

Chapter 4

Study on the organic thin film transistors based on Poly (3-hexylthiophenes) (P3HT)

4.1 Introduction

Poly (3-hexylthiophenes) (P3HT) are preferred materials because they have high hole mobilities and can be solution processed. The normally p-type films enable transistors to operate in accumulation mode, typically with ohmic contacts. It has been demonstrated that, as the concentration of acceptors is increased, the electrical conductivity also increase because of additional holes, but also enhanced carrier mobility [1] [2]. TFT performance depends largely on the semiconductor/ dielectric interface [3~7]. To improve mobility, the molecules must be close together and orderly. However, individual molecules are held together by relatively weak van der Waals forces. The molecular vibrations and steric hinderance tend to push them apart. In addition, the electronic properties of the material are primarily determined by the molecular properties like the length of conjugated band, bandgap, purity and ionic content... etc. In previous study, the transistor action takes place only within the first 5 nm from the surface of gate dielectric layer. Therefore, the degree of molecular order in that region is very important for the electrical properties of devices. In this study, the thermal SiO₂ used as the dielectric because of its well-characterized properties (dielectric constant, breakdown voltage, and surface roughness) and ease of chemical modification. Derivatizing the dielectric surface with self-assembled monolayers (SAMs)

prior to the deposition of the organic semiconductor leads to the highest reported carrier mobility in the unoriented phase.

Two different structures organic thin film transistors were fabricated: Top contact and bottom contact structure. In this study, the effects of various surface treatments of gate insulator on the performance of poly (3-hexylthiophene) thin film transistors were investigated. The use of the self-assembly materials (hexamethyldisilazane, octadecyltrichlorosilane, and chlorotrimethylsilane) for chemically modifying the surface of silicon dioxide gate insulator prior to the deposition of the organic semiconductor is effective to enhance the field effect mobility.

4.2 Experiment

First, we use the self-assembly materials {hexamethyldisilazane (HMDS), octadecyltrichlorosilane (OTS), and chlorotrimethylsilane (TMS)} to modify the surface of silicon dioxide. Then, the highly region-regular poly (3-hexylthiophene) (P3HT) film was spin-coating or drop-casting on the treated dielectric surface. Two different kinds of the organic thin film transistors structures were fabricated: Top contact and bottom contact structure.

4.2.1 The fabrication of the bottom contact OTFT:

(1) 200nm thermal oxide is first grown on the Si wafer. In order to define the source/drain metal pad, we use the positive photoresist to define the pattern.

(2) Using the HF solution to remove the backside native oxide.

(3) The source/drain metal and the backside metal are thermal evaporated chromium (10nm) and gold (90nm) step by step.

(4) The sample is then immersed in the acetone solution. By using the ultrasonic shock, the photoresist will be removed and the source/drain metal will appear. This process is called the lift-off process.

(5) Successively washed the surface with DI-water and acetone. Then, the oxygen plasma is used to remove the organic matter on the surface.

(6) The sample is dealt with various surface treatments. The substrate was immersed in different organic solutions.

(a)HMDS immersing: the substrate was immersed in the HMDS solution at 120°C for one hour.

(b)OTS immersing: the substrate was immersed in the 2% OTS solution in anhydrous isopropanol at 50°C for one hour.

(c)TMS immersing: the substrate was immersed in the 2% TMS solution in anhydrous isopropanol at 50°C for one hour.

(7)After the treatment of the surface, the P3HT organic semiconductor is coated on the surface by using spin-coating and drop-casting from a 0.2 wt% solution in chloroform. The sample is annealing at 100°C for one hour and quench to the room temperature. The structure of the bottom contact device is shown in Fig. 4-1.

4.2.2 The fabrication of the Top contact OTFT:

(1) 200nm thermal oxide is first grown on the Si wafer. The HF solution is used to remove the backside native oxide.

(2)We use the DI-water, IPA and acetone to clean the wafer step by step. After that we bake the sample at 150°C for 10 min.

(3) The backside metal is thermal evaporated chromium (10nm) and gold (90nm) step by step. After that we use the DI-water, acetone and oxygen

plasma to remove the organic matter on the surface.

(4) The sample is dealt with various surface treatments. The substrate was immersed in different organic solutions.

(a) HMDS immersing: the substrate was immersed in the HMDS solution at 120°C for one hour.

(b) OTS immersing: the substrate was immersed in the 2% OTS solution in anhydrous isopropanol at 50°C for one hour.

(c) TMS immersing: the substrate was immersed in the 2% TMS solution in anhydrous isopropanol at 50°C for one hour.

(5) After the treatment of the surface, the P3HT organic semiconductor is coated on the surface by using spin-coating and drop-casting from a 0.2 wt% solution in chloroform. The sample is annealing at 100°C for one hour and quench to the room temperature.

(6) Source and drain gold contact metals are thermally evaporated through a shadow mask. The structure of the top contact device is shown in Fig. 4-1.

4.3 Measurement

The current–voltage characteristic measurement of organic thin film transistor devices is performed by HP 4156 semiconductor parameter analyzer with source grounded and body floating. The channel width and channel length of the bottom contact are 50 μm and 10 μm respectively. The channel width and channel length of top contact are 600 μm and 100 μm respectively.

4.4 Results and Discussion

4.4.1 Surface treatment of the dielectrical layer

The surface of oxide and P3HT is hydrophilic and hydrophobic, respectively. The difference of surface polarity between oxide and P3HT will result in poor adhesion. TFT performance depends largely on the semiconductor/dielectric interface. The purpose of this work is to show that improved characteristics of P3HT based TFT are obtained by controlling the chemistry of the dielectric/polymer interface. Transistor action takes place only within the first 5 nm or so from the gate dielectric, so only molecules in that region must be orderly. The effects of various surface treatments of gate insulator on the performance of poly (3-hexylthiophene) thin film transistors were investigated. The treatments of the interface include:

(1)The cleaning: to remove the organic and inorganic contaminants.

(2)The cleaning and oxygen plasma treatments: to remove the organic and inorganic containments and to decrease the roughness at the interface.

(3)The use of the cleaning, oxygen plasma treatment and the self-assembly materials modify the surface of silicon dioxide.

The 0.2 wt% P3HT solution is coated after various surface treatment methods. After that, we use the optical microscope to observe the shape and uniformity of the P3HT film.

Fig.4-2 is the photograph of the P3HT film which is coated by the spin coating after the surface of dielectric layer by cleaning, oxygen plasma treatment or without any cleaning process. Fig. 4-2 shows that the P3HT film is uniform without any surface treatment but the P3HT film is very none uniform after the cleaning or oxygen plasma treatment. These results consist with the water contact angle measurement. (Table 4-1) The surface without any treatment contains various containments, organic containments especially.

Therefore, the surface of oxide becomes hydrophobic, the hydrophobic P3HT is easy to adhesive. On the contrary, the surface of oxide will become more hydrophyllic after the cleaning or oxygen plasma treatment, so the P3HT solution will be swung away from the surface of oxide during spin-coating process. Therefore, we must modify the surface of oxide to make the P3HT film become more uniform.

Fig.4-3 is the photograph of the P3HT film which is coated by the spin coating and drop casting after the cleaning, oxygen plasma treatment and modification the surface of oxide by the self assembly materials (HMDS, OTS and TMS). Fig. 4-3 shows that the P3HT film is uniform regardless of using HMDS, OTS or TMS.

4.4.2 The performance of the bottom contact device

Fig. 4-4~6 are the transfer characteristic and output characteristic of the P3HT FET under different surface treatment. Table 4-2 lists the electric characteristic of the different device. From the result, we observe that the devices without any FET characteristic regardless of the cleaning or the oxygen plasma treatment. These results are comparison with Fig 4-2 and Table 4-1. Because the surface of oxide becomes more hydrophyllic , the P3HT cannot be coated uniformly on the surface of oxide. It may result that the carriers cannot transport at the interface.

Fig. 4-7~10 is the transfer characteristic and output characteristic of the P3HT FET by various surface treatment methods and different coating methods. Table 4-3 lists the electric characteristic of the different device. Fig. 4-3 shows that the P3HT film is coated uniformly on the surface of oxide with various surface treatment methods. The hole mobility of P3HT devices

after HMDS, OTS and TMS surface treatment is about 4×10^{-3} , 3×10^{-3} and $2 \times 10^{-3} \text{ cm}^2/\text{V.s}$, respectively. It is obvious that using surface treatment agent (HMDS, OTS and TMS) not only makes the P3HT film become uniform but also improves the carrier transportation. If the P3HT film was coated by drop casting, the hole mobility will increase one order to reach about $10^{-2} \text{ cm}^2/\text{V.s}$. It may result from the volatility of solvent. In this study, chloroform was used as solvent. Chloroform has low boiling temperature and high volatility. There is not enough time for the P3HT molecule to arrange orderly, when the P3HT is coated by spin coating. On the contrary, the P3HT molecule has enough time to arrange orderly, when the P3HT is coated by drop casting. Although we observe that the P3HT is more uniform by spin coating under the optical microscopy, the behavior of the carrier transportation is mainly at the P3HT and oxide interface not at the P3HT air-side surface. Moreover, the hole transportation is the microcosmic behavior between molecule and molecule. The behavior can't be observed by using optical microscopy. Comparison with the HMDS, OTS and TMS, the performance of the device is not different from each other.

4.4.3 The performance of the top contact device

Fig. 4-11~13 is the transfer characteristic and output characteristic of the P3HT FET by various surface treatment methods and different coating methods. Table 4-4 lists the electric characteristic of the devices. If the P3HT film was coated by drop casting, the hole mobility will reach $2 \sim 3 \times 10^{-2} \text{ cm}^2/\text{V.s}$. Comparison with the HMDS and OTS, the performance of the device is not

different from each other.

4.5 Conclusion

It is effective to enhance the field effect mobility of P3HT devices by using the self-assembly materials (hexamethyldisilazane, octadecyltrichlorosilane, and chlorotrimethylsilane) to modifying the surface of silicon dioxide gate insulator prior to the deposition of the organic semiconductor. The self-assembly materials can make the surface of oxide more hydrophobic, and then improve the adhesion between P3HT film and oxide layer. By using the surface treatment, the OTFT will have the output characteristic and transfer characteristic, and the hole mobility can reach about $10^{-2} \text{ cm}^2/\text{V.s}$.

