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Title:

Poly (sodium-4-styrene sulfonate) (PSSNa)-Assisted Transferable Flexible, Top-Contact High-Resolution Free-Standing Organic Field-Effect Transistors†

Authors:

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Abstract

The development of high-integration, flexible and transferable devices is a very important premise to realize authentically wearable applications in the future. Here, we report how to fabricate flexible, free-standing and high-resolution (down to 5 μm) top-contact OFETs based on polystyrene (PS) dielectric layer. In this process, we use a special sacrificial layer, poly (sodium-4-styrene sulfonate) (PSSNa). It is low-cost, dissolves quickly in water at room temperature and has good compatibility with most organic material processing techniques. With the help of this sacrificial layer, this kind of free-standing transistors can be successfully transferred onto arbitrary substrates. Furthermore, the degradation of the performance of the devices after multiple and successive transfer is tolerated.

Introduction

Motivated by the significant progress of organic electronics in the past decade, [1-6] the pursuit of high integration has gradually represented the primary trend in this field, which conforms to the guidance by the famous Moore's law [7] as well. Nowadays, the feature size of the transistors has been reduced to the nanoscale, [8-14] and even to the molecular level. [15-17] However, these available technologies are mostly based on the strength of inorganic surfaces of which the most predominant one is silicon dioxide (SiO_2). It has been acknowledged that organic materials including dielectric materials and semiconductor materials are considered as ideal candidates due to their remarkable merits contributing to flexible and low-cost electronic devices with high performance. [18-20] Regrettably, the progress of the control of the feature size of transistors based on organic surfaces is still limited. One of the main factors restricting the development of this area is that most of the organic materials cannot withstand to chemical solution processing during the micromachining. To date, there have been some fruitful results reported to overcome this problem. Polyvinylphenol (PVP) mixtured with special components [21, 22] and polyimide [23-27] can both serve as dielectrics, which are processable in photolithography with the feature size of transistors reduced to 5 μm, but they require high annealing temperature (above 200 ^{o}C). Another significant breakthrough made by "Double exposure method" [28] is to apply low-annealing-temperature (80 ^{o}C) polystyrene (PS) and polymethyl methacrylate (PMMA) feasible in the process of microfabrication with the size down to 5 μm. However, these above-mentioned methods are based on bottom-contact configuration, which possess less injection areas and less favourable injection paths compared with top-contact devices. [29] Although, high-resolution top-contact transistors are achieved by some reliable methods, such as orthogonal photolithography [30, 31] and high-resolution mask method, [32-34] these applications are still limited to inorganic dielectric layers. Simultaneously, the introduction of organic materials into devices can not only help to realize higher flexibility, but also provide a platform to achieve transferable devices. Actually, there are some unconventional substrates which cannot be used to directly built devices on them. Therefore, the

whole device should be transferrable. Here, we demonstrate an approach to successfully transfer free-standing, flexible, high-resolution top-contact OFETs based on polystyrene insulators to arbitrary substrates. Furthermore, the degradation of the performance of the devices after multiple and successive transfer is tolerated**.** In particular, we show the first successful kind of transfer based on polystyrene insulator.

Experimental section

Poly (sodium-4-styrene sulfonate), polystyrene, ITO/Glass, pentacene and flexible polyethylene terephthalate (PET) were purchased from Aldrich. Pentacene was used as received without further purification.

ITO/Glass wafers used in the present study were successively cleaned with deionized water, acetone, pure ethanol, deionized water and isopropanol. Plasma treatment (300 W, 10min) was carried out before spin-coating the PSSNa layer. PSSNa with the concentration of 30 mg/ml in deionized water was spin-coated onto the clean ITO surface with 3000 rpm speed for 30 s. and then this film was annealing at 100 ^{o}C about half an hour to remove the deionized water. After that, the morphology and thickness of this film were investigated by atomic force microscope (AFM, a Multimode Nanoscope IIIa instrument (Digital Instrument)) with tapping mode. Polystyrene (PS) with the concentration of 80 mg/ml in toluene was spin-coated on the surface of gold to serve as the insulator layer and the thickness of this film was measured by AFM.

In order to measure the unit-area capacitance of PS film, the devices with ITO/PS/Al (100 nm) sandwich structure were fabricated. The specific capacitance as a function of frequency based on PS film was tested by Keithley 4200-SCS capacitance unit. Bottom-gate top-contact OFETs were fabricated using the PS as dielectric layers, pentacene film as the active layer. 50nm-thick pentacene film was thermally evaporated with a rate of 0.1 Å/s, and then the 20 nm Au electrode deposited through a polymer mask, and all the devices were tested by Keithley 4200-SCS semiconductor analyzer and a Micromanipulator 6150 probe station at ambient atmosphere.

Metal deposition was carried out in a vacuum chamber using W wire as heating

source under a vacuum of 10^{-4} Pa. Semiconductor deposition was performed in a vacuum system under 10^{-4} Pa.

Results and discussion

Herein, an essential sacrificial layer, poly (sodium-4-styrene sulfonate) (PSSNa), was used in our work. Compared with other available sacrificial layers, [35-38] it is low-cost and dissolves quickly in water at room temperature. The most important thing is that it has good compatibility with most organic material processing techniques due to its insoluble property in common organic solvents, such as acetone, toluene, and chloroform etc. The chemical structure of poly (sodium-4-styrene sulfonate) (PSSNa) is shown in Fig. 1a. PSSNa was spin-coated onto the clean ITO surface to form ~32 nm films with the cross-sectional of the thickness shown in Figure S1. Interestingly, this treatment effectively improved the smoothness of the ITO surface from 2.41 nm (root-mean-square roughness) (Fig. 1b) to 0.65 nm (Fig. 1c) as analyzed by atomic force microscopy (AFM). This improvement assists in forming uniform films on its smoother surface compared with that of ITO and floating the upper layers rapidly on the deionized water due to its hydrosoluble property. Figure 1d demonstrates the process to float the polystyrene film onto the deionized water within less than 20 seconds, which greatly increases the efficiency of the transfer. As a result, a uniform polystyrene film was observed from Fig. 1d due to the same color covering the whole surface, which was beneficial to the growth of semiconductor on its surface.

Fig. 2 schematically illustrates our experimental design for the process of fabricating the devices. The first step was to have the aid of this PSSNa to produce polymer masks to fabricate high-resolution top-contact OFETs. Here, we used a PS polymer mask with 5 μm channel length and 40 μm channel width and this high-resolution channel length (5 μm) was further measured by AFM (Figure S2) after depositing gold. The details to prepare this polymer mask were recorded in our previous work. [39] However, in this work, we extended our polymer masks to fabricate flexible and transferable devices instead of the previous SiO_2/Si substrate and this

kind of transfer method provided an approach to build devices on some special substrates, such as skin, money, and bus card etc. We believed that this application was a very important premise to realize authentically wearable applications in the future. Here the material for this polymer mask was polystyrene. This polymer mask was used to build the top-contact source/drain electrodes on the surface of semiconductor and minimized any possible damage to the organic semiconductor film. Secondly, glass with indium tin oxide (ITO) was served as the intermediary substrate for the transferable device preparation. As shown in Fig. 2a, a 30 nm PSSNa smooth film was formed on ITO surface by spin-coating method and a 100 nm gold film was chosen as the gate electrode to deposit on the surface of PSSNa. Subsequently, a 600 nm polystyrene (PS) with the cross-sectional thickness shown in Figure S3 was spin-coated on the surface of gold as the dielectric layer; and 50 nm pentacene as the active layers and 20 nm gold as the source/drain electrodes were deposited in turn to finish the whole device. This 600 nm PS layers produced a capacitance per unit of 3 nF cm^{-2} (Figure S4). Subsequently, the edge of the device was slowly immersed into the deionized water to float the free-standing part (Au/pentacene/PS/Au) on the deionized water (Fig. 2b). Finally, the free-standing device could be transferred to the target substrate (Fig. 2c). Different from the previous reports [40-42] using PSSNa as a sacrificial layer, we liberated the poly (dimethylsiloxane) (PDMS) stamp and floated the free-standing devices on the deionized water. It was believed that this arrangement was to the benefit of transferring the devices to flexible substrates. Considering the pentacene sensitive to water, the whole process successfully guaranteed the pentacene not in contact with the deionized water by increasing the area of lift-off layer (Au/PS) and keeping the area of semiconductor (pentacene) away from the edge. The corresponding physical presentation is shown in Fig. 3a and 3b. The floating device without the PSSNa and glass layer could be readily transferred to arbitrary substrates, such as a flexible polyethylene terephthalate (PET) (Fig. 3c), a bus card (Fig. 3d) and an RMB (Fig. 3e). Such attempts are reported successfully for the first time. It is noted that after one-time transfer, the device was easy to float again back to the surface of water and ready for the next transfer (multiply transfer). Representative

transfer characteristics of the transistors (with V_{DS} = -80 V) are shown in Fig. 4a. A comparison (see Table 1) with devices before and after transfer provided important parameters, such as the maximum current, mobility, on/off current ratio, threshold voltage and subthreshold swing. It was observed that the maximum current of the device on the RMB (the third transfer) was only reduced by 5.7% (from 2.10 μA to 1.98μA) compared with the device on the ITO/Glass (the original device) and the saturation mobility (from 0.11 cm^2 V^{-1} s^{-1} to 0.09 cm^2 V^{-1} s^{-1}) accordingly by 18 %. We believed that the reason for this reduction was possibly ascribed to some uncertain factors during the transfer and non-ignorable aqueous vapor influencing on the pentacene. Even so, there was a tolerated change for the overall level of the performance of device. Representative output characteristics of the transistors are shown in Fig. 4b. These devices also showed the expected gate modulation of the drain current (I_D) in both the linear and saturation regimes. Although, the output current was reduced slightly after each transfer, we believe that this change was in the tolerated range. As seen from the gate current shown in Fig. 5, it was smaller than the drain current by more than two to three orders of magnitude, and even after three transfers, the gate current still maintained at 10^{-8} A level, confirming the high quality of the gate dielectric after multi-transfer. Notably, this is the first report on high-resolution (5 μm), free-standing, top-contact and transferable OFETs based on PS dielectric layer and also the first time to transfer this kind of OFETs to arbitrary substrates. Certainly, this kind of transfer could also be applied to other insulators, such as polymethyl methacrylate (PMMA) and polyimide (PI).

Conclusions

In summary, poly (sodium-4-styrene sulfonate) is low-cost and hydrosoluble sacrificial layer. It can fast dissolves in the water at room temperature. With the help of poly (sodium-4-styrene sulfonate), flexible, free-standing and high-resolution (5 μm) top-contact OFETs based on PS dielectric layer the first time can successfully transferred onto arbitrary substrates. Furthermore, the degradation of the performance

of the devices after multiple and successive transfer is tolerated**.** We believe this transfer method has significant potential applications in organic electronics.

Acknowledgements

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Figure captions:

Figure-1: (a) The chemical structure of PSSNa, (b) AFM image of the morphology of ITO surface, (c) AFM image of the morphology of PSSNa surface, (d) The physical presentation to float the PS film on the water and the physical presentation of PS film floating on the water.

Figure-2: (a) The schematic diagram of the device ready for transfer, (b) The schematic diagram of the floating device, (c) The schematic diagram of the device transferred onto target substrate.

Figure-3: (a) The corresponding physical presentation to float the device on the water, (b) The corresponding physical presentation of device floating on the water, (c) device on flexible polyethylene terephthalate (PET), (d) device on bus card, (e) device on RMB

Figure-4: (a) The transfer curve of the device before and after three transfer, (b) the output curve of the device before and after transfer.

Figure-5: Gate current as a function of gate–source voltage based on devices before and after transfer.

Table 1: Numerical results of pentacen-based OFETs before and after transfer.

Figures:

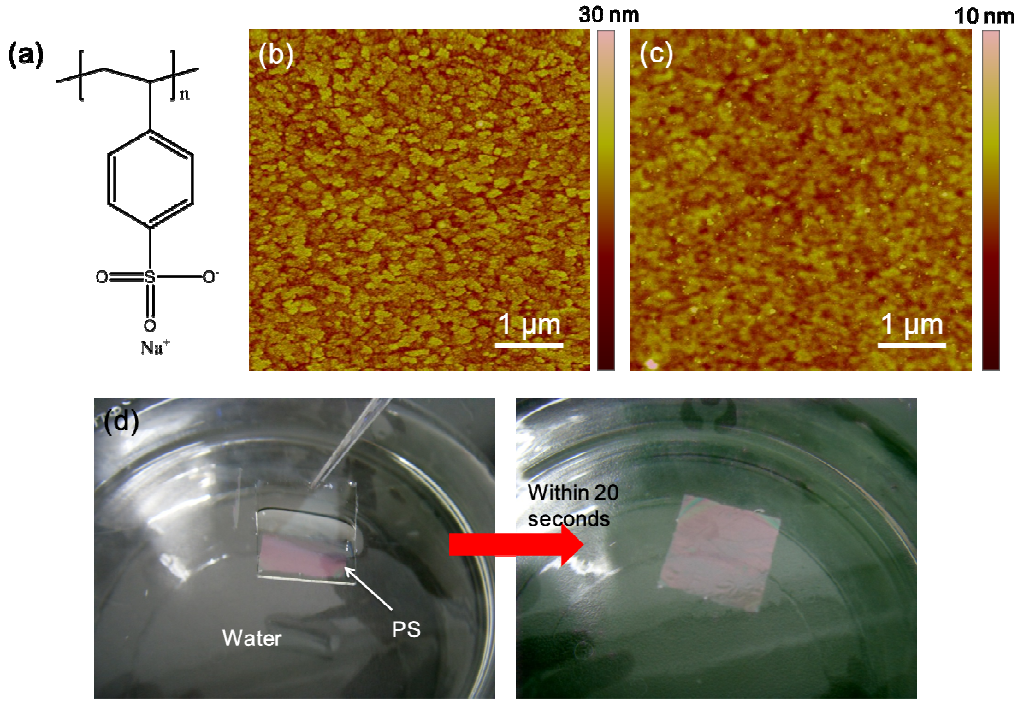

Figure-1

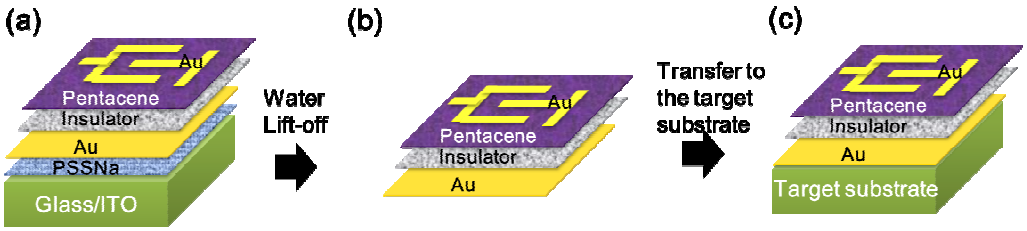

Figure-2

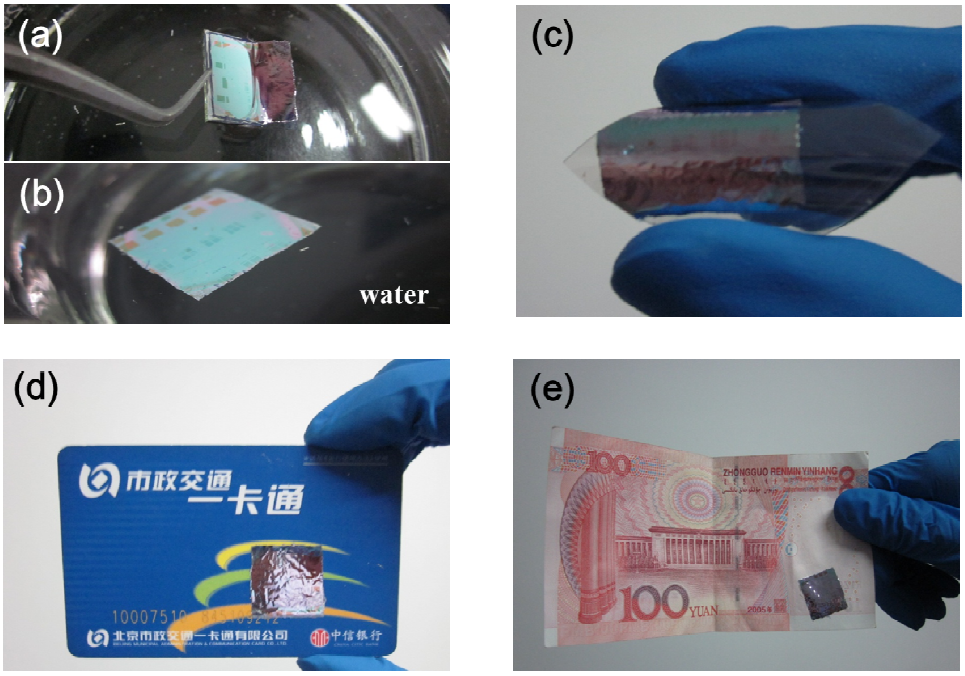

Figure-3

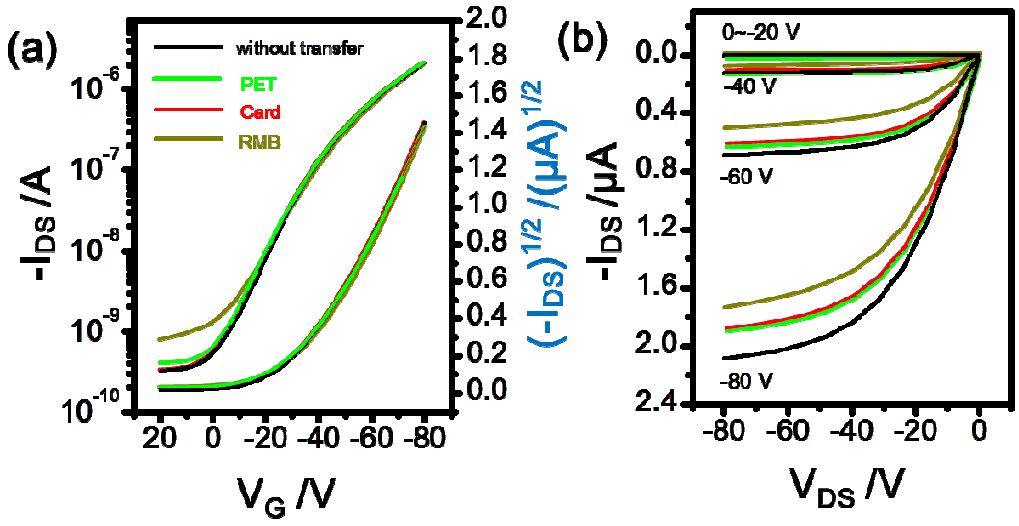

Figure-4

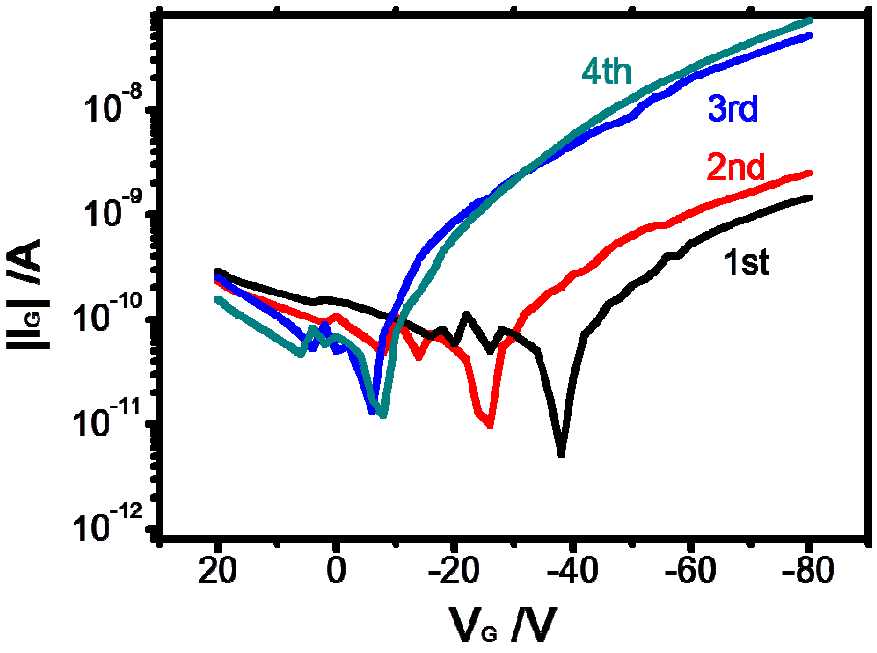

Figure-5

	Imax (μA)	μ ($cm^2 V^{-1} s^{-1}$)	ON/OFF	VT (V)	S ($mV\ dec^{-1}$)
1st	2.10	0.11	6.5×10^3	-35	-14.5
2nd	2.10	0.10	6.3×10^3	-34.4	-15.4
3rd	2.02	0.10	5.3×10^3	-34.6	-17.2
4th	1.98	0.09	2.8×10^3	-36.7	-17.5

Table-1

The table of contents entry

Here we demonstrate how, by means of poly (sodium-4-styrene sulfonate), one can successfully transfer the free-standing, flexible, high-resolution top-contact OFETs based on polystyrene insulator to arbitrary substrates. In particular we show the first successful this kind of transfer based on polystyrene insulator.

Keywords: Poly (sodium-4-styrene sulfonate), transfer method, transistor, organic electronics

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