

Fabrication and characterization of organic thin-film transistors based on Peri-xanthenoxanthene (PXX) derivative

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ABSTRACT

Over the past decade, OTFTs (Organic Thin-Film Transistors) act as a key component of the radio frequency identification (RFID) tags, biological sensors and flexible display have a broad application prospects because of the advantages of low cost, large area and flexible substrate^[1]. Material design and device engineering are both important approaches to generate performance enhancement. In this study, we demonstrate high-performance OTFTs with mobility of $0.15\text{cm}^2\text{V}^{-1}\text{S}^{-1}$ using a novel semiconductor based on Peri-xanthenoxanthene^[2] derivative, we also aim to reduce threshold voltage through the modification of insulator layer and using different structure of device. The result shows that the modification of insulator layer using a thin film of polymer is one useful strategy for reduce threshold voltage of device.

Keywords: OTFTs, charge mobility, threshold voltage, insulator, flexible electronics.

1 INTRODUCTION

It is known that organic semiconductor materials such as benzene and thiophene derivatives are susceptible to oxygen and light. Devices made from these materials in air can degrade rapidly, which considerably limits their applications^[3]. Therefore, researchers in organic electronics field have been focusing on improvements both charge transfer characteristics and ambient stability of organic electronic devices^[4, 5].

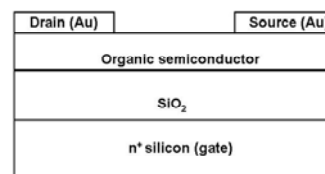
There are mainly two factors which influence the charge transfer characteristics in an organic thin film transistor (OTFT), the intrinsic charge transfer capacity of the semiconductor material^[6] and the interface property of different function layers in a device^[7, 8]. The intrinsic charge transfer capacity of the semiconductor material determines the maximum charge mobility of OTFT. An optimized device mobility, measured by the time of flight (TOF) method, is considered infinitely closed to the mobility of semiconductor material. The interface property, such as the contact between the electrode and the active layer, can have

great impact on the device performance. Researches have shown that modification of electrode work function is an effective approach to improve carrier injection and device performance; The roughness of dielectric layer can affect the threshold voltage of OTFT; Smooth surface and low defect density can facilitate charge transport and reduce operating voltage.

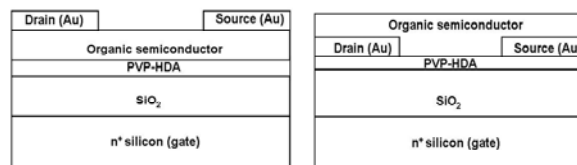
In this work, OTFTs based on 3,9-Bis-(4-hexyloxy-phenyl)-Peri-xanthenoxanthene as semiconductor material is presented. The material was synthesized from PXX and is a PXX derivative (Ph-PXX). For fabrication of OTFT, the Ph-PXX was deposited both by vacuum evaporation and by drop-casting in solution. Aging experiment proved that the device has a good environmental stability. The threshold voltage significantly reduces from 12.3V to 1.4V through modification of SiO₂ insulator layer with a 20nm thickness of PVP-HAD film.

2 EXPERIMENT

Figure 1 shows the cross-section structure of the three OTFT devices.



(a) bottom gate top contact without polymer modified layer



(b) bottom gate top contact (BGTC) and (c) bottom gate bottom contact (BGBC) with polymer modified layer

Figure 1: Schematics of OTFT layer structures

Heavily doped n-type Si wafers were used as substrates and served also as gate contacts. The wafer was coated with a thermal SiO₂ layer (300 nm in thickness). The substrates were cleaned through ultrasonic bath in acetone, isopropanol and deionized water, respectively, then placed in oven at 100°C for 1h to remove the residual solvent. For polymer modification, standard solutions of poly-4-vinylphenol (PVP, MW=25000) were prepared with a cross-linking agent (CL) at ratio of 10:1 (PVP:CL) by weight in propylene glycol monomethyl ether acetate (PGMEA). Cross-linked polymer films were formed through the esterification of (4-vinylphenol) (PVP) with 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (HDA) at 200°C for 1 hour. The solutions were filtered through a 0.2µm syringe filter and spin-coated onto the substrates. Prior to spin-coating, the substrates were cleaned in an oxygen plasma for 5 min. Film thicknesses were measured using ellipsometry. The Infrared spectroscopic measurements were performed to confirm the formation of polymer films.

For vacuum deposited OTFT, Ph-PXX was deposited by thermal evaporation in a high-vacuum chamber at a rate of about 1Å/s ($p < 1 \times 10^{-5}$ Pa). The film thickness was 50nm. The substrate temperature was kept at room temperature. The structure and morphology of the films were characterized by X-ray diffraction (XRD) and AFM in tapping mode. Gold electrodes were deposited through a metallic shadow mask by thermal evaporation under high vacuum ($p < 1 \times 10^{-6}$ Pa) and have a thickness of 80nm. The gate channel has a length of 75 µm and a width of 3mm. For solution deposited OTFT, 0.5wt % solution of Ph-PXX in dichlorobenzene was applied by drop-casting and followed by oven bake at ~80°C for ~30 min to remove residual solvent. The electrodes were fabricated by standard photolithography to define gate channel of 20 µm in length and aspect ratio of W/L=45.

Electrical characterization of OTFTs was performed with a Keithley 4200SCS semiconductor parameter analyzer connected to a probe station setup. Capacitance measurements were carried out using a sandwich electrode configuration with a capacitance-voltage model for frequencies ranging between 1KHz and 100 kHz.

3 RESULTS AND DISCUSSION

The polymer modified substrate was characterized by IR spectrometry. The spectra in Fig.2 shows that there is a significant change at peaks of 1770-1870cm⁻¹ corresponding to the *c = o* stretch in HDA. The peaks of after cross linking in IR spectra are weaker and less sharp compare with the as spin coating sample. This phenomenon confirmed that the esterification reaction occurred between PVP and HDA after heated at 200°C for 1hour. It is also noteworthy that the *o - H* stretch in PVP does not appear in IR spectra because the peaks lager than 3000cm⁻¹ were absorbed by the substrate.

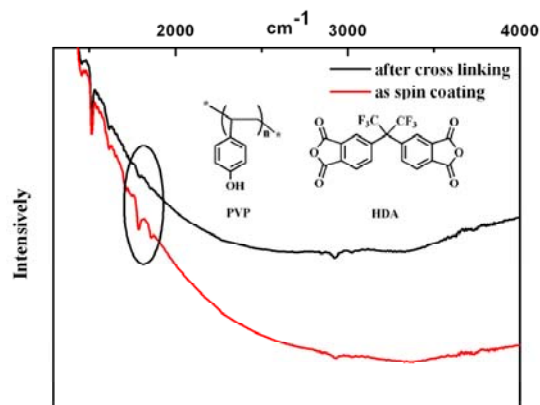


Figure 2: IR spectra for substrate with a thin film of PVP-HAD

In order to study the film structure, Ph-PXX thin film was examined by X-ray diffraction (XRD), which showed two peaks assignable to (001) and (003) diffractions, meaning that the film has a highly ordered structure (Figure 3). On the basis of the diffraction pattern, the monolayer thickness (d-spacing) was determined to be 30.86 Å. AFM image showed that the Ph-PXX formed continuous thin film with good quality by thermal evaporation and the growth direction tends to be in two-dimensional plane. From this result as well as the XRD spectrum, it can be concluded that the molecules of Ph-PXX in the film are nearly perpendicular to the substrate and have a tight π - overlapping structure, allowing for the effective contribution of aromatic atoms to charge migration.

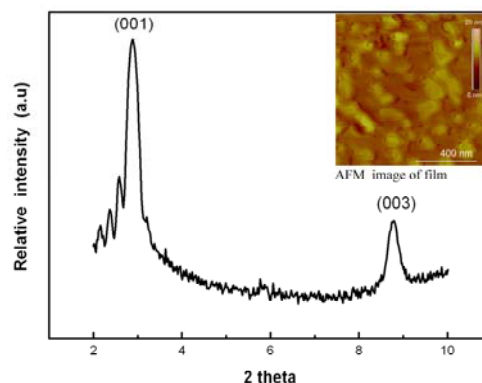


Figure 3: X-ray diffraction of Ph-PXX film and (Insert) The AFM image of film morphology

Figure 4 shows the typical characteristics of p-channel OTFT. The ohmic characteristic in the linear region of the output characteristics (Fig.4 B/D) ensures efficient carrier injection with low contact resistance between metal electrodes and the Ph-PXX film. However, the contact resistance of OTFT fabricated by drop-casting was two orders of magnitude greater than that of vacuum deposited OTFT. This was probably due to the fact that vacuum deposited layer formed a conformal contact between

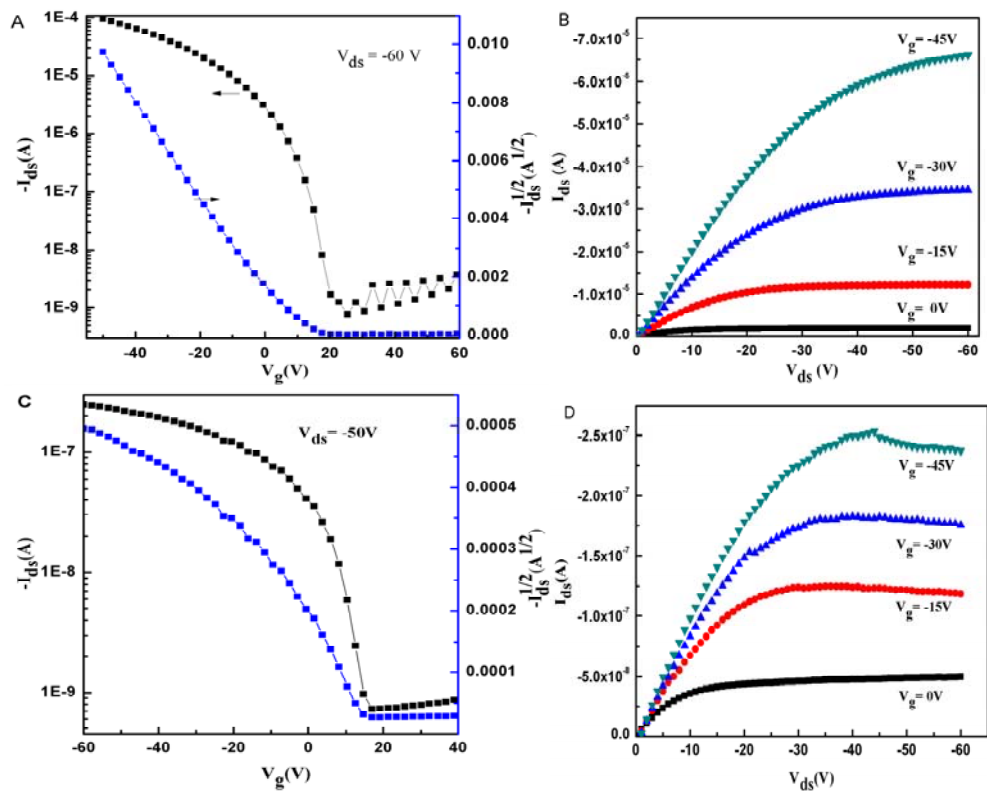


Figure 4: (A)/ (B), (C)/(D) Transfer and output characteristics of the Ph-PXX OTFTs fabricated by vacuum evaporation and drop-casting process

source/drain electrodes and underlying organic semiconductor layer for top-contact structure. The calculated effective field-effect mobility (μ_{sat}) in the saturation regime and extracted threshold voltage (V_T) are $0.15\text{cm}^2\text{V}^{-1}\text{S}^{-1}$ and 12.3V for vacuum deposited OTFT and $2.0 \times 10^{-4}\text{cm}^2\text{V}^{-1}\text{S}^{-1}$ and 17.3V for drop-cast OTFT, respectively (Fig.4 A/C).

Surface properties of a dielectric layer, i.e., surface energy and surface roughness, were also the key factors that determine the electric characteristics of OTFTs. Modification of surface with 20nm PVP-HAD polymer film was carried out and the resulted OTFT structures are shown in Fig.1 (b)/(c). The electrical characteristics of modified OTFTs are shown in Figure 5. The threshold voltage was reduced to 1.4V for BGBC structure and 6.5V for BGTC structure, though the mobility for BGBC structure decreased to $0.03\text{cm}^2\text{V}^{-1}\text{S}^{-1}$. Meanwhile, the current I_{ds} of BGTC structure is higher than that of BGBC structure, confirming the advantage of BGTC structure^[9].

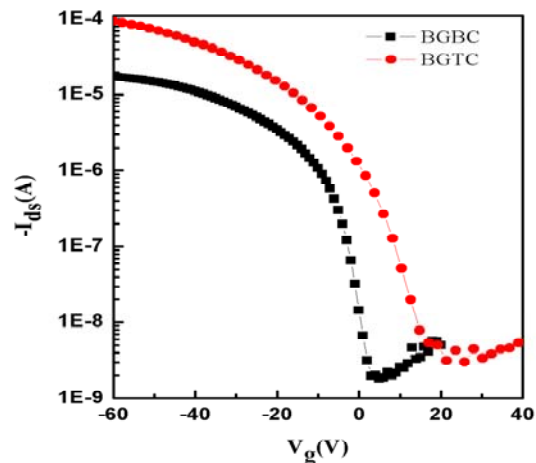
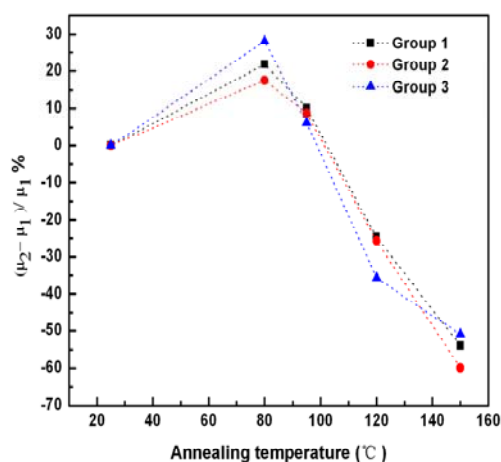


Figure 5: Transfer characteristics of devices with structure of Fig 1 b, c



μ_1/μ_2 refer to the mobility of devices of as-deposition and after annealing at different annealing temperature

Figure 6: Trend in mobility by annealing in air condition

The environmental stability of the device was demonstrated by aging test. Twelve devices fabricated by vacuum evaporation was divided into three groups and annealed in air at different temperatures for 1 hour. Figure 6 shows the correlation between change in charge mobility and the annealing temperature. The results show that the charge mobility dropped to 50% even after annealing in the air at 150°C for 1 hour, indicating that the OTFTs based on Ph-PXX have a good stability when exposed to light, oxygen and thermal environment. Previous reports have shown that the pentacene OTFT exhibited more sensitive to oxygen and water under the similar experimental conditions^[10-12]. We concluded that the OTFTs based on Ph-PXX have the better stability comparing to the pentacene or other benzene derivatives when exposed to light and oxygen.

4 CONCLUSION

OTFTs fabricated from a new organic semiconductor material are presented. The material is a derivative of Perixanthoxanthene (Ph-Pxx). The devices were fabricated both by vacuum deposition and solution processing of Ph-Pxx. Electrical characterization of OTFTs have demonstrated high charge mobility. A new surface modification method has been proposed. The threshold voltage of device with insulator layer of SiO₂ can be effectively reduced by modified with PVP-HDA polymer film. Aging test also indicates that the Ph-Pxx material is highly stable in ambient environment.

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