Bilayer Ambipolar Organic Thin-Film Transistors and Inverters Prepared by the Contact-Film-Transfer Method

Qingshuo Wei,[†] Keisuke Tajima,[*,†] and Kazuhito Hashimoto[*,†,‡]

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and Hashimoto Light Energy Conversion Project, Exploratory Research for Advanced Technology, Japan Science Technology Agency, Japan

ABSTRACT Ambipolar organic thin-film transistors with a bilayer structure of poly(3-hexylthiophene) and [6,6]phenyl C_{61} butyric acid methyl ester were fabricated using a simple solution-based, contact-film-transfer method. The transistors exhibited balanced electron and hole mobilities of 2.1×10^{-2} and 1.1×10^{-2} cm^2 V^{-1} s^{-1}, respectively. Complementary inverters based on two identical ambipolar transistors showed good performance with a gain of 14.

KEYWORDS: ambipolar transistor • film transfer • polythiophene • fullerene

Organic thin-film transistors (OTFTs) have drawn tremendous attention because of their potential applications as mechanically flexible, lightweight, and inexpensive electronic devices (1−4). OTFTs have generally operated as either n- or p-channel transistors (unipolar devices) depending on the injection efficiency for the charge carriers. Therefore, for the fabrication of electronic circuits, it is necessary to pattern both n- and p-type organic semiconducting materials on the same substrate (5). This requirement increases the process complexity and thus the manufacturing cost. The realization of ambipolar OTFTs containing both p- and n-channel transistors in one device would represent a step forward in the development of complex digital circuits, enabling the fabrication of electronic circuits such as complementary inverters without relying on advanced patterning techniques (6).

To obtain ambipolar behavior in OTFTs, a promising approach is the use of a bilayer film of n- and p-type semiconducting materials (7). The construction of such layered structures can be easily accomplished by successive depositions using dry processes; therefore, almost all examples of bilayer ambipolar transistors reported to date are based on vacuum-evaporated organic molecules (7−13). Solution-based processing of semiconducting materials is more attractive because it is scalable, low cost, and compatible with the various mass printing and coating techniques currently used in the industry. However, the fabrication of bilayer devices based on solution processes is very limited (14). This is mainly due to the technical difficulty of obtaining well-defined smooth interfaces when using solution-based processes. Because the polymers are generally soluble in the same solvents, it is difficult to cast the second polymer layer from solution without dissolving the first layer. Recently, we reported a novel and simple contact-film-transfer method at ambient conditions and its utilization in the fabrication of high-performance polymer TFTs using the polymer/air interface as a charge-transport layer (15). This approach also has advantages for preparing multilayered structures free from the constraints of conventional solution-based processes. In this paper, we report the fabrication of ambipolar OTFTs and inverters based on a bilayer film of poly(3-hexylthiophene) (P3HT) and [6,6]phenyl C_{61} butyric acid methyl ester (PCBM). Although several organic film transfer techniques have been reported recently (16−21), there have been no reports on the fabrication of ambipolar OTFTs via these methods.

The schematic drawing in Figure 1 shows the device fabrication process for the contact-film-transfer method. First, a film with the structure of glass/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/P3HT was prepared by successive spin coating of an aqueous solution of PEDOT:PSS and a chlorobenzene solution of P3HT. This P3HT film was lightly contacted onto an n-channel top-contact OTFT transistor with a structure of Si/SiO_2/divinyltetramethyldisiloxanebis(benzocyclobutene) (BCB)/PCBM/Au. A total of 1 drop of water was placed on the edge of the stacked substrates. The water selectively penetrated into the PEDOT:PSS layer. After the PEDOT:PSS layer was completely dissolved, the glass substrate was easily detached from the organic layer, resulting in the transfer of the P3HT film from the glass to the PCBM transistors.

The output characteristics of the prepared transistors are shown in Figure 2a. The gate voltage was changed from

* Corresponding authors. E-mail:k-tajima@light.t.u-tokyo.ac.jp (K.T.), hashimoto@light.t.u-tokyo.ac.jp (K.H.).
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† The University of Tokyo.
‡ Japan Science Technology Agency.
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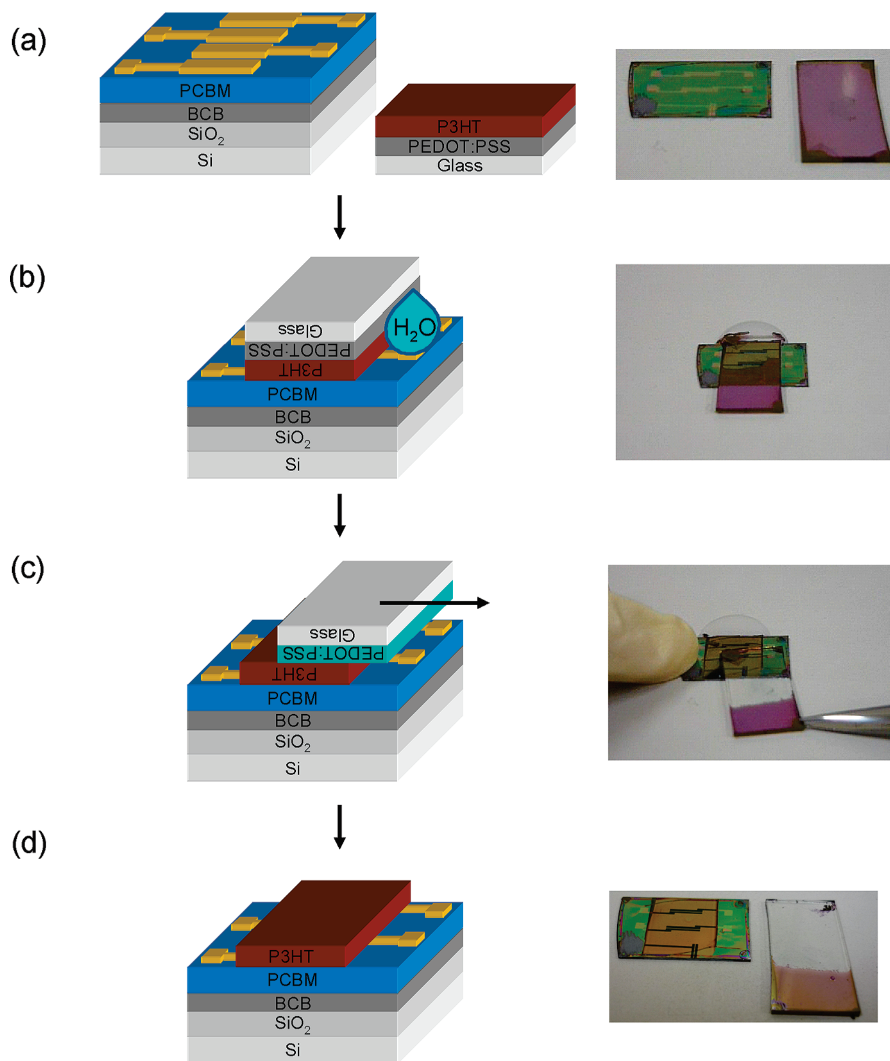

FIGURE 1. Schematic (left) and photographic (right) images showing the transfer process applied to the deposition of a P3HT film onto a PCBM transistor: (a) two organic layers were prepared on different structures; (b) the substrates were lightly contacted, and a drop of water was placed on the edge; (c) P3HT was detached from the glass substrate after PEDOT:PSS was dissolved; (d) the glass substrate was removed, leaving P3HT on the target substrate.

0 to −60 V for the p channel and from 0 to 60 V for the n channel. A clear field effect was observed in both p- and n-channel operations. The output curve shows diodelike behavior at a low gate voltage (V_G) and a high drain-to-source voltage (V_{DS}) because electrons are injected into the p channel at high V_{DS} and vice versa. This is a typical characteristic of ambipolar transistors, which can be observed in neither P3HT nor PCBM unipolar transistors.

The transfer characteristics of the devices are shown in Figure 2b,c. V_G was swept from −60 to +60 V in 1 V steps with V_{DS} of −60, −30, +30, and +60 V, respectively. The change in the minimum of the transfer curve under different V_{DS} values can be explained by a spatial shift of the ambipolar regime in the channel, as described by the model given by Smits et al. (22) From the slope of $I_D^{1/2}$ vs V_G at $V_D = +30$ and 30 V, we determined the electron mobility of 2.1×10^{-2} $cm^2\ V^{-1}\ s^{-1}$ and the hole mobility of 1.1×10^{-2} $cm^2\ V^{-1}\ s^{-1}$ for the ambipolar device. More than 20 devices were fabricated by using the contact film transfer, and over 80% of the prepared devices clearly showed the ambipolar transport properties with hole mobilities in the range of $(0.6-1.1) \times 10^{-2}$ $cm^2\ V^{-1}\ s^{-1}$ and electron mobilities in the range of $(1.5-2.1) \times 10^{-2}$ $cm^2\ V^{-1}\ s^{-1}$. The values of both the electron and hole mobilities for the present ambipolar device are 1−2 orders of magnitude higher than those reported previously for devices based on a mixture of P3HT and PCBM, in which the disordered structure of the blended films has a detrimental effect on carrier transport (23, 24). To the best of our knowledge, the ambipolar mobility values observed here are the highest values among two-component transistors based on solution-based processes reported to date (14, 25, 26). Although it is still lower than the highest value for single-component ambipolar OTFTs (27), our approach can be easily applied to other organic materials with higher mobilities. It is noteworthy that these mobility values were obtained under ambient conditions and no significant change in the device performance was observed compared with the measurements under vacuum. This suggests that the P3HT layer can protect the n-channel transport in PCBM

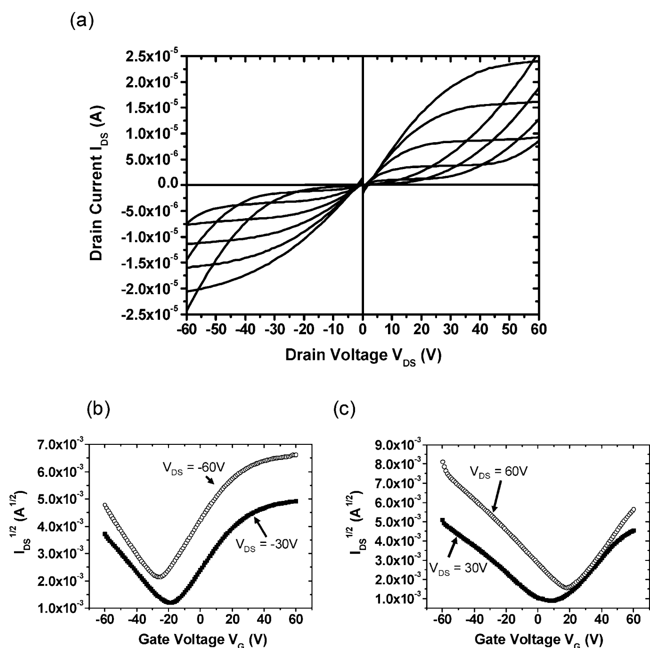

FIGURE 2. (a) Output characteristics of the P3HT/PCBM bilayer transistor. The gate voltage ranges from 0 to −60 V (−10 V increments) for holes and from 0 to 60 V (+10 V increments) for electrons. (b) Transfer characteristics: V_G vs $I_{DS}^{1/2}$. Filled squares refer to $V_{DS} = -30$ V; open circles refer to $V_{DS} = -60$ V. (c) Transfer characteristics: V_G vs $I_{DS}^{1/2}$. Filled squares refer to $V_{DS} = 30$ V; open circles refer to $V_{DS} = 60$ V.

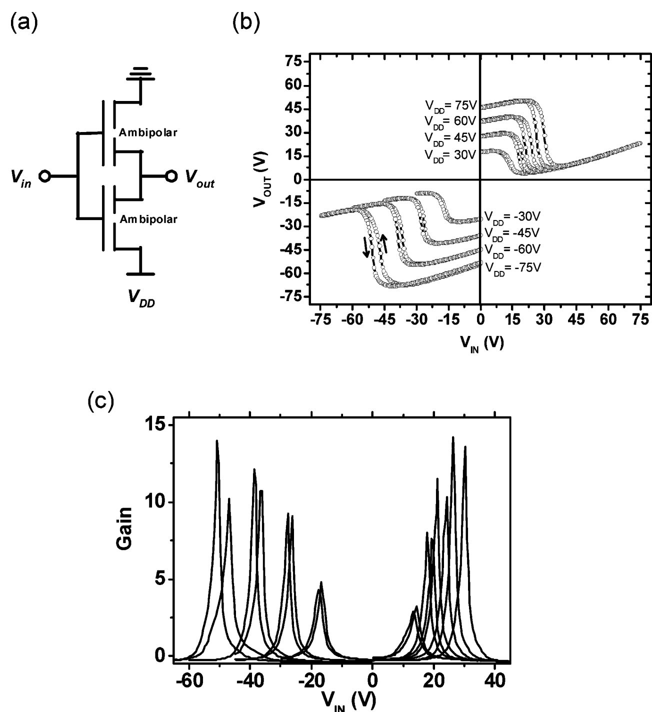

FIGURE 3. (a) Schematic representation of the electrical connections for the inverter based on two identical ambipolar transistors. (b) Transfer characteristics and (c) gain curves of the complementary inverters under the application of different V_{DD} values.

Table 1. Summary of the Transistor Properties for Different Structures

	electron mobility μ_e (cm^2 V^{-1} s^{-1})	hole mobility μ_h (cm^2 V^{-1} s^{-1})	threshold voltage V_T (V)	on/off ratio
transferred P3HT		9×10^{-2}	−1	10^3
spin-coated PCBM	3×10^{-2}		9	10^4
P3HT/PCBM ambipolar		1×10^{-2}	−7	10
	2×10^{-2}		8	25

against the penetration of oxygen during the electric measurements for a period of at least several hours.

As summarized in Table 1, the electron mobility of the ambipolar devices is close to that of unipolar transistors based on a single layer of PCBM. This result is reasonable because the electron-transport channel is exactly the same in both devices. On the other hand, the ambipolar transistor has a lower hole mobility than P3HT unipolar transistors prepared by contact film transfer onto a dielectric layer (15). This can be attributed to several factors. First, the P3HT/PCBM interface could be rougher than the P3HT/BCB interface. Carrier transport would be adversely affected by rough interfaces, as reported in the case of layered ambipolar transistors fabricated by vacuum evaporation (11). The second possibility is that more trap sites for holes exist on the surface of the PCBM layer compared with the BCB layer. Also, the difference in the geometry of drain-source electrodes for P3HT, namely, top contact for the unipolar transistor and bottom contact for the ambipolar transistor, one possible reason for the mobility difference. Detailed analysis of the interfacial properties is underway. It is noteworthy that the on/off ratios of the ambipolar transistors are generally much lower than those of the unipolar devices because the ambipolar transistors are never fully switched off, and therefore leakage currents always exist (6).

The bilayer ambipolar transistors had electron and hole mobilities that were highly balanced. Therefore, they were expected to be applicable to organic complementary inverters. The inverters were fabricated by the same procedure as that used for the ambipolar OTFTs except that a gold electrode pattern was used to connect two identical ambipolar P3HT/PCBM transistors on a single substrate. The schematic representation of the electrical connections is shown in Figure 3a. In the circuit, the input voltage V_{in} was applied to the common gate for both transistors. Plots of the output voltage V_{out} as a function of V_{in} under the different supply voltages V_{DD} are shown in Figure 3b. When positive V_{DD} and V_{in} are applied, the inverter works in the first quadrant. When V_{DD} and V_{in} are negative, the inverter works in the third quadrant. This is a characteristic behavior of ambipolar transistor-based inverters that cannot be observed in inverters based on unipolar transistors that work only in one quadrant (6). With $V_{DD} = +75$ and -75 V, a high output voltage gain of 14 was obtained (Figure 3c), which is defined as the steepness of the transitions between the high and low voltage states. The output voltage swing could be controlled by changing the supply voltage V_{DD} from −75 to +75 V. This result demonstrates the usefulness of the contact-film-transfer approach for fabricating various electronic devices in very simple steps.

LETTER

In summary, we successfully fabricated ambipolar OTFTs and inverters based on a bilayer structure of P3HT and PCBM by using a contact-film-transfer method. These results indicate that contact film transfer provides a facile way to construct multilayered structures with well-defined smooth interfaces and to fabricate complicated organic electronic devices. Further improvement may be achieved by using other organic materials with higher mobilities. This transfer technique could also be applicable to the fabrication of bilayer organic solar cells.

EXPERIMENTAL SECTION

Chemicals. Poly(3-hexylthiophene) (P3HT; Lisicon SP001) was used as received from Merck Chemicals. PCBM (E100) was purchased from Frontier Carbon Corp., Tokyo, Japan. Chlorobenzene (C_6H_5Cl; 99.8%) was purchased from Aldrich, Madison, WI. Divinyltetramethyldisiloxanebis(benzocyclobutene) (BCB; CYCLOTENE 3000) was received from Nissan Chemical, Tokyo, Japan.

Device Fabrication and Characterization. Transistors were fabricated on highly doped n-type (100) Si substrates (<0.02 Ω cm) with 300-nm thermally grown silicon dioxide. The SiO_2 surface was passivated with BCB (CYCLOTENE 3000), which was spin-coated from a dilute trimethylbenzene solution, and cross-linked at 250 °C on a hot plate for 3 h in a nitrogen-filled glovebox. The capacitance of the gate dielectric was $C_i = 10.7 \pm 0.7$ nF cm^{-2}, which was measured by using the charging time. For film preparation, chlorobenzene solutions (10 mg mL^{-1}) of P3HT or PCBM were spin-coated onto the substrates (600 rpm, 30 s). Gold electrodes were evaporated on top through a metal mask ($L = 70$ μm and $W = 6$ mm). The electrical characteristics of the transistors were measured using Keithley 2400 and 6430 source/measurement units at room temperature. The measurements for the PCBM transistors (n channel) were performed under vacuum (<1 × 10^{-4} Torr), and the measurements for the P3HT transistors (p channel), ambipolar transistors, and inverters were performed under ambient conditions.

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