 and chapter 7, the situation of P3HT active layer was controlled carefully by keeping the same quench time from run to run. Besides, the as-fabricated OTFTs were all stored in a high vacuum chamber (10^{-6} torr) for two days to restore the initial properties of P3HT as good as possible. The measurement time of each sample was kept to no longer than 2 hours and the other samples waiting for measurement after being taking out from the high vacuum chamber were temporarily stored in a low vacuum chamber (50 torr).

The electrical reliability of OTFTs was also examined in this chapter. Although no degradation about the I_{ON} or μ_{FE} was observed, the V_{th} of OTFTs shifts obviously with respect to different stress conditions. A polarization effect model was therefore proposed to explain the hysteresis phenomenon under bias stresses.