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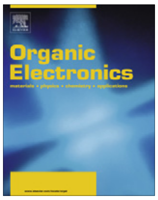

Two-dimensional crystal growth of thermally converted organic semiconductors at the surface of ionic liquid and high-mobility organic field-effect transistors

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ABSTRACT

We report a novel solution-crystallization method to grow two-dimensional platelet-shaped single-crystals of well-known insoluble organic semiconductors via thermal conversion of their precursor molecules dissolved in ionic liquids (ILs). By optimizing conditions of the crystal growth regarding physical properties of ILs such as density and viscosity, we successfully and reproducibly obtained thin platelets of pentacene and dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (DNTT) single-crystals, with which nearly the best performing field-effect transistors are constructed for the two compounds. The prompt and simple technique has opened the way to use practically insoluble organic semiconductor materials for high-performance printed electronics, which enables mass-producible and large-area organic circuitry devices.

1. Introduction

Organic field-effect transistors (OFETs) based on single crystals were first developed for fundamental studies to investigate intrinsic charge transport [1–4] and are now of growing interest for industrial application because of newly developed solution-crystallized high-mobility devices with the mobility exceeding 10 cm^2/Vs [5,6]. In addition to general material advantages such as absence of grain boundaries and minimum densities of disorders, defects and impurities, which can all slow down the charge transport, spontaneous emergence of molecularly flat crystalline surface plays an essential role in realizing the high performance in the practical devices. We note that the electric-field induced charge accumulates only at the first mono-molecular layer [7]. Such an ultra-flat crystalline surface is resulted from extremely large anisotropy between in-plane and out-of-plane growth speed, producing platelet-shaped crystals whose surface molecular arrangement is characterized by π–π interactions between adjacent molecules. Developing general methods to drive the two-dimensional crystal growth for such π-conjugated systems gives additional step to advance studies in the organic semiconductor materials.

Here, we introduce a novel method to grow platelet-shaped organic semiconductor crystals preferably at the liquid-to-gas phase boundaries so that charge transport performance at their molecularly flat surfaces is maximized. Indeed, the OFETs of pentacene and dinaphtho[2,3-*b*:2′,3′-*f*]thieno[3,2-*b*]thiophene (DNTT), which are fabricated by laminating the floating crystals on substrates,

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show nearly the highest values of mobility reported for both compounds.

2. Results and Discussion

We employ solution of precursors that are thermally converted to organic semiconductor molecules such as pentacene and DNTT in order to control the rate of generating poorly soluble organic semiconductor molecules in the liquid [8,9]. By choosing solvents with high density, much higher boiling point than the conversion temperature of the precursors and reasonable solubility for precursors, we expect that the thermally converted insoluble semiconductor compounds are promoted to rapidly reach the surface and to crystallize into the two-dimensional shape preferably at the surface of the liquid. As compared to recently developed solution-crystallizing techniques, in which molecules originally dissolved in the solvent crystallize into thin-film like crystals at the surface of the solution with diminishing solvents due to vaporization, the present method is similar in that the thin crystals appear at the surface but is contrasting in that the resultant organic semiconductors are insoluble. Since many of high-mobility organic semiconductor compounds are poorly soluble inherently due to large π-conjugated cores, applicability of the present method is diverse as long as one can prepare precursors for the thermal conversion.

Such materials were originally developed mostly for processes to first form films of the precursors from solution by spin-coating, for example, and thermally converted to organic semiconductor layers in the next step [8–10]. Though transistor operations are reported for such systems, the maximum performance can be difficult to achieve due to intrinsic difficulty that crystal structure is disordered after the molecular conversion. On the other hand, the crystals are formed after the conversion in the present process to produce fully crystallized high-mobility semiconductors. Similarly to recently developed crystallization methods from solution, which presents a route to mass-production with the development of large-area printing technology, these methods utilizes molecular self-assembly at the surface of the solvents so that highly mobile molecules forms periodic crystal structures very quickly on the liquid. Other methods such as double ink-jet technique have the same advantage reported for producing single crystals at the two-liquid boundary [6]. We also note that a unique experiment of crystallization is reported by depositing organic semiconductors at the surface of ionic liquid in a vacuum chamber [11]. Pentacene single crystals have been successfully grown into a millimeter size as the result.

The molecular structure of 13,6-*N*-sulfinylacetamidopentacene (pentacene precursor), which is available commercially, and the thermal conversion reaction in this study are shown in Fig. 1a. The precursor molecules are thermally transformed to pentacene at the temperature of above 120–200 °C [8]. In the present experiment, the precursor is dissolved in an ionic liquid (IL) of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (emim-TFSI, depicted in Fig. 1b) at the concentration of 0.05 wt.% at 65 °C. A droplet of the solution is mounted on a glass slide and then heated on a hot plate in a glove-box in argon atmosphere up to 120 °C, at which the elimination reaction just starts [8] to supply the converted pentacene slowly as indicated in Fig. 1c.

Exhibited in Fig. 2a is time evolution of the appearance of the droplet during the conversion process. Though the converted pentacene is slightly dissolved in the IL at the very beginning of the process, the solution quickly reaches saturation concentration with the continuous supply of the converted pentacene, so that tiny crystals of pentacene precipitate in the droplets. Because of their smaller density of pentacene than that of the emim-TFSI IL, the solid flakes of pentacene reaches the surface and grows to form submillimeter size crystals on the surface with further supply of the pentacene due to the continuous conversion reaction (Fig. 2b). Interestingly, the resultant pentacene single crystals are shaped to two-dimensional plates with the typical thickness of 50–200 nm preferably located at the top of the IL with their planar directions parallel to the surface plane of the liquid–gas boundary. Since pentacene and IL are in the vicinity of solubility equilibrium at the IL surface, boundaries of the crystals repeat appending and removing pentacene molecules. We suspect that the continuous generation of the pentacene molecules drives further growth of the planar-shaped crystals, which preferentially takes place in the planar directions because of the in-plane interactions. The platelets of the single crystals are easily transferred from the IL surface to substrates with gate insulators to form devices of OFETs, as illustrated in Fig. 1c.

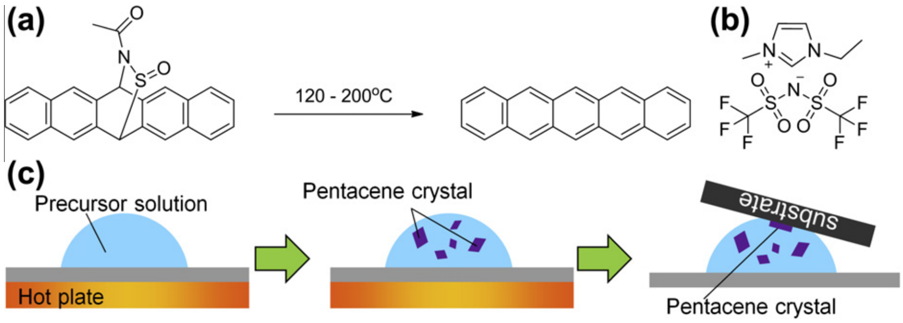

Fig. 1. (a) Molecular structure of 13,6-*N*-sulfinylacetamidopentacene (pentacene precursor) and a scheme of thermal conversion to pentacene. (b) Molecular structures of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (emim-TFSI). (c) Schematics of the method of fabricating organic semiconductor single crystals and the method to transfer the crystals onto substrates.