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Two-step surface modification for bottom-contact structured pentacene thin-film transistors

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ABSTRACT

We investigated surface treatment effects of hexamethyldisilazane (HMDS), poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and L-cysteine on gold source/drain electrodes in bottom-contact structured pentacene thin-film transistors (TFTs). The treatment methods include spin coating and immersing. We have also researched on two-step treatment based on the combination of each treatment methods. The highest device performance was achieved by treating gold S/D electrodes with L-cysteine first and PEDOT:PSS afterwards, showing field effect mobility up to 0.35 $cm^2/V \cdot s$. L-cysteine can reduce the contact resistance between metal and semiconductor layer, and PEDOT:PSS acted as a hole transporting layer while HMDS decreased the surface energy, which enlarged the grain size of pentacene on it.

1. Introduction

There are two common device configurations used in organic thin-film transistors (OTFTs) for possible source and drain (S/D) contacts: top contact (TC) and bottom-contact (BC) structures. In TC structured devices, S/D electrodes are deposited onto the organic semiconducting layer while in BC structured devices, this deposition sequence is reversed. TC structure has revealed superior electrical properties than its BC counterpart [1] due to smaller contact resistance [2,3]. However BC structure has more commercial potential than TC configuration as photolithography has to be used in contacts patterning but pentacene cannot be exposed to solvents involved in this process. 'Recently, orthogonal processing has been developed for patterning pentacene [4] and has great potential to be applied in industry.

At elevate temperatures, pentacene is in polycrystalline phase through thermal evaporation and its film quality influences the device performance [5,6]. Larger grain size and less grain boundaries can help increase the mobility of the device. In BC structure, pentacene consists small grain size on metal S/D electrodes which results in large contact resistance especially in the linear region [7]. If pentacene molecules are perpendicular to the substrate, large grain size will be formed [8]. However, metal has the ability of rearranging its surface energy to accommodate nearby molecules. As a result, pentacene molecules tend to lie on metal film surface [7]. Self-assemble monolayers (SAMs) containing thiol group have been widely studied to enlarge pentacene grain size on metal [7–10]. SAMs of alkanethiol derivatives can form closely packed monolayers on the gold surface, with the alkyl chains extending towards the surface. Repulsion between pentacene molecules and alkanethiol molecules help form larger grains on SAM treated gold surface than on bare surface [8,10]. However, SAM modification methods were reported with only inorganic insulators because devices should be immersed in SAM material dissolved ethanol for several hours and ethanol will damage the organic insulator surface.

Aparting from modifying the S/D electrodes, adding a hole injection layer is also a common way to improve the performance of OTFTs. For electrode and organic film interface, low energy barrier is preferred for easier charge injection. Molybdenum trioxide (MoO_3) [11] and PEDOT:PSS [12] have been studied as hole injection layer in OTFTs.

In our work, we focused on the gold surface treatment method in devices with polymer insulator. We introduced hexamethyldisilazane (HMDS), poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and L-cysteine as modification material on

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the gold surface. Only spin coating and immersing method were included in this process, which made the modification process easy and can be applied to devices with polymer dielectric layers containing low surface energy. Apart from single treatment method, we also researched on the two-step modification methods using the materials mentioned above. The two-step modification methods included PEDOT:PSS coating followed by HMDS coating (PEDOT:PSS & HMDS, hereafter), L-cysteine treatment followed by PEDOT:PSS coating (L-cysteine & PEDOT:PSS, hereafter) and L-cysteine treatment followed by HMDS coating (L-cysteine & HMDS, hereafter). Because in L-cysteine single treatment, we need to immerse the devices in aqueous solution for 2 h and both PEDOT:PSS and HMDS will be dissolved to some extent, we have not researched on PEDOT:PSS & L-cysteine and HMDS & L-cysteine two-step treatments. In addition, we have implemented a simple inverter circuit with L-cysteine and PEDOT:PSS two-step modification to show the potential of this treatment method in circuit fabrication.

2. Material and methods

For performance comparison, both TC and BC OTFTs were fabricated following the same procedure except for the S/D electrodes' position. Rigid glass was used as the substrate and was ultrasonic cleaned by acetone and isopropyl alcohol for 20 min separately. Aluminum (80 nm) was thermally evaporated through a shadow mask as the gate electrode. PMMA powder (purchased from Sigma Aldrich, Mw~120,000) was mixed with toluene and then spin coated onto the substrate forming the gate insulator with 220 nm thick. To form the active layer, pentacene (purchased from TCI) was evaporated at a rate of 0.3 Å/s to 70 nm thick and also patterned by shadow mask. For TC structure, gold S/D electrodes (40 nm) were evaporated after the deposition of the pentacene layer while for BC structure, the deposition sequence was reversed. As BC structured devices have inferior electrical properties than TC structured devices, we modified the gold S/D electrodes before the deposition of pentacene. For PEDOT:PSS modification method, PEDOT:PSS (purchased from AGFA, 1.3 wt% with 0.5 wt% PEDOT and 0.8 wt% PSS in H_2O) was spin coated at 4000 rpm for 30 s to form a 13 nm thick film on gold S/D electrodes. For HMDS modification method, HMDS (purchased from Merck) was spin coated at 3000 rpm for 30 s. After that, the devices were annealed at 130 °C in air for 10 min. For L-cysteine treatment, the device was immersed in 100 mM L-cysteine (purchased from Sigma Aldrich) dissolved aqueous solution for 2 h and was rinsed by deionized water and dried in nitrogen atmosphere. All devices except for ones in contact resistance measurement were fabricated at the same time with the same channel length of 100 μm and width of 1000 μm. In addition, the inverter circuit was also fabricated under the same fabrication process mentioned above.

Electrical characteristics of the devices were measured using semiconductor parameter analyzer HP Agilent 4145B. To analyze the surface property of the gold surface with different modification methods, water contact angle was also measured. AFM (Park system XE-100) images were taken to show the grain size of pentacene on gold S/D treated by different materials. To perform an explicit analysis of contact resistance, the contact resistance was extracted using the transmission line method. As we assume that the resistance at the S/D electrodes is the same regardless of the channel length variation. We plotted the total resistance of the channel length from 100 μm to 400 μm with an interval of 50 μm. Then the contact resistance can be extracted under extrapolation of channel length to zero. The total resistance of each device was calculated in the linear region when gate bias is −10 V and drain bias is −5 V.

3. Results and discussion

The performances of bare TC and BC structured devices are first examined, and the transfer and output curves are shown respectively in Fig. 1. BC structured device shows inferior performance to TC structured device which only differs in sequence of the gold and pentacene deposition. The saturation drain current of top and bottom-contact devices is around 11 μA and 0.6 μA, respectively at the gate voltage of −30 V and drain voltage of −40 V. In Fig. 1(c), when the gate bias is −30 V, the drain current in TC structured device saturates at −20 V while Fig. 1(d) shows that BC structured devices cannot saturate even at −40 V and we can observe a high contact resistance. As shown in Table 1, the field effect mobility in TC structure is almost 80 times larger than that of its BC counterpart. The contact resistance we measured using transmission line method is around 251 MΩ shown in Fig. 4. Three reasons are believed to have relationship with the high contact resistance in BC structured devices. The first cause is the limited charge injection region. The effective charge injection region is the side area of source and drain which height is the thickness of source and drain and length is the channel width. The second reason is the step difference between source/drain gold layer and insulator layer. We can observe small crystallized pentacene at the interface between the source/drain and the active layer. Yong Xu et al. [13] have found out that reducing the contact thickness, one can reduce the small grain size region near the interface, which results in reduction in contact resistance. Ching-Lin Fan et al. [14] have suggest a planar structure which eliminates the step difference to provide a better deposition condition for pentacene. The third reason is the small grain size of pentacene on the metal source and drain surface. In order to improve the electrical properties of BC structured devices, we researched on the chemical modification methods on source and drain to improve the grain size of pentacene on it and reduce the hole injection barrier. The modification methods are divided into single chemical treatment methods and two-step chemical treatment methods.

For single chemical treatment methods, we introduced three materials: HMDS, L-cysteine and PEDOT:PSS. HMDS has been reported as modification material on dielectric layer such as SiO_2 due to its amphipathy. After being modified by HMDS, SiO_2 layer has shown a reduced surface free energy which results in increase of crystallinity of pentacene [15]. HMDS was considered impossible to attach on gold surface. Jangdae Youn et al. [16] have shown a bad device performance after HMDS treatment on gold S/D while in our research, we have shown an improvement after HDMS treatment after annealing at 130 °C. We have also observed a worse performance after HDMS treatment without annealing. The device performances after HMDS treatment with and without annealing are shown in Fig. 2. As a result, annealing is the key factor deciding the treatment effects. We have observed a surface free energy variation between gold surface with and without HMDS treatment. From Table 2, the water contact angle on HMDS treated gold surface is 5° larger than that on bare gold surface. HMDS with annealing has turned the gold surface more hydrophobic, which enlarges the pentacene grain size from 0.5 μm to 0.8 μm according to Fig. 5(a) and (b). Compared with bare BC structured devices, HMDS treated devices have shown an increased field effect mobility from 0.006 $cm^2/V\cdot s$ to 0.036 $cm^2/V\cdot s$ and a decrease in contact resistance from 251 MΩ to 21 MΩ shown in Fig. 3 and Fig. 4, respectively.

The most reliable method to improve the device performance of bottom-contact structured devices is to treat S/D with a self-assembled monolayer (SAM). Regarding SAM on the gold surface, alkane thiol and aromatic thiol are widely researched. The improved device performance can be explained in two reasons. In thiol treatment, thiol group is attached to one gold atom leaving the

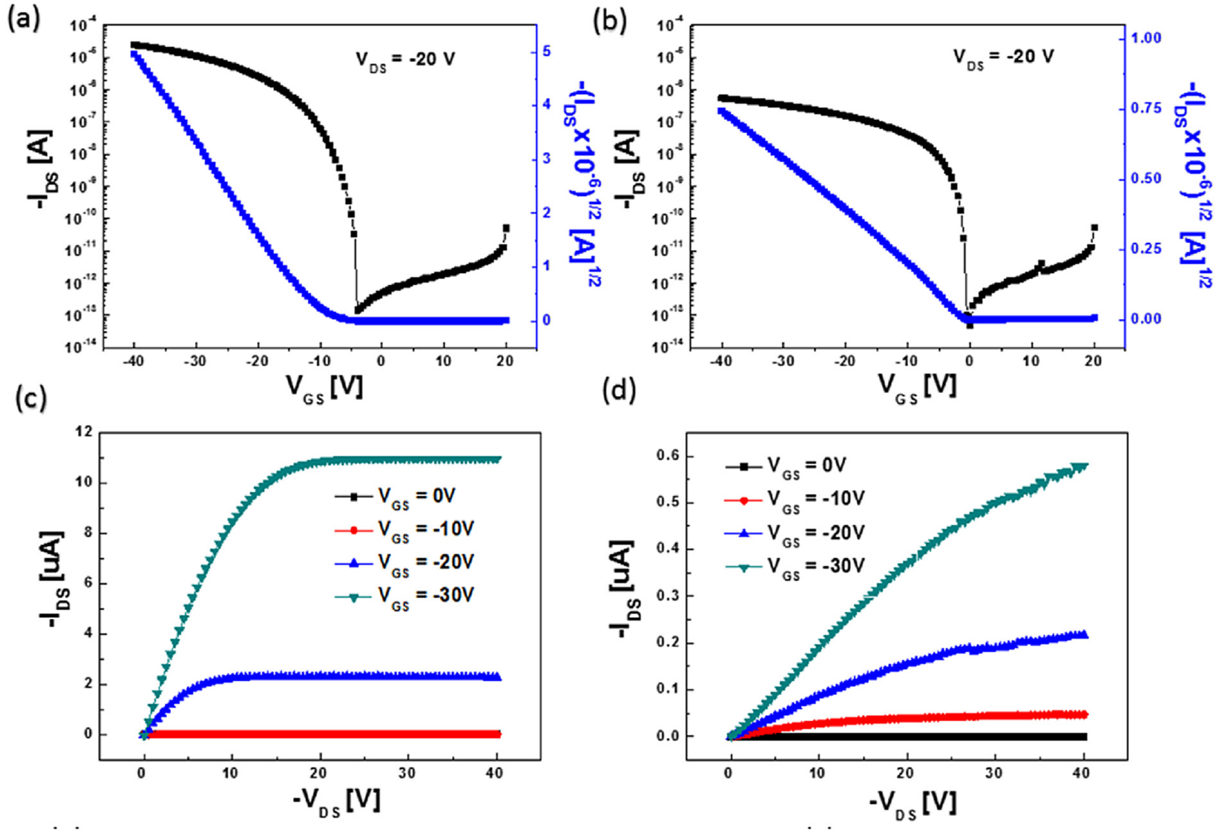

Fig. 1. (a) Transfer characteristics under drain bias $V_D = -20$ V and (c) output characteristic of TC structured devices. (b) Transfer characteristics under drain bias $V_D = -20$ V and (d) output characteristic of BC structured devices.

Table 1
Electrical property of each device.

	TC	BC	BC with HMDS	BC with L-cysteine	BC with PEDOT:PSS	BC with PEDOT:PSS &HMDS	BC with L-cysteine & HMDS	BC with L-cysteine & PEDOT:PSS
V_{th} (V)	−9.5	−1.3	−2.7	−3.4	−1.9	−1.4	−2.6	−1.8
μ_{fet} (cm^2/V·s)	0.468	0.006	0.036	0.048	0.16	0.31	0.043	0.35

functional group to the air. The functional group usually turns the gold surface from hydrophilic to hydrophobic which enlarges the grain size of pentacene on it. The second reason is that it can reduce the hole injection barrier between gold and pentacene. M. Kawasaki et al. [17] found out SAM treated gold surface has shown an increased work function and thus resulting in a decrease of the Schottky barrier height. Alkane or aromatic thiol is dissolved in ethanol with a certain concentration, and devices are dipped in this solution for 1 min to 1 day to form a self-assembled monolayer on the gold surface. In our devices, PMMA was used as gate insulator and can be damaged by ethanol which was used to dissolve alkanethiol. Instead of using alkanethiol, we chose L-cysteine, one kind of protein which can be dissolved in water, as the SAM material. However because the endgroup of L-cysteine is −COOH, the gold surface was more hydrophilic after modification which leads to a decrease in pentacene grain size shown in Fig. 5(c). As a result, L-cysteine treated devices have not shown a good performance as much as alkanethiol treated devices. Due to the decreased contact resistance, compared with bare BC structured devices, the field effect mobility of L-cysteine treated devices was improved to 0.048 cm^2/V·s and the contact resistance was reduced to 13 MΩ.

The energy difference between the electrode's work function and HOMO level of p-type semiconductors is a hole injection barrier from metal to the organic material. Adding a buffer layer such as PEDOT:PSS which is widely used as a hole transport layer, can effectively reduce the hole injection barrier [12]. In our devices, PEDOT:PSS can be coated only on gold surface rather than on PMMA surface. Even though water contact angle on PEDOT:PSS coated gold surface was 31.1°, pentacene grain size on PEDOT:PSS coated gold surface was still larger than that on bare gold surface. PEDOT:PSS treated device has shown the highest field effect mobility among the single treated OTFTs, reaching to 0.16 cm^2/V·s.

Based on the three single treatment methods, we researched on a combined effect of three two-step modification methods which is one single treatment process followed by another single treatment process. The two-step modification methods include L-cysteine & HMDS, PEDOT:PSS & HMDS and L-cysteine & PEDOT:PSS. The former material means the foremost single treatment method. We excluded HMDS & L-cysteine and PEDOT:PSS & L-cysteine conditions because both HMDS and PEDOT:PSS will dissolve to some extent in L-cysteine solution and their residues will prevent the attachment of L-cysteine molecules on the gold surface. As a result,

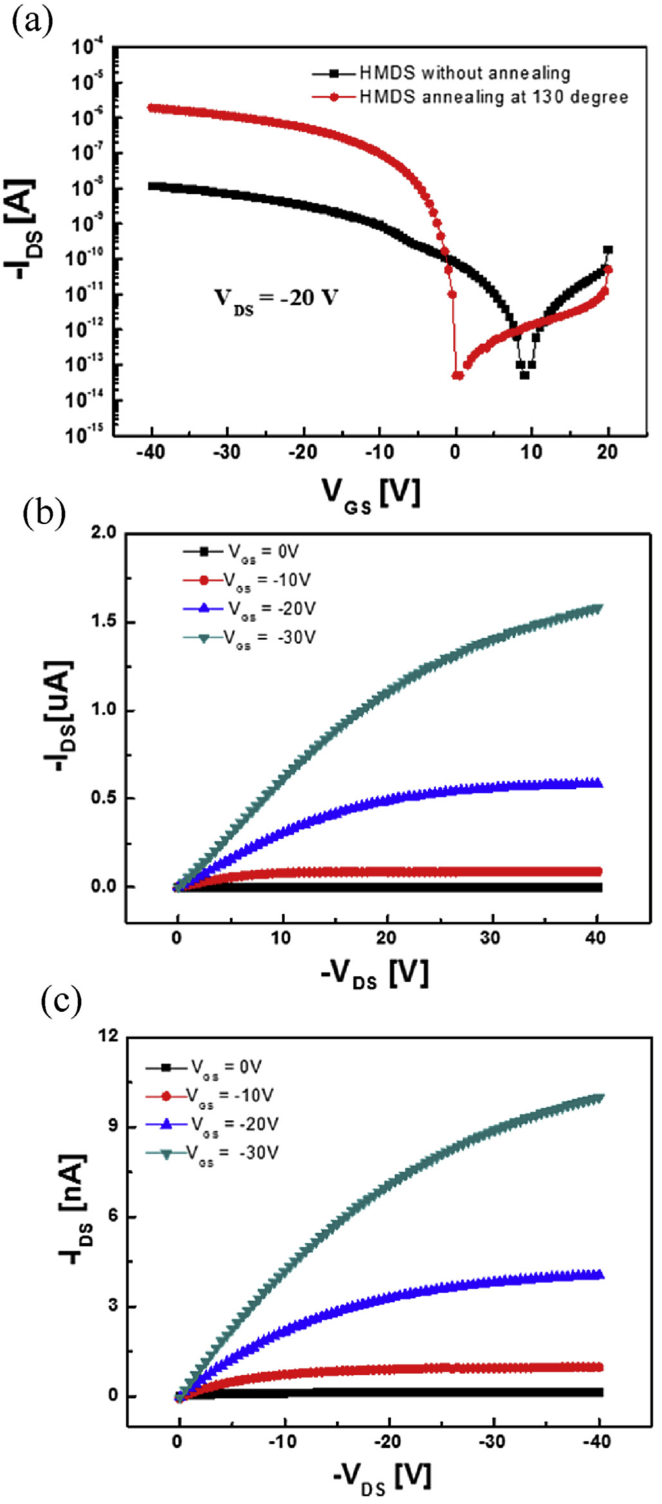

Fig. 2. (a) Transfer characteristics under drain bias $V_D = -20$ V of BC structured devices after HMDS treatment with and without annealing, output characteristic of BC structured devices after HMDS treatment (b) with annealing and (c) without annealing.

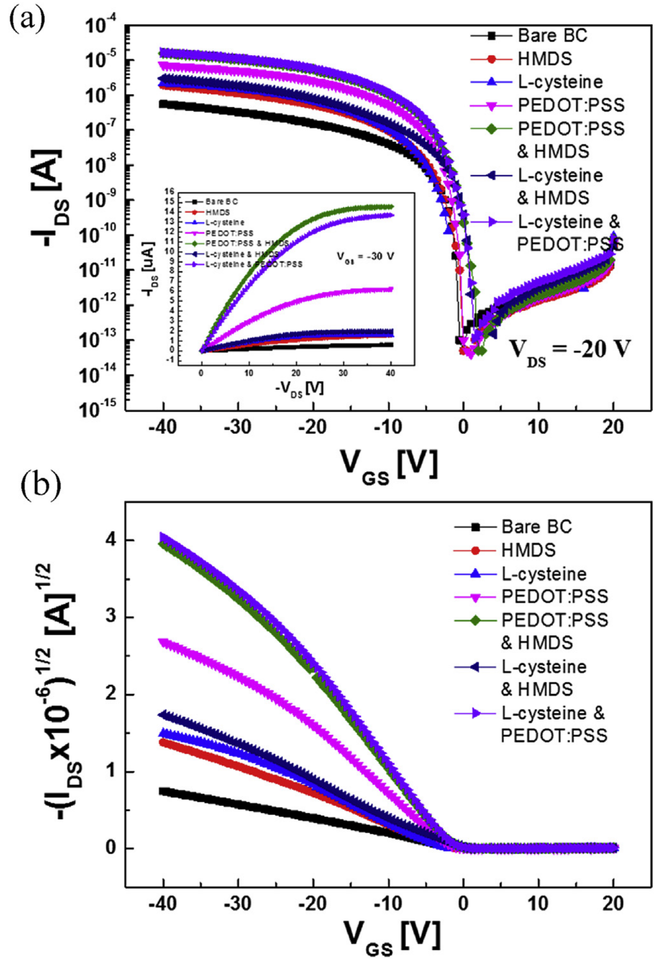

Fig. 3. (a) Transfer characteristics under drain bias $V_D = -20$ V and (b) output characteristics of BC structured devices with chemically treated gold S/D electrodes.

instead of showing a combined effect, the device performance of these two conditions will be worse than only L-cysteine single treatment.

For L-cysteine & HMDS condition, the first layer of L-cysteine made the gold surface more hydrophilic as we can observe a water contact angle reduction from 74.8° to 11.1° because of the functional group –COOH of L-cysteine. The smaller grain size of pentacene on L-cysteine treated gold surface than on bare gold surface is the shortcome of single L-cysteine treatment, and we expected the second layer HMDS will reduce the surface free energy to favour the crystallization of pentacene. However we can observe the device performance of L-cysteine & HMDS treatment is almost the same with only L-cysteine single treatment. The field effect mobility was 0.043 $cm^2/V \cdot s$ which is similar with 0.048 $cm^2/V \cdot s$ of only L-cysteine single treatment. We considered the reason was that after the formation of L-cysteine self-assembled monolayer on the gold surface, it was hard for HMDS to form another layer of SAM on it. As a result, the device performance with this two-step treatment showed no obvious difference comparing with only L-cysteine

Table 2
Water contact angle of gold surface with and without HMDS and PEDOT:PSS modification.

	Bare surface	Coated with HMDS without annealing	Coated with HMDS annealing at 130 °C	Coated with PEDOT:PSS	Coated with PEDOT:PSS & HMDS	Coated with L-cysteine
Gold surface	74.8°	77.2°	79.7°	31.1°	34.4°	11.1°

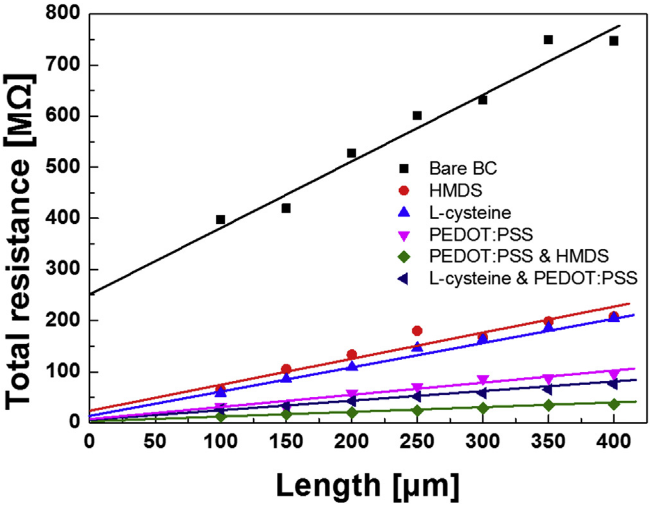

Fig. 4. Total resistance of BC structured devices with chemically treated gold S/D electrodes. The channel length varies from 100 μm to 400 μm with an interval of 50 μm. The total resistance was measured at the drain voltage $V_D = -5$ V and the gate voltage $V_G = -10$ V. The contact resistance was extracted using transmission line method.

treated devices.

Different from L-cysteine & HMDS condition, PEDOT:PSS & HMDS two-step modification method showed combined effects of single PEDOT:PSS and single HMDS treatments. PEDOT:PSS reduces the hole injection barrier and HMDS changes the surface free energy of PEDOT:PSS film. The water contact angle on PEDOT:PSS coated gold surface is 31.1° and was increased by 3.3° after HMDS coating. In single PEDOT:PSS treatment, we can already observe an increase in pentacene grain size on PEDOT:PSS coated gold surface. After spin coating another HMDS layer on PEDOT:PSS layer, we can observe larger grain size of pentacene than on only PEDOT:PSS or only HMDS coated gold surface in Fig. 5(b), (d) and (e). After being modified with both PEDOT:PSS and HMDS, the field effect mobility of bottom-contact structured devices was improved from 0.006 $cm^2/V\cdot s$ to 0.31 $cm^2/V\cdot s$ and contact resistance was reduced to 5 MΩ.

Gold surface is not a good substrate for spin coating PEDOT:PSS on, and thermal evaporated gold surface ⟨1,1,1⟩ presents low surface free energy (water contact angle on it is 74.8° in Table 2) which makes it more difficult for forming a uniform PEDOT:PSS film. Usually we need to add surfactant into PEDOT:PSS solution in order to acquire a uniform PEDOT:PSS film. However in our device, PEDOT:PSS is highly conductive and adding surfactant to PEDOT:PSS will induce a short channel between source and drain electrodes. This problem can be easily solved by L-cysteine. After L-cysteine treatment, the contact angle on the gold surface was dramatically reduced from 74.8° to 11.1°, which provides a good condition for PEDOT:PSS coating. However, we can observe from Fig. 5(f), the grain size was smaller on L-cysteine and PEDOT:PSS coated gold surface than only PEDOT:PSS coated gold surface. It has shown a combined effect on pentacene crystallization. Thanks to the two times reduction of the hole injection barrier, the final device property was improved with field effect mobility reaching 0.35 $cm^2/V\cdot s$ which is the highest mobility among all treatment methods and the contact resistance was reduced to 5 MΩ.

In order to check the compatibility of L-cysteine & PEDOT:PSS two-step modification method with circuit implementation. We designed a simple inverter circuit and included this treatment method in the fabrication process. The inverter consists of a driving transistor (length of 100 μm and width of 6000 μm) and a load transistor (length of 100 μm and width of 600 μm). Fig. 6 shows the voltage transfer curve of this inverter with gain of 3.1.

4. Conclusion

Bottom-gate bottom-contact structured organic thin-film transistors with various kinds of chemical treatments were researched.

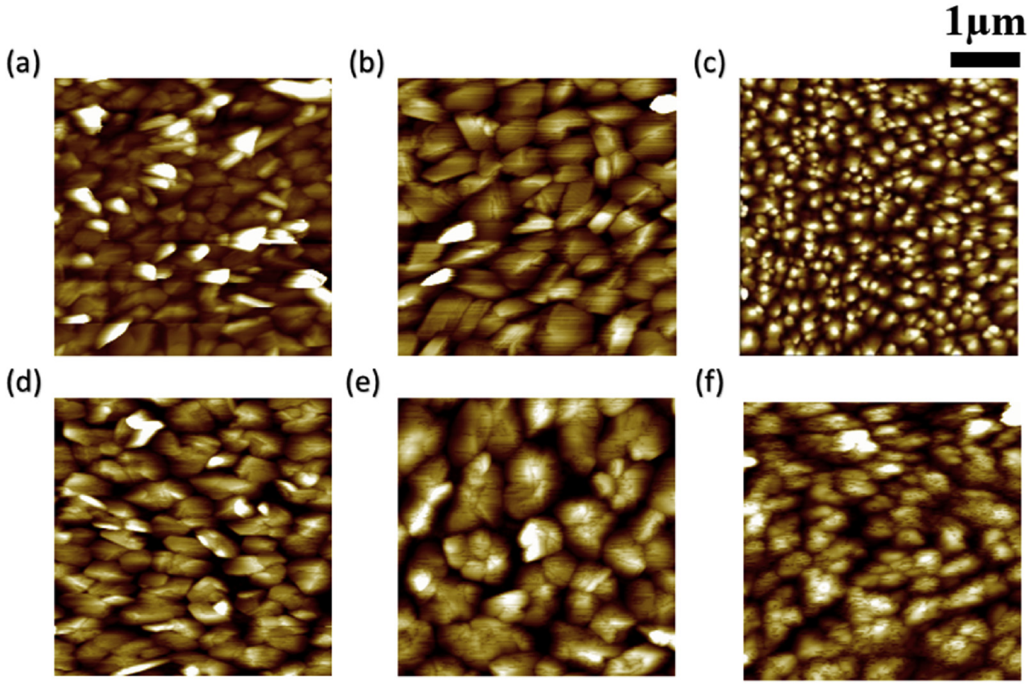

Fig. 5. AFM images (4 μm × 4 μm) of pentacene on (a) bare, (b) HMDS coated, (c) L-cysteine treated, (d) PEDOT:PSS coated, (e) both PEDOT:PSS and HMDS coated and (f) both L-cysteine treated and PEDOT:PSS coated gold surface.

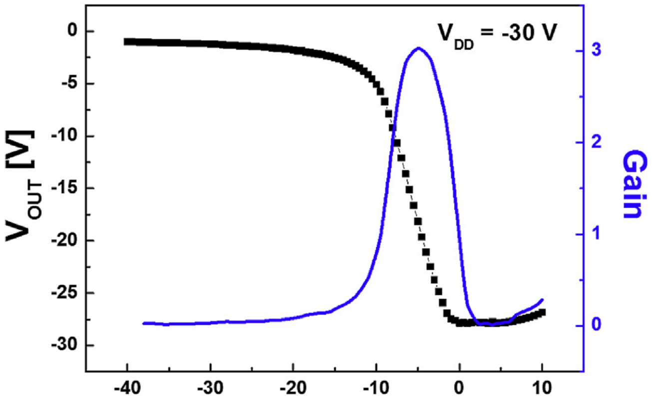

Fig. 6. Voltage transfer characteristic of inverter with L-cysteine and PEDOT:PSS treated bottom-contact structured organic thin-film transistors under V_{DD} of −30 V. The inset is the schematic inverter circuit with driving transistor length of 100 μm and width of 6000 μm and load transistor length of 100 μm and width of 600 μm.

The single treatment methods include materials like HMDS, L-cysteine and PEDOT:PSS. The two-step treatment methods are the combination of the single treatments and under the same experimental process. HMDS changes the surface free energy of the underneath surface which favoured the crystallization of pentacene on it. L-cysteine and PEDOT:PSS reduce the hole injection barrier between gold and pentacene. Among the single treatment, PEDOT:PSS is the most effective one showing mobility up to 0.16 $cm^2/V\cdot s$ by almost 27 times than bare bottom-contact structured devices. The L-cysteine and PEDOT:PSS two-step modification method shows a combined effect of single L-cysteine and PEDOT:PSS treatment methods, and improves the field effect mobility in the saturation region up to 0.35 $cm^2/V\cdot s$ by almost twice comparing with single PEDOT:PSS treatment, due to the reduced contact resistance from 251 MΩ to 5 MΩ.

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