Crystal Growth

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Solution-Based Direct Growth of Organic Crystals on an Active Channel Region for Printable Bottom-Contact Organic Field-Effect Transistors**

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In an attempt to gain a fundamental and rigorous understanding of the charge transport in and electrical properties of crystalline organic transistors at a microscopic or molecular level and to develop printing methods for cost-effective and mass-producible electronic devices, considerable effort has been expended in the study of organic crystals composed of π-conjugated organic molecules.[1] Generally, in comparison with networked organic thin-film field-effect transistors (OTFTs), crystalline organic transistors exhibit better electrical properties, such as higher carrier mobility, as a result of the regular orientation of molecules in the crystal, the absence of grain boundaries, and the low trap densities. However, the growth of crystals in the highest-mobility direction on an active channel region in organic field-effect transistors (OFETs) is technically a significant challenge.[2] Moreover, in solution-based processes, which are generally favorable for isotropic growth, it is very difficult to grow a well-oriented organic single crystal in an active channel region in transistors.[3] Thus, a practical solution-based approach to place crystalline organic materials in an active channel region in organic transistors involves the development of a direct growth method for the growth of dozens of well-oriented organic crystals in the channel. Research has been focused on organic semiconductor materials that can be processed in solution to create printed electronic devices, such as flexible displays, electronic signage, photovoltaic panels, membrane keyboards, radio-frequency identification tags (RFIDs), electronic sensors, and integrated electronic circuits. Printing methods are considered to be cost-effective and suitable for mass production.

In a living cell, functional structures are made through sequential ejections of constituent materials in a process similar to ink-jet printing. Ink-jet printing methods are the natural and appropriate choice for the production of low-cost printed electronic devices. Herein, we propose a simple and innovative method for the fabrication of bottom-contact well-oriented crystalline organic transistors. In this approach, which takes advantage of the hydrophobic–hydrophilic interaction between xylene and water, crystals are grown directly by using a micropipette and a modified drop-cast method similar to ink-jet printing. We were able to grow 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS pentacene) crystals on an active channel region in transistors by controlling the solvent-evaporation rates in a two-liquid system. Thus, we fabricated transistors with dozens of well-oriented organic TIPS pentacene crystals in the active channel region and with source/drain electrodes made from chemically modified Ag electrodes for efficient hole injection. The transistors exhibit a practical carrier mobility of $0.30\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$ and current on/off ratio of 4×10^8.

A number of solution-processable pentacene derivatives have been synthesized, characterized, and fabricated as organic transistors.[4] Among them, TIPS pentacene[5] has been widely used to fabricate high-performance OTFTs, as it has high solubility in most organic solvents and a high degree of π overlap; these features are responsible for the high charge-carrier mobility of OTFTs.[6] In the present study, to produce well-oriented TIPS pentacene crystals on an active channel region in bottom-contact OFETs, we controlled the evaporation rates of xylene solvent through its interaction with polar H_2O.

Figure 1 shows a schematic illustration of the direct growth of well-oriented TIPS pentacene crystals in a two-liquid system on an active channel region in bottom-contact OFETs. Dozens of TIPS pentacene crystals were grown directly along the radial direction in the xylene–water system on the circular active region of the OFETs. We used a heavily doped silicon wafer as the gate electrode and a hydrophobic hexamethyldisilazane-treated SiO_2 layer as the gate dielectric. Silver electrodes patterned by conventional photolithography and coated with a self-assembled monolayer of pentafluorothiophenol (PFTP) were used as the source/drain electrodes; PFTP–Ag electrodes facilitated efficient hole injection to TIPS pentacene in the active circular channel.[7] The bottom-contact electrodes consisted of a circular drain electrode located in the center region and an annular source electrode positioned in the periphery region (Figure 1a). The active region in transistors is an annular strip located between source and drain electrodes. To form highly ordered self-organized TIPS pentacene crystals on an active channel region, we placed a drop of water on the drain-electrode region by using a micropipette (Figure 1b). TIPS pentacene dissolved in *o*-xylene was then dropped on top of the water droplet with a micropipette (Figure 1c). Because *o*-xylene is immiscible with water, the TIPS pentacene solution in

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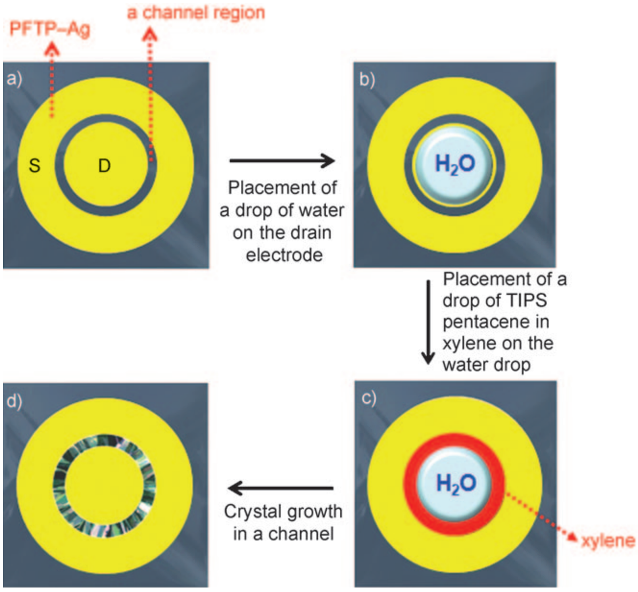

Figure 1. Schematic illustration of the procedure for the direct growth of well-oriented TIPS pentacene crystals on an active channel region in bottom-contact OFETs. Crystal growth occurs as a result of the evaporation of the volatile solvent and the hydrophobic–hydrophilic interaction between xylene and water. S = source electrode, D = drain electrode.

o-xylene spread out immediately from the center of the surface of the water droplet over the whole surface of the water droplet. As the *o*-xylene solvent started to evaporate from the outermost circumference, the crystallization of TIPS pentacene began at the outermost periphery of the area covered by the solution in *o*-xylene. The crystallization of TIPS pentacene continued until the *o*-xylene solvent had completely evaporated (Figure 1 d). Owing to the presence of the water droplet during the evaporation of the *o*-xylene solvent, the crystallization proceeded isothermally. Thus, it was possible to grow well-oriented TIPS pentacene crystals directly on an active channel region in transistors.

Figure 2 shows a polarized optical micrograph (POM) of a transistor with TIPS pentacene crystals and the X-ray diffraction (XRD) pattern of the directly grown TIPS pentacene crystals. The observation of thermal cracking in the TIPS pentacene crystals indicated that the crystal growth direction was [210], which is the best hole-transport pathway in the TIPS pentacene transistor.[8] Furthermore, the XRD pattern of these TIPS pentacene crystals contained diffraction peaks for the (001) reflection, which indicated that the TIPS pentacene molecules in the crystals had their bulky silyl groups positioned vertically on the substrate.[6b]

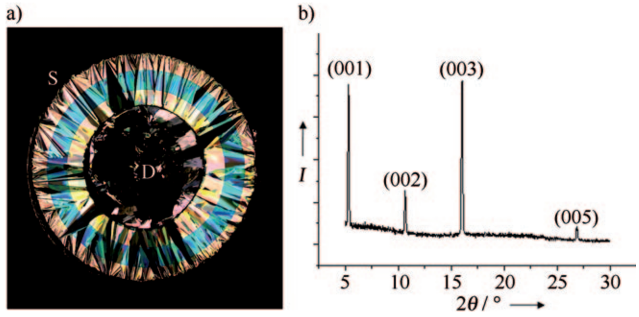

Figure 2. a) Polarized optical micrograph of a TIPS pentacene crystal transistor. b) XRD pattern of the corresponding TIPS pentacene crystals.

The output (a) and transfer characteristics (b) of the TIPS pentacene crystal transistors are shown in Figure 3. The field-effect mobility (μ) was obtained from the slope in the saturation region ($V_{DS} = -40$ V), and the W/L ratio was defined as the ratio of the circumference of the inner boundary of the source electrode to the radial distance between the source and the drain electrodes. The TIPS pentacene crystal transistors with PFTP–Ag electrodes exhibited a *p*-type mobility of 0.30 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ in the saturation region and a current on/off ratio of 4×10^8. We fabricated 16 devices and found the following average values: mobility, $(0.25 \pm 0.05)\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$; current on/off ratio, 2×10^8; threshold voltage, -1.3 V; and subthreshold slope, 0.7 V $\mathrm{decade^{-1}}$. These average values are similar to those of transistors with gold source/drain electrodes: An average mobility of $(0.24 \pm 0.05)\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$ and an average current on/off ratio of 10^8 were observed for TIPS pentacene crystal transistors with gold source and drain electrodes.

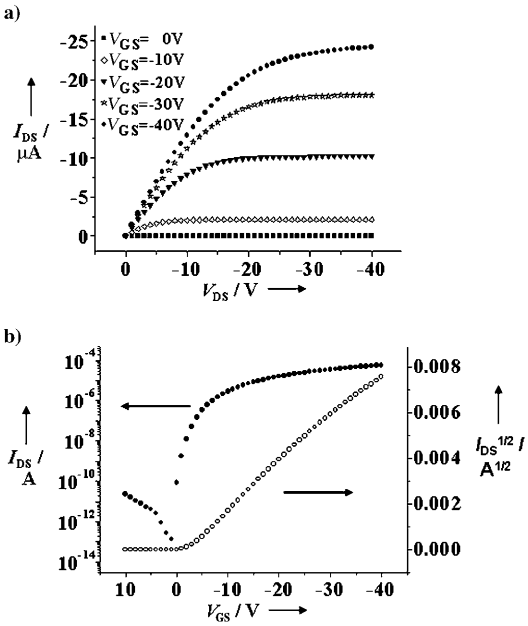

Figure 3. a) Output and b) transfer characteristics of TIPS pentacene crystal transistors.

In summary, we have developed a simple and innovative method for the fabrication of bottom-contact well-oriented crystalline OFETs. In an approach similar to ink-jet printing, crystals are grown directly by using a micropipette and a modified drop-cast method. A two-liquid system (xylene–water) was used, and dozens of TIPS pentacene crystals were grown directly on an active channel region in the highest-mobility direction through self-organization and the isothermal evaporation of the solvent in the two-liquid system. The

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obtained TIPS pentacene crystal transistors with PFTP–Ag electrodes exhibit a p-type mobility of 0.30 $cm^2 V^{-1} s^{-1}$ in the saturation region and a large current on/off ratio of 4×10^8. Our innovative method for the direct growth of organic crystals on patterned channel regions by utilizing a micropipette and taking advantage of the hydrophobic–hydrophilic interaction between the two constituents of a two-liquid system is expected to be suitable for the fabrication of low-cost and mass-producible printed electronic devices. Further studies on similar organic-crystal transistors are in progress.

Experimental Section

The transistors based on TIPS pentacene crystals were fabricated with the bottom-contact geometry. We used a heavily doped Si wafer as the gate electrode and a SiO_2 layer treated with hexamethyldisilazane (thickness ca. 300 nm) as the gate dielectric. A thermally evaporated layer of Ag (40 nm) was used as the source/drain electrodes and patterned by using a photolithography and lift-off method. The resulting bottom-contact electrodes were circular; they had a channel length, L (the length between the source and drain electrodes along the radial direction), of 200 μm and width (circumference of the inner circle of the annular source electrode) of 6280 μm. The self-assembled monolayers (SAMs) were formed on the patterned Ag electrodes by immersing them in a 1 mM ethanolic solution of pentafluorothiophenol (PFTP; Aldrich) for 1 h. The coated Ag electrodes were then taken out of the solution, rinsed with ethanol several times, and dried with N_2 gas. To form TIPS pentacene crystals on the active channel region, we placed a drop of deionzed water (ca. 0.05 μL) at the center of the circular drain region and then a drop of o-xylene solution (ca. 0.03 μL) containing TIPS pentacene (0.8 wt %) on top of the water droplet by using a micropipette. The crystallization of TIPS pentacene proceeded for about 1 min. The devices were then annealed at 90 °C for 10 min. Electrical characterization of the transistors was performed at room temperature in air by using a Keithley 4200-SCS semiconductor analyzer. The field-effect mobility (μ) was calculated in the saturation region ($V_{DS} = -40$ V) from the plot of the square root of the drain current versus V_{GS} by using Equation (1):

$$I_{DS} = \frac{W\,C_i}{2\,L}\,\mu(V_{GS} - V_T)^2 \tag{1}$$

in which I_{DS} is the source–drain saturation current, C_i (1.1×10^{-8} F) is the capacitance of the SiO_2 insulator, W/L is the ratio of the width to the channel length, and V_{GS} and V_T are the gate-source and threshold voltages, respectively.

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