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Letter

High performance organic thin film transistors using chemically modified bottom contacts and dielectric surfaces

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ABSTRACT

A compatible process of orthogonal self-assembled monolayers (SAMs) is applied to intentionally modify the bottom contacts and gate dielectric surfaces of organic thin film transistors (OTFTs). This efficient interface modification is first achieved by 4-fluorothiophenol (4-FTP) SAM to chemically treat the silver source–drain (S/D) contacts while the silicon oxide (SiO_2) dielectric interface is further primed by either hexamethyldisilazane (HMDS) or octyltrichlorosilane (OTS-C8). Results show that the field effect mobilities of the bottom-gate bottom-contact PTDPPTFT4 transistors were significantly improved to 0.91 $cm^2\ V^{-1}\ s^{-1}$.

1. Introduction

Organic thin-film transistors (OTFTs) have great potential to be used in thin, lightweight, flexible and unbreakable printed electronics. OTFTs are particularly promising for use in flexible display devices [1], such as electronic papers [2–4], and organic light-emitting diodes (OLED) [5]. Bottom-contact OTFTs are technologically important because the channel length defined by the source-drain (S/D) of bottom contacts (BC) can be scaled by photolithography or by a variety of contact printing techniques. This advantage makes the BC transistor a priority candidate for large-scale manufacturing. However, BC OTFTs typically show lower performance due to substantial contact resistance compared to the corresponding top-contact OTFTs [6–8].

In order to improve the performance of bottom contact OTFTs, self-assembled monolayers (SAMs) are widely used to modify the bottom contacts and dielectric interfaces, where functionalized interfaces facilitate better charge injection and transport [9–11]. For instance, the thiol (R–SH) and dithiol (HS–R–SH) SAMs are effective for modification of gold surface [12,13]. Generally the SAM treatment of metal contacts allows tuning of the work function so as to match the energy level of the highest occupied molecular orbital (HOMO) of the organic semiconductor (OSC), leading to better ohmic contacts [14–17]. Moreover, lowering the surface energy of the metal surface is energetically favorable for the alignment of the OSC over the surface of bottom contacts [18–23]. The SAM treatment of dielectrics helps passivate trap sites at the dielectric surface [24–26] and enhances the molecular packing of the organic semiconductor along the interface, due to favorable surface assembly [27–31].

Modification of bottom contacts and dielectric interfaces can be achieved in different manners. The first

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approach is to simultaneously modify both bottom-contact Ag electrodes and oxide dielectric surfaces using a single SAM. For example, Acton et al. [32] recently introduce a single n-alkyl phosphonic acid SAM to simultaneously modify both bottom-contact Ag electrodes and hafnium oxide (HfO_2) dielectric surfaces so as to achieve desirable properties. However, it is difficult to find out the appropriate SAM material to simultaneously modify the metal and dielectric interfaces. The second approach is to modify the bottom contacts and dielectric interfaces separately using two different SAMs [15,16,22]. The problem of this method is chemical compatibility of double SAMs treatment. As yet, literature discussing the compatibility of double SAMs treatment on bottom contacts and dielectrics is limited.

In this paper, the compatibility of orthogonal self-assembly to treat bottom contacts and dielectrics independently is evaluated based on a high performance organic semiconductor (PTDPPTFT4) that possesses mobilities >2 $cm^2\ V^{-1}\ s^{-1}$ for its corresponding top-contact structure [33]. Orthogonal self-assembly means the first SAM reacts with the bottom contacts while the second SAM interacts only with the dielectric surface. In our bottom contact OTFT studies, Ag was treated with 4-fluorothiophenol (4-FTP) [34] while the silicon dioxide (SiO_2) gate insulator was primed with hexamethyldisilazane (HMDS) or octyltrichlorosilane (OTS-C8) (Fig. 1). Influence of surface modification is studied and the devices are labeled as shown in Table 1.

2. Experimental

OTFT devices were fabricated using a bottom-contact geometry where Ag is used to form S/D contacts. Heavily doped Si ⟨100⟩ wafers were used as gate electrodes where a 200 nm thermally grown silicon dioxide layer acts as the gate dielectric layer. The substrates were cleaned by sonication in semiconductor grade acetone and isopropanol, and then given a 2 min O_2 plasma treatment at 20 W under an operating pressure of 0.1 Torr. Silver was thermally evaporated to form the S/D contacts through a metal shadow mask which defines the transistor physical dimension (L = 50–150 μm, W = 1000 μm). 4-FTP SAM treatment was used to modify the pre-patterned Ag bottom electrodes through immersing samples into a 1 mM ethanolic solution of 4-fluorothiophenol (4-FTP from TCI) for 1 h. The 4-FTP-treated Ag electrodes were then removed from 4-FTP solution and rinsed extensively with anhydrous ethanol and blown dry with N_2. The gate oxide is intentionally modified by either HMDS or OTS-C8. In the case of HMDS modification, HMDS is spin-coated at a rate of 3000 rpm for 60 s and baked at 120 °C for 120 s. For the OTS-C8 modification, samples were dipped into a p-xylene diluted OTS-C8 solution (1.3 vol%) at room temperature for 60 min, followed by an isopropanol rinse.

A 5 mg/mL solution of PTDPPTFT4 in a p-xylene was prepared by stirring at 120 °C for 20 min. Polymer films were then deposited by spin-coating with the sequence of: 0 RPM for 10 s, 500 RPM for 5 s, 1000 RPM for 60 s. The samples were annealed in a nitrogen environment at 190 °C for 60 min and then cooled to room temperature. Electrical characteristics of all transistors were measured by Keithley 4200 SCS in air. All film thicknesses were measured by a KLA-Tencor XP-200 step profiler.

3. Results and discussion

Fig. 2(a) shows the mobilities of bottom-contact transistors of device A (4-FTP treated Ag S/D) and a control device (Ag S/D only) under different channel lengths from L = 50–150 μm. The control device shows a linear reduction in mobility from 0.22 to 0.12 $cm^2\ V^{-1}\ s^{-1}$ upon decreasing the channel length while the one with 4-FTP treated Ag S/D contacts (device A) exhibits a constant mobility against the channel length. The corresponding output characteristics under a gate bias from 0 to −30 V are shown in Fig. 2(b) and (c). In the control device, its initial IV characteristics (Fig. 2(b)) behaves superlinearly, which suggests that the OSC/Ag interface is non-ohmic. The enhancement in mobility due to 4-FTP treatment is attributed to better alignment between the HOMO of PTDPPTFT4 (5.3 eV) [33] and the work function of the 4-FTP-treated Ag S/D contact (5.21 eV) [34]. This 4-FTP treatment raises the work function of the Ag by 0.51 eV compared to typical Ag electrode (4.6 eV) [34], resulting in lowering the hole injection barrier.

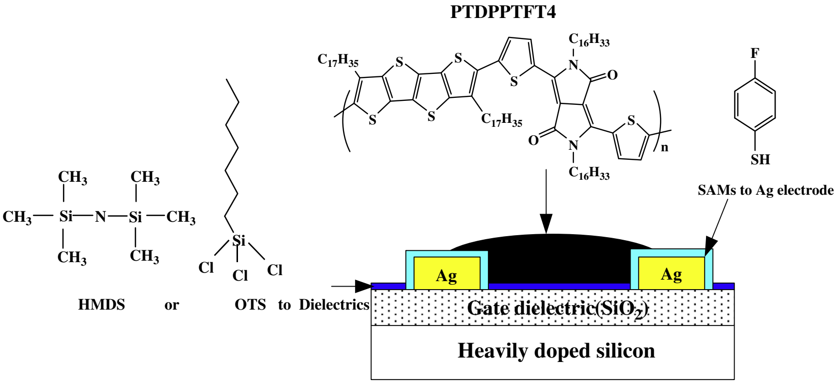

Fig. 1. Bottom-contact PTDPPTFT4 OTFT with chemically modified Ag contacts and dielectric surfaces.