Two-dimensional organic single-crystalline p-n junctions for ambipolar field transistors

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ABSTRACT Two-dimensional single-crystalline p-n junctions of organic semiconductors (pn-2DCOSs) show great potential in organic logic circuits due to their single crystal nature and excellent ambipolar charge transport. However, there are only few reports on pn-2DCOSs because it is difficult to obtain such highly ordered structure in p-n junction. Herein, a novel and effective solution processing method of secondary transfer technology based on the facile drop casting is used to fabricate devices of pn-2DCOSs based on C₈-BTBT (p-type) and TFT-CN (n-type) successfully. The high-performance ambipolar field transistors based on such ultrathin pn-2DCOSs with several molecular layers thickness show well-balanced ambipolar charge transport behaviors with hole mobility as high as 0.43 cm² V⁻¹ s⁻¹ and electron mobility up to 0.11 cm² V⁻¹ s⁻¹, respectively. This work is essential for studying the intrinsic properties of organic p-n junctions and achieving high performance in organic complementary circuits.

Keywords: two-dimensional materials, ambipolar field transistors, p-n junctions, single crystals

INTRODUCTION

Single crystals are widely used in semiconductor devices due to their potential for studying the relationship between molecular structure and charge transport [1–3]. Two-dimensional crystals of organic semiconductors (2DCOSs) have attracted wide attention because of the unique advantages of organic materials [4–7] as a new research issue of organic electronics and two-dimensional crystals in recent years [8–12]. 2DCOSs possess the advantages of long-range ordering, no grain boundary, few impurities and defects in the organic single crystal structures [13]. They were widely used in high-performance stretchable devices for their good flexibility [14].

Moreover, ultra-thin nature of 2DCOSs endows them with high transparency which is expected to make transparent devices [15]. In addition, 2DCOSs have ideal band gaps and specific functions (electronic, optical, or magnetic) by molecular design [16]. The array and integration of large-area single crystals provide the possibility to prepare large-scale integrated flexible circuits [17,18].

Ambipolar field transistors are one of the important parts of circuits, especially complementary circuits [19]. p-n junctions are the basic elements to realize ambipolar field transistors and the foundation of modern electronic technology [20,21]. 2D single-crystalline p-n junctions of organic semiconductors (pn-2DCOSs) become a potential research due to their abundant raw materials and highly ordered molecular packing. Regrettably, the preparation of 2DCOSs is still in the primary stage, and the preparation of pn-2DCOSs is rarely reported [22]. Therefore, the development of highly efficient methods for fabricating highly ordered pn-2DCOSs is of great significance for the study of p-n junctions.

Here, we described an ingenious growth method of pn-2DCOSs based on C₈-BTBT and TFT-CN with few molecular layers thickness by “secondary transfer method”, which was based on the facile drop casting method [23]. This new method to prepare pn-2DCOSs is simple and convenient with no need to design the molecules with ambipolar characteristic and find suitable orthogonal solvents. The pn-2DCOSs are expected to help study the intrinsic properties of organic p-n junctions. Impressively, the pn-2DCOSs showed ambipolar charge transport characteristics in field-effect transistors (FETs) with the best performance of 0.43 cm² V⁻¹ s⁻¹ for hole mobility and 0.11 cm² V⁻¹ s⁻¹ for electron mobility. This work provides a new method for fabricating two-di-

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mensional organic single crystalline p-n junctions.

EXPERIMENTAL SECTION

C₈-BTBT and TFT-CN 2DCOSs

C₈-BTBT (in Fig. 1a) bought from Daeyeon chemicals without further purification was dissolved in chlorobenzene with the concentration of 1 mg mL⁻¹ and the weighting bottles (60 mm × 30 mm) were cleaned by sonication in acetone and isopropyl alcohol for 20 min successively. Next, 25 mL deionized water was added into the weighting bottles as a substrate for crystal growth. Then, 20 μ L of the chlorobenzene solution of C₈-BTBT was drop-cast onto the deionized water surface and then set quickly. When the solvent evaporated entirely, the C₈-BTBT 2DCOSs were obtained floating on the water surface. With the same procedure, TFT-CN (in Fig. 1b) 2DCOS was produced. TFT-CN was synthesized and purified according to previous reports [23,24].

pn 2DCOS fabrication

As described in Scheme 1, a SiO₂ (300 nm)/Si substrate was inserted at an angle into the water below the water surface, and TFT-CN 2DCOS on the water surface was easily transferred to the SiO₂ (300 nm)/Si substrate. When water evaporated, TFT-CN 2DCOS fell tightly and smoothly on the substrate automatically. Then the location of TFT-CN 2DCOS on the substrate was confirmed by optical and crosspolarized optical microscope, and C₈-BTBT 2DCOS can be transferred on the substrate with TFT-CN 2DCOS by using the same transferring method. Thus, C₈-BTBT 2DCOS and TFT-CN 2DCOS were

overlapped and pn-2DCOS with C₈-BTBT and TFT-CN were prepared.

Device fabrication

SiO₂ (300 nm)/Si wafers were cleaned by deionized water, isopropanol, deionized water, piranha solution (70/30 vol/vol H₂SO₄/H₂O₂), deionized water, isopropanol and oxygen plasma, successively. Devices were fabricated with bottom-gate/top-contact (BGTC) configuration using Au (160 nm) as source and drain electrodes by stamping method on SiO₂ (300 nm)/Si.

Characterization

Optical and crosspolarized optical microscopy images were taken with Nikon ECLIPSE Ci-POL polarized optical microscope with a blue filter. Typical bright-field transmission electronic microscopy (TEM) image and selected area electron diffraction (SEAD) were conducted on a Tecnai G² F20 S-TWIN. The floating TFT-CN and C₈-BTBT 2DCOS were transferred onto the Cu grid directly for TEM measurement. X-ray diffraction (XRD) for investigating the crystallinity and orientation of single crystal films was carried out in reflection mode at 45 kV and 200 mA with monochromatic Cu K α radiation utilizing a Rigaku Smartlab diffractometer. The general (Bragg-Brentano focusing) package measurement mode was used to realize out-of-plane 2θ scan XRD measurement, where 2θ represented the angle between incident beam and diffracted beam. Atomic force microscopy (AFM) images were obtained using a Bruker Dimension Icon with intelligent mode. The FET characteristics were measured using a micromanipulator 6150 probe station

Figure 1 Optical micrographs of C₈-BTBT, TFT-CN and pn-2DCOS. Crosspolarized optical micrographs (a–c); polarized optical microscopy photo rotated 45 degrees (d–f) of C₈-BTBT, TFT-CN and pn-2DCOS.

connected to a Keithley 4200-SCS in a clean and shielded box. All measurements were carried out in the air at room temperature.

RESULTS AND DISCUSSION

As shown in Scheme 1, the fabrication of pn-2DCOSs is very facile. By casting chlorobenzene solutions of C₈-BTBT and TFT-CN on the surface of water with pipette, high-quality ultrathin C₈-BTBT and TFT-CN 2DCOS can be easily prepared. When solution dropped onto the water surface, they spread over the whole water surface quickly on account of the surface tension. Coffee-ring effect can be suppressed by eliminating the pinned three-phase contact line, while the nucleation density can be reduced due to the larger spread area compared with a solid substrate. Under intermolecular van der Waals forces, solute molecules can self-assemble with solvent evaporation. Hence, large-area uniform crystalline ultrathin single crystal films were obtained on the water surface. The single crystal films can be easily transferred to silicon substrates. A substrate was inserted into TFT-CN solution with a very tiny angle, and TFT-CN 2DCOS was transferred onto the substrate. When the water was pumped away, the TFT-CN 2DCOS fell on the substrate. And then, using the same method C₈-BTBT 2DCOS can be easily transferred to the substrate with TFT-CN 2DCOS. As a result, TFT-CN 2DCOS and C₈-BTBT 2DCOS overlapped. In this way, pn-2DCOS with C₈-BTBT and TFT-CN were prepared.

Scheme 1 Flow chart of preparing pn-2DCOS.

We successfully prepared C₈-BTBT 2DCOS, TFT-CN 2DCOS and pn-2DCOS of C₈-BTBT and TFT-CN. Fig. 1a–c display bright-field optical and crosspolarized optical microscopy images of C₈-BTBT 2DCOS, TFT-CN 2DCOS and pn-2DCOS on a treated SiO₂ (300 nm)/Si wafer. Each of images shows a clear and regular boundary between the single crystal film and substrate with no obvious cracks or grain boundaries on the single crystal film in the field of view. Under a crosspolarized optical microscope (Fig. 1d–f), the colors and shades of C₈-BTBT 2DCOS, TFT-CN 2DCOS and pn-2DCOS change uniformly, when the samples are rotated under polarized light due to the long-range alignment of C₈-BTBT and TFT-CN crystals.

XRD patterns of C₈-BTBT 2DCOS, TFT-CN 2DCOS and pn-2DCOS were characterized to assess the quality and molecular packing of the crystal (Fig. 2a). The smooth baseline and sharp diffraction can be seen, indicating the highly order and crystalline quality of C₈-BTBT 2DCOS, TFT-CN 2DCOS and pn-2DCOS. The corresponding secondary diffraction peaks were also observed, manifesting the layer-by-layer growth of organic semiconducting molecules on the substrate. The diffraction peak at $2\theta=5.5^\circ$ is well assigned to the (001) diffraction peak of TFT-CN according to the simulated single crystal data. The corresponding second-order diffraction peak of TFT-CN at 11.2° (002) was also observed. At the same time, the corresponding second-order and third-order diffraction peak of C₈-BTBT at 6.1° (002) and 9.1° (003) can be observed at the patterns of C₈-BTBT and pn-2DCOS. The single crystal structure diagram of C₈-BTBT shows that the molecule adopts typical herringbone packing (Fig. 2b), while TFT-CN adopts a slipped face-to-face packing with a strong π - π partial overlap between adjacent molecules in ab plane of single crystal film (Fig. 2c). As shown in Fig. 2d, the C₈-BTBT 2DCOS has a thickness of 21.796 nm, corresponding to ~ 7 stacked monolayers (ML) of C₈-BTBT. What's more, the root mean square roughness (RMS) is ~ 0.30 nm when sampled over $3\ \mu\text{m} \times 6\ \mu\text{m}$. As RMS is close to atomic flatness, the crystallinity of C₈-BTBT 2DCOS was pretty good. TEM image and SEAD patterns of C₈-BTBT 2DCOS transferred to a copper grid are shown in Fig. 2e, f. The C₈-BTBT 2DCOS displays a uniform morphology over the entire selected area and there is no change in the SEAD patterns at different parts of the same film, certifying the single crystal nature in the entire film. In Fig. 2g, AFM image shows that the TFT-CN 2DCOS has a thickness of 4.332 nm. Considering the packing of TFT-CN molecules on the substrate and the layer spacing of

Figure 2 Structure characterization of C_8 -BTBT, TFT-CN and pn-2DCOS. (a) XRD patterns of C_8 -BTBT, TFT-CN and pn-2DCOS; (b, c) molecule packing of C_8 -BTBT, TFT-CN; (d) AFM image of the typical C_8 -BTBT 2DCOS on a silicon substrate with the RMS roughness estimated at ~ 0.30 nm and thickness of 21.796 nm; (e, f) TEM image and its corresponding SAED patterns of individual C_8 -BTBT 2DCOS; (g) AFM image of the typical TFT-CN 2DCOS on a silicon substrate with the RMS roughness estimated at 0.35 nm and thickness of 4.332 nm; (h, i) TEM image and its corresponding SAED pattern of individual TFT-CN 2DCOS.

1.6 nm from the single crystal structure information of TFT-CN [23], the 2DCOS has three molecule layers. The RMS is ~ 0.35 nm when sampled over $10\ \mu\text{m} \times 20\ \mu\text{m}$, approaching atomic flatness. In Fig. 2h, i, the TEM image and SEAD patterns of TFT-CN 2DCOS transferred to a copper grid indicate that the whole film is a single crystal. All the above results indicate the 2DCOS are ultrathin with good crystallinity.

We fabricated bottom-gate and top-contact FETs with the obtained p-n junctions of C_8 -BTBT and TFT-CN (Fig. 3a, Fig. S1), and measured the charge transport properties in air. In Fig. 3b, c, the pn-2DCOS devices display the typical transfer characteristics with classic V-shaped curves, wherein the two arms stand for electron transport and hole transport, respectively. The transfer characteristics in p-channel (Fig. 3b) and n-channel (Fig. 3c) operation modes confirm the excellent gate

modulation. The channel width of the device is $149.4\ \mu\text{m}$ (for p channel) and $95.5\ \mu\text{m}$ (for n channel), while the channel length is $58.4\ \mu\text{m}$ (Fig. S1). The best FET performance was achieved from the C_8 -BTBT and TFT-CN pn-2DCOS grown from a solution ($[C_8\text{-BTBT}] = 1\ \text{mg mL}^{-1}$, $[TFT\text{-CN}] = 1\ \text{mg mL}^{-1}$), with the most balanced hole mobility of $0.43\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ and electron mobility of $0.11\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$. For hole transport, on-to-off current ratio ($I_{\text{on}}/I_{\text{off}}$) is $>10^5$ and threshold voltage (V_T) is about -10 V, while for electron transport, $I_{\text{on}}/I_{\text{off}}$ is $>10^3$ and V_T is about 15 V. Compared with the hole and electron mobility of the single crystal devices, the mobility of the p-n junctions is comparable but slightly lower [23,25]. The highest mobility of pure p-type C_8 -BTBT 2DCOS devices is up to $2.1\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ (Fig. S2a, b), while the highest mobility of pure n-type TFT-CN 2DCOS devices is up to $0.8\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ (Fig. S2c, d). This may

Figure 3 Structure and transfer curves of pn-2DCOS. (a) Three dimensional device schematic of ultrathin pn-2DCOS; (b, c) transfer curves of the ultrathin pn-2DCOS FET with $V_{ds}=-40$ V and $V_{ds}=40$ V.

result from trace amount of water between C_8 -BTBT 2DCOS and TFT-CN 2DCOS. The water is introduced during the transfer which is inevitable and leads to the lower hole and electron mobility compared with that of individual materials.

CONCLUSIONS

In summary, an ultrathin pn-2DCOS of C_8 -BTBT and TFT-CN with thickness of few nanometers was fabricated by a simple method on water surface by which the size of pn-2DCOS can reach up to millimeter size with thickness of several molecular layers by molecular interaction. The FETs based on the junctions show ambipolar charge transport characteristics, with the best performance of $0.43 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for hole mobility and $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electron mobility, respectively, indicating well-balanced ambipolar charge transport behaviors. This efficient method for the preparation of highly ordered organic semiconductor single crystal p-n junctions is of great significance for the study of high performance organic electronic devices and the construction of high-speed circuits.

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Supplementary information Supporting data are available in the online version of the paper.

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二维有机单晶p-n结用于双极晶体管

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摘要 有机二维单晶半导体p-n结(pn-2DCOS)因其单晶性质和出色的双极性电荷传输特点, 在有机逻辑电路领域具有巨大的应用潜力. 然而, 在p-n结中获得高度有序的单晶结构异常困难, 因此关于pn-2DCOS的文献报道很少. 本文基于简单滴注法和有效的二次转移技术成功得到基于C₈-BTBT(p型)和TFT-CN(n型)的pn-2DCOS器件. 这种具有几个分子层厚度的超薄pn-2DCOS的高性能双极场效应晶体管具有良好的平衡双极电荷传输性质, 空穴迁移率高达0.43 cm² V⁻¹ s⁻¹, 电子迁移率高达0.11 cm² V⁻¹ s⁻¹. 这项工作作为研究有机p-n结的固有特性提供了有效方法, 并可为实现高性能有机互补电路提供借鉴.