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Large-scale fabrication of field-effect transistors based on solution-grown organic single crystals

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Abstract A simple solution processing method was developed to grow large-scale well-aligned single crystals including 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene), anthracene, tetracene, perylene, C_{60} and tetracyanoquinodimethane. As pinned by a solid needle, a droplet of semiconductor solution dried into single-crystal arrays on a 1 cm × 2 cm substrate. TIPS-pentacene was used to demonstrate the fabrication of hundreds of field-effect transistors (FETs) with the hole mobility as high as 6.46 $cm^2\ V^{-1}\ s^{-1}$. As such, this work provides a high-throughput, yet efficient approach for statistical examination on the FET performance of organic single crystals.

Keywords Organic single-crystal transistors · Large scale · High mobility · Solution process

1 Introduction

Field-effect transistors (FETs) made of organic single crystals show superior mobility values [1–8] as organic single crystals have fewer structural defects than their amorphous and polycrystalline counterparts [9–12]. In fundamental research, organic single-crystal FETs are ideal for studying the charge transport characteristics of organic semiconductors [13–15]. From a technological standpoint, organic single crystals are attractive candidates for applications in low-cost microelectronics and optoelectronics [16, 17]. For both fundamental studies and technological applications, high-throughput fabrication of single-crystal FETs is highly desired for either examination of device performance statistics or realization of a large array of devices. Initially, bottom-up strategies were used to achieve device arrays through either patterning the crystal nucleation sites or patterning the crystallization media [18–23]. Alternatively, once large-sized single crystals were, occasionally, obtained [24], top-down patterning techniques could become possible [25]. Compared to patterning, crystal alignment is a much more simple approach to fabricate device array in large scale as the source and drain electrodes can be easily deposited perpendicular to the alignment direction [6, 22, 26–28].

Crystal alignments of organic semiconductors were achieved by either templating (e.g., polydimethylsiloxane (PDMS)) [27, 29] or template-free methods [30, 31]. Recently, unidirectional receding of a droplet regulated by the capillary force has been found to be an efficient and facile approach to align single crystals of organic semiconductors [6, 32–36]. As an evaporating droplet of a semiconductor solution was pinned, typically, by a small piece of solid (termed "pinner") such as silicon wafer, its directional receding led to aligned crystallization with a direction followed that of the droplet receding. Given that a very limited number of crystals were grown using these droplet-pinned methods, it is necessary to see how general this

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aligned crystallization is. In this work, we examined the crystallization of six organic semiconductors and obtained aligned crystals on 1 cm × 2 cm substrates. Also, we modified the previously reported droplet-pinned crystallization (DPC) method [6] by using metal needles as more convenient pinners to achieve higher surface coverage of the crystals.

2 Materials and methods

2.1 Materials

6,13-Bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene, ≥99 %), tetracene (≥99 %), perylene (≥99 %), and tetracyanoquinodimethane (TCNQ, 98 %) were purchased from Sigma-Aldrich, while anthracene (≥99 %) was purchased from Fluka and C_{60} (≥99 %) from Alfa Aesar. All the reagents were used without further purification. Polyvinyl alcohol (PVA) was purchased from Sinopharm Chemical Reagent Co. A 15 wt% water solution of PVA was prepared by heating and stirring.

2.2 Crystallization

Crystals were grown in situ on substrates for FETs, highly doped silicon substrates (1 cm × 2 cm) with 300 nm SiO_2. Before crystallization, the substrates were modified by divinyltetramethyldisiloxane bis(benzocyclobutene) (BCB, Dow Chemicals) thin layers that were spin-coated from a mesitylene (Acros) solution (v_{BCB}:$v_{mesitylene}$ = 1:30) and thermally cross-linked on a hot plate in a N_2 glove box at the temperature of 120 °C (30 min), 180 °C (30 min) and 240 °C (30 min). Organic semiconductor solution (0.4 mg/mL, 40 μL) was dropped onto a substrate. Pinners were placed on the substrates to pin the solution droplets. Three types of pinners were used, including 4 mm × 15 mm silicon wafers, nickel-plated needles and PVA ribbons. The silicon substrate with the droplet was placed on a Teflon slide inside a Petri dish (35 mm × 10 mm) sealed with parafilm. Crystals formed on the silicon substrate after the solvent slowly evaporated on a hot plate (25 °C for anthracene, 30 °C for TIPS-pentacene, perylene and C_{60}, 50 °C for tetracene and TCNQ). Ribbon-shaped crystals were grown from different solvents (CCl_4, HPLC, Aladdin) for anthracene, *p*-xylene (TCI, HPLC, Sigma-Aldrich) for tetracene, *m*-xylene (HPLC, Sigma-Aldrich) for perylene, toluene (HPLC, Tedia) for TCNQ, mixed solvents (v_{CCl_4}:$v_{m\text{-xylene}}$ = 1:1) for TIPS-pentacene and mixed solvents (v_{CCl_4}:$v_{m\text{-xylene}}$ = 4:3) for C_{60}, and the solution dried out in 0.5–2 h.

2.3 Characterization

The morphology and crystalline structures were characterized by optical microscopy (OM, Nikon LV100 POL, Nikon) and atomic force microscope (AFM, Veeco 3D, Veeco). The single-crystalline structures were examined by selected area electron diffraction (SAED, JEOL 1400, JEOL). FETs were constructed by depositing top-contact source and drain electrodes (80–100 nm Au, depending on the thickness of the crystals) in a bottom-gated configuration. The channel length and width were 50 μm and 1 mm separately. Current–voltage characteristics of the devices were measured using a Keithley 4200-SCS semiconductor parameter analyser (Keithley) in a N_2 glovebox. The measured capacitance of the BCB-covered SiO_2/Si substrates was 10 nF cm^{-2}, and this value was used for mobility calculation. For statistics, data of crystal heights, widths and hole mobility are presented as mean ± SD.

3 Results and discussion

We first improved the DPC method [6] for crystallization. The silicon pinner is the key component for the DPC method as it pins the droplet of semiconductor solution to provide a steady droplet receding and continuous crystallization. Although a few crystals and their junctions were obtained using silicon pinner [6, 35–37], shortcomings of this pinner were clearly seen. First, as the silicon pinner is typically 4 mm wide, a large portion (~40 %) of the substrate surface is covered by the wafer and, thus, is not accessible to the crystals (Fig. 1a). Second, cutting wafer into smaller millimetre-sized pinners with sharp edge is a non-trivial process prohibitive for producing devices with reasonable throughput. In order to avoid these two shortcomings, pinners of varied materials were tested. One of the requirements of the pinner is that it will not be dissolved by organic solvents during crystallization. As such, water-soluble PVA was used, 15 % of PVA aqueous solution was injected through a syringe onto a substrate and dried into a stripy PVA pinner (Fig. 1c). A droplet of TIPS-pentacene solution pinned by the PVA pinner crystallized into well-aligned crystal arrays on a 1 cm × 2 cm substrate (Fig. 1d). Although the PVA pinner was about 2–3 mm wide, further studies on rheology might lead to narrower size and eventually realize printable pinners for crystallization in large area.

Another pinner material we examined was nickel-plated needle with a diameter of 0.7–0.8 mm that occupies much less space than the 4-mm-wide silicon pinner.