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Directed self-assembly of organic semiconductors via confined evaporative capillary flows for use in organic field-effect transistors

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ABSTRACT

We fabricated well-defined 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-PEN) crystal arrays for use in electronic applications via a simple but effective method, the confined evaporative capillary flow (CEC) method. This has been accomplished by systematically controlling the contact line pinning at the edge of glass stylus and the outward hydrodynamic flow within the drying droplet with various processing solvents and surface properties of the substrate during solidification. We found that after CEC coating of TIPS-PEN solution dissolved into toluene onto SiO_2 surface, ribbon-shaped TIPS-PEN crystals were well developed with a width of 20–100 μm and length of 300 μm – 2 mm, which is presumably owing to optimized capillary evaporation. Specifically, TIPS-PEN crystals present highly preferred crystal orientation along the (*l* 0 0) axis, which can lead to efficient charge transport in a lateral direction. Thus, TIPS-PEN field-effect transistors (FETs) exhibited a good hole mobility of 0.72 cm^2/Vs.

1. Introduction

Organic field-effect transistors (OFETs) based on solution-processed organic semiconductors (OSCs) offer a viable alternative to amorphous silicon (a-Si:H)-based FETs because they are easily processed and provide good optoelectrical properties for use in low-cost flexible integrated circuits, displays, and sensors [1–6]. The fabrication of organic crystalline films from solution-state small molecule OSCs, such as 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-PEN) or triethylsilylethynyl anthradithiophene (TES-ADT), is advantageous in that it avoids vacuum deposition techniques and may potentially be used to prepare large-area OFETs with mobilities exceeding 1 cm^2/Vs [7–9]. The direct preparation of highly ordered crystals through solution coating methods remains a challenge, in part because solvents tend to evaporate rapidly, crystal nucleation is stochastic, and the fluid flows include instabilities [9]. It is worth noting that conventional solution-coating methods, such as spin-coating or drop-casting, do not allow for control over the crystal growth and orientation, which are required for the fabrication of

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high-performance large-area films. In an attempt to address these problems, several solution processing approaches have been tested for their utility in preparing aligned OSC crystals with large domains and over large areas. Some of the techniques tested include dip coating [10], zone casting [11], solution shearing [8,9], hollow pen writing [12], and pinned drop casting on an inclined substrate [13]. Well-defined single crystalline patterns rely, above all else, on controlling the nucleation and growth of OSC materials from solution. Such control requires optimization of the solvent boiling temperature, the substrate's wettability in the presence of the solution, and the affinity of the solvent for the OSC solute.

Adopting a similar principle of crystal growth, in this study, we designed a simple, but very effective confined evaporative capillary flow (CEC) method (Scheme 1) to enable directed self-assembly of OSCs over large area during solidification. Our method utilizes confining evaporative droplet in the geometry consisting of curved upper surface on flat lower substrate, in which OSC molecules are self-organized to form highly ordered crystals as a result of the outward capillary flow driven by confined evaporating meniscus during solvent evaporation. The crystal morphologies could be tuned by adjusting the solvent type and substrate surface energy, because hydrodynamic flows inside the confined evaporative droplet is influenced by the boiling point of the solvent and the interaction between a droplet and its substrate [14–16]. The molecular orientations within the TIPS-PEN crystals grown using the CEC method were investigated, and OFETs based on the self-assembled TIPS-PEN and TES-ADT organic crystals were fabricated on SiO_2/Si substrates.

2. Experimental

2.1. Device fabrication

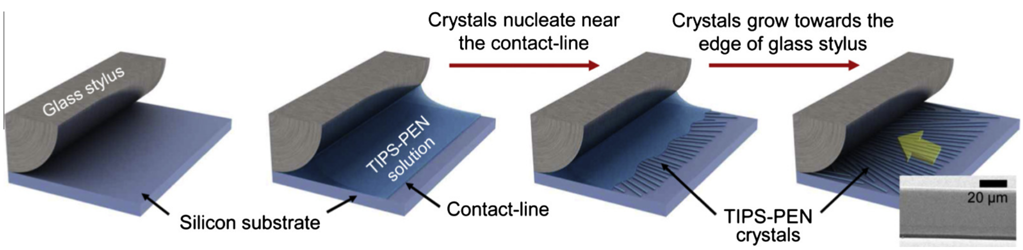
OFETs were fabricated using a highly doped *n*-type Si wafer with a thermally grown 300 nm thick oxide layer as the substrate. The wafer served as the gate electrode, whereas the oxide layer acted as a gate insulator. Prior to treating the silicon oxide surface, the wafer was cleaned in piranha solution for 30 min at 100 °C, then washed with copious amounts of distilled water. The SiO_2 substrate was treated using octadecyltrichlorosilane (ODTS, Gelest, Inc.) and hexamethyldisilazane (HMDS, Aldrich Chemical Co.) to control the surface characteristics by a previously reported method [14]. A semicylindrical glass stylus with an outer wall diameter of 3 cm was placed on top of the substrate. A 0.5 mg/mL TIPS-PEN solution (tetrahydrofuran (THF), chloroform, toluene, and chlorobenzene) was then dropped onto the substrate adjacent to the glass stylus. After dying the solvents, 50 nm-thick Au was thermally deposited through a shadow mask to define the source and drain contact electrodes on the TIPS-PEN crystal films.

2.2. Characterization

The film morphologies were imaged by optical microscopy (SOMTECH I-MEGASCOPE). The crystalline structure of the TIPS-PEN films was characterized by synchrotron X-ray diffraction (XRD) studies at the 5Abeamline of the Pohang Accelerator Laboratory (PAL), Korea. Transistor current–voltage characteristics were measured using Keithley 2400 and 236 source/measure units at room temperature under ambient conditions in a dark environment.

3. Results and discussion

The directed self-assembly of TIPS-PEN over a large area, using the CEC method, was accomplished by placing a semicylindrical glass stylus with an outer wall diameter of 3 cm on top of a silicon wafer substrate, as shown in Scheme 1. Next, a 0.5 mg/mL TIPS-PEN solution (tetrahydrofuran (THF), chloroform, toluene, and chlorobenzene) was dropped onto the substrate adjacent to the glass stylus. TIPS-PEN solution was confined in the gap between the glass stylus and flat substrate. We noted that confining evaporating droplet allows the solvent to evaporate preferably at the droplet contact line because of imposed geometrical constrain, rather than solvent evaporates over the entire droplet surface in the case of the drying droplet on a single surface [17,18]. This approach is beneficial to induce the directional hydrodynamic flows towards the contact line (outward hydrodynamic flows) in the drying droplet which is driven by the faster evaporation of solvent at the pinned contact line, commonly referred as "coffee-ring" effect [19]. Recently, periodic concentric patterns of various materials including carbon nanotubes and polymers have been successfully demonstrated by controlling the droplet evaporation in a confined geometry [17,20,21]. As the solvent evaporated slowly, the TIPS-PEN



Scheme 1. Schematic representation of the confined evaporative capillary flow (CEC) method. A TIPS-PEN solution droplet was pinned by a semicylindrical glass capillary. As the solvent evaporated slowly, the TIPS-PEN crystals nucleated near the contact line of the droplet. The nuclei then grew along the direction in which the contact line receded, toward the edge of the glass stylus. The inset shows the SEM image of TIP PEN crystals fabricated by CEC method.