Chapter 3

Plasma Treatment Effects On OTFTs

3.1 Introduction

Recently, organic materials such as pentacene and poly(3-alkylthiophene) have attracted considerable attention due to their potentials for semiconductor's electronics [3.1],[3.2],[3.3],[3.4]. In particular, the characteristics of P3AT field-effect transistors(FETs) have made such devices feasible for applications requiring mechanical flexibility, large-area coverage, and low overall cost. Poly(3-hexylthiophene) (P3HT) is a well-known polymer as an organic semiconductor and has shown the field-effect mobility as high as $0.1 \text{ cm}^2/\text{V-s}$ in earlier works[1.8]. However, the performance of P3HT FETs was severely changed by the conditions of preparation process and the interface states between P3HT and insulator materials[3.5]. The field-effect mobility is usually determined by scatterings inside of the P3HT film, such as phono scattering, grain boundary scattering, and impurity scattering. In addition, scatterings due to the gate insulator such as interface roughness scattering, and surface state scattering affect the field-effect mobility as well. Therefore, in order to enhance the mobility, it is essential to purify P3HT and grow it with larger grains. Moreover, the grain size and the crystallinity of P3HT film also depend on the surface state of the gate insulator. Various attempts have been made to modify the surface potential energy like the work function or the electron affinity by a self-assembling (SA) molecular monolayer such as hexamethyldisilane (HMDS) or octadecyltrichloro-silane (OTS) on the surface, and also to enhance the crystallinity of pentacene.

However, SA is a wet process and OTFTs are immersed in SA vapor or solution for a long time, such as 24h. Sometimes, the long immersion may take off contact metals, and the solvent or vapor used in SA may attack the plastic substrate which is employed for the flexible display. In our experiments, the gate surface has been treated by the dry process of O₂, N₂O, and NH₃ plasma prior to the deposition of P3HT. The effects of various plasma treatment on the performance of P3HT OTFTs were discussed.

3.2 Experimental Detail

The detailed process flow were shown in Fig 3-1. OTFTs in this experiment are fabricated with a stacked structure described in 2.4.2, except for the surface treatment on SiO₂ prior to the deposition of P3HT film. After IPA and DI water cleaning the surface of SiO₂, the devices were treated with O₂, N₂O, and NH₃ plasma respectively. All plasma treatments were formed under the conditions of gas flow gate of 20 sccm and radio-frequency power 30 W. The plasma treatment time was varied from 1 min to 5 min. After being treated with various plasma and with various exposure time, the devices were then spun onto P3HT film. The detailed spin-coating parameters of P3HT film were also described in chapter 2. The devices were annealed at 120°C for 3 mins and then stored in vacuum for 2 days. The electric characteristics were measured by HP 4156 in atmosphere.

3.3 Results and Discussion

The surface of SiO₂ and P3HT are hydrophilic and hydrophobic respectively. The difference of surface polarity between SiO₂ and P3HT resulted in the poor adhesion. The performance of OTFTs greatly depends on the interface of SiO2/P3HT. In previous work, we found self-assembling monolayers(SAMs) such as HMDS, OTS, and TMS can provided better adhesion due to controlling the chemistry of the interface of SiO2/P3HT. However, some organic contaminant may residue on the surface of SiO₂ and polluted the interface of SiO2/P3HT. Instead of SAMs which can provide better adhesion between SiO2/P3HT, plasma treatment can effectively remove residual organic and inorganic contaminant on the surface of SiO₂. In our experiments of plasma treatment, we considered soft plasma conditions. All plasma treatments on SO₂ in our experiments were based on the conditions of low gas flow rate and low radio-frequency power. Under soft plasma treatments, roughness of SiO₂ did not change obviously and interface roughness scattering would not affect the performance of OTFTs.

Fig 3-2, 3-6, and 3-10 show the output characteristics I_S -V_G of OTFTs with O₂, N₂O, and NH₃ plasma treatment prior to the deposition of P3HT respectively. The electrical characteristics of OTFTs with plasma treatment show irregular variation due to plasma treatment on SiO₂. Carriers transport in benzene faster than those transport between benzene. This is because carriers suffer from more repulsive force due to interface charges, surface roughness, and residual contaminants on SiO₂ when carriers transport between benzene. On the contrary, carriers remain higher transport velocities due to the π - π bonds in benzene. Under soft plasma treatments, roughness did not change obviously and residual contaminants were removed. Furthermore, the interface charges decreased and the electrical characteristics improved. However, the atoms from plasma on SiO₂ affected the crystallinity and resulted in irregular variation of electrical characteristics.

Fig 3-3, 3-7, and 3-11 show the variation of field-effect mobility with respect to O_2 , N_2O , and NH_3 plasma exposure time respectively. With various plasma treatment and exposure time, the performance of OTFTs improved remarkably. The interface charges on SiO₂ decreased after plasma treatment. Compared with N_2O plasma and NH_3 plasma, O_2 plasma decreased interface charges most effectively and devices showed highest mobility up to 0.044 (cm²/V-s) with O_2 plasma treatment for 1 min.

Fig 3-3, 3-7, and 3-11 show the variation of threshold voltage with respect to O_2 , N_2O , and NH_3 plasma exposure time respectively. The threshold voltage is closely related to the oxide charge. Generally, the threshold voltage is shifted to the positive bias direction with the increase of exposure time, which implies that negative charges are induced in the oxide or that residual positive positive charges in the oxide decrease with exposure time. Devices showed largest threshold voltage up to 62.8 V with N₂O plasma treatment for 3 min.

Fig 3-4, 3-8, and 3-12 show the the output characteristics I_S-V_D of OTFTs with O_2 , N_2O , and NH_3 plasma treatment prior to the deposition of P3HT respectively. In our experiment, we got optimum condition for OTFTs with plasma treatments. Devices with O_2 plasma treatment for 5 min show the largest on current. Variations of mobilities and threshold voltages with various plasma treatment and exposure time are shown in Table 3-1, 3-2, and 3-3.

3.4 Summary

The performance of OTFTs is closely related to the surface states of the gate insulator. In our experiment, the effects of various plasma treatment prior to the deposition of P3HT have been investigated. The plasma treatments cause irregular variation in field-effect mobility and threshold voltage. Plasma treatments can remove residual contaminants and decrease interface charges while HMDS can change the chemistry and enhance the adhesion of P3HT on SiO₂. Compared with HMDS treatment, plasma treatments improve the OTFTs performance more effectively. We also got the optimum condition for OTFTs with O₂ plasma treatment for 5 min.



Figure 3-1 Process flow of OTFTs with plasma treatment on SiO₂ prior to the deposition of P3HT. (continue)



Figure 3-1 Process flow of OTFTs with plasma treatment on SiO₂ prior to the deposition of P3HT.



Figure 3-2 The output characteristics I_S - V_G of OTFTs with O_2 plasma treatment prior to the deposition of P3HT.



Figure 3-3 Variation of field-effect mobility with respect to O₂ plasma exposure time.



Figure 3-4 Variation of threshold voltage with respect to O₂ plasma exposure time.



Figure 3-5 The output characteristics I_S-V_D of OTFTs with O₂ plasma treatment prior to the deposition of P3HT.



Figure 3-6 The output characteristics I_S - V_G of OTFTs with N_2O plasma treatment prior to the deposition of P3HT



Figure 3-7 Variation of field-effect mobility with respect to N₂O plasma exposure time.



Figure 3-8 Variation of threshold voltage with respect to N_2O plasma exposure time.



Figure 3-9 The output characteristics I_S-V_D of OTFTs with N_2O plasma treatment prior to the deposition of P3HT



Figure 3-10 The output characteristics I_S-V_G of OTFTs with NH_3 plasma treatment prior to the deposition of P3HT



Figure 3-11 Variation of field-effect mobility with respect to NH₃ plasma exposure time



Figure 3-12 Variation of threshold voltage with respect to NH₃ plasma exposure time



Figure 3-13 The output characteristics I_S - V_D of OTFTs with NH₃ plasma treatment prior to the deposition of P3HT

Time	HMDS	1 min	2 min	3 min	4 min	5 min
Mobility (cm ² /V-s)	0.0015	0.044	0.016	0.042	0.024	0.042
V _{TH} (V)	25	57.6	55.9	51.7	60	57

Table 3-1Summary of field-effect mobility and threshold voltage with respect to O2plasma exposure time.



Time	HMDS	1 min	2 min	3 min	4 min	5 min
Mobility (cm ² /V-s)	0.0015	0.0064	0.0011	0.0012	0.02	0.008
V _{TH} (V)	25	64.5	49.6	62.8	48.3	63.7

Table 3-2Summary of field-effect mobility and threshold voltage with respect to
N2O plasma exposure time.

Time	HMDS	1 min	2 min	3 min	4 min	5 min
Mobility (cm ² /V-s)	0.0015	0.005	0.0041	0.0016	0.006	0.0015
V _{TH} (V)	25	42.7	48.2	46.8	53.6	54.1

Table 3-3Summary of field-effect mobility and threshold voltage with respect to
NH3 plasma exposure time.

