



## Controlling the crystal formation in solution-process for organic field-effect transistors with high-performance

Chuan Liu<sup>a,\*</sup>, Yun Li<sup>d</sup>, Yong Xu<sup>a</sup>, Takeo Minari<sup>a,b</sup>, Songlin Li<sup>a</sup>, Kazuo Takimiya<sup>c</sup>, Kazuhito Tsukagoshi<sup>a</sup>

<sup>a</sup> International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305 0044, Japan

<sup>b</sup> RIKEN, Wako, Saitama 351 0198, Japan

<sup>c</sup> Hiroshima University, Department of Applied Chemistry, Graduate School of Engineering, Higashi-Hiroshima, Japan

<sup>d</sup> School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, People's Republic of China

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### ABSTRACT

We control the growth of high-quality organic semiconducting crystals in the aim of transistor application. By finely tuning the processing parameters, both isolated crystals showing characteristic facet angles and irregular-shaped, thin crystalline domains are obtained in large sizes (>400 μm). Structural investigations indicate that the various shapes of crystals are in the same crystal structure, and reveal that the irregular-shaped crystalline domains are composed by terrace of molecularly flat regions, which can be up to hundreds of microns in size. When applied in field-effect transistors, the thin crystalline domains exhibit the best performance showing  $\mu_{\text{FET}}$  up to 4.4 cm<sup>2</sup>/V s. This is an order of magnitude higher than that of the transistors made from as-spun films and thick crystals. The approach well demonstrates the importance of fine control of crystal formation and can be generally used for getting organic crystal transistors.

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## 1. Introduction

Research of organic semiconductors aims at meeting the needs of industry, which asks for fabricating electronic devices with simple process, low cost, and high performance [1,2]. In particular, ideal organic field-effect transistors (OFETs) are expected to be solution-processed and exhibit high carrier mobility. A variety of organic single crystals have been reported to exhibit large mobility values (~10 cm<sup>2</sup>/V s) [3–6] that are able to compete with the conventional vacuum processed inorganic semiconductor devices, and hence attract a broad range of research activities. Understanding of crystal formation enables precise control of crystal patterning for circuits [7–11] and improvement in the crystal quality, especially for those ob-

tained by inkjet-printing [4,12,13]. Also, the single crystal without structural disorder is an ideal media to study the basic electrical properties, such as charge transport properties [14–18], electronic structure [19], and spin injection [20]. Hence studying the growth of organic single crystals and manipulating the crystal properties in solution process can advance research in both device application and fundamental physics [3,21].

In this report, we focus on growing high-quality single crystals from solution that has the optimal properties for the application in FETs. The object material is 2,7-dialkyl[1]benzothieno[3,2-b][1]benzothiophenes (C12-BTBT) [22], as the classes of benzo-fused thienothiophenes exhibit remarkable charge carrier mobility and good stability in ambient air when applied in transistors [23]. Moreover, the molecules of group feature high solubility in common organic solvents and thus imply the possibility to fabricate single crystals by solution process. We adapt the method of solution drying for its simplicity in processing and

\* Corresponding author.

E-mail addresses: [liu.chuan@nims.go.jp](mailto:liu.chuan@nims.go.jp) (C. Liu), [TSUKAGOSHI.kazuhiito@nims.go.jp](mailto:TSUKAGOSHI.kazuhiito@nims.go.jp) (K. Tsukagoshi).

capability for controlling. By using appropriate solvent and concentration, we are able to obtain crystals with various quality and morphology. After analyzing the molecular packing structure, the crystals are applied to FETs. The best performance exhibits mobility up to  $4.4 \text{ cm}^2/\text{V s}$ , well illustrating the importance of fine control of crystal formation.

## 2. Experimental

**Crystal growth:** The experimental processes were carried out in ambient atmosphere unless stated. Highly doped n-type silicon wafers with 50 nm  $\text{SiO}_2$  layers were cleaned in an ultrasonic bath in a succession of de-ionized water, acetone and iso-propanol for about 5 min each and treated by ultraviolet light and ozone for 5 min. For growing crystals by solution drying,  $\text{SiO}_2/\text{Si}$  substrate was put onto the glass slides inside a Petri-dish, and 60  $\mu\text{l}$  solution of C12-BTBT (synthesized according to [24]) in the selected solvent was dropped onto the substrates. The solution was dried in a Petri-dish covered with a lid at room temperature.

**Crystal characterization:** Optical images were captured by a digital microscope, with or without a polarizer. Topological micro-graphs were taken by an Atomic Force Microscope (AFM) in the tapping mode (SPA-500 scanning probe microscope, Seiko Instruments Inc). Signals of X-ray diffraction were measured by D/MAX-2000/PC (Rigaku Corporation,  $\text{CuK}\alpha$ ).

**FET fabrication and characterization:** Before crystal growth,  $\text{SiO}_2/\text{Si}$  substrates were modified with a self-assembly monolayer (SAM) of phenethyltrichlorosilane (PhTS), via soaking substrates in the solution of PhTS in chloroform for 12 h. Afterwards crystals were grown as described above and samples were heated at  $70^\circ\text{C}$  in vacuum for 3 h to get rid of any residues. Consequently source and drain electrodes were made by evaporating  $\text{FeCl}_3$  and Au (1/50 nm,  $0.1 \text{ \AA/s}$ ) [25,26] through a shadow mask in vacuum ( $<4 \times 10^{-4} \text{ Pa}$ ). Measurement of FETs was carried out in vacuum ( $<2 \times 10^{-2} \text{ Pa}$ ). Mobility of FET ( $\mu_{\text{FET}}$ ) is extracted from transfer characteristics in saturated regime by fitting  $-I_d = [W/(2L) \times C_i \times \mu_{\text{FET}}] \times (V_g - V_{\text{th}})^2$ , where  $W$  and  $L$  are channel width and length,  $I_d$  is drain current,  $C_i$  is capacitance per unit area (70 nF/cm for 50 nm  $\text{SiO}_2$ ),  $V_g$  is gate voltage, and  $V_{\text{th}}$  is threshold voltage.

## 3. Results and discussion

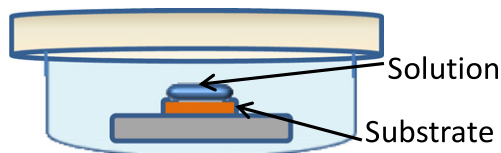
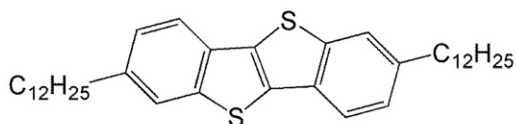
### 3.1. Crystal formation control

To obtain crystals suitable for OFET, we investigated the crystal formation by drop-casting, i.e. gradually evaporat-

ing solution of C12-BTBT (Scheme 1), where the saturation degree of solution is enhanced gradually to intrigue nuclei formation and the consequent crystal growth [27]. The advantage of using drop-casting is that the set-up is simple and it allows fine control on the processing factors, such as solvent, concentration and temperature, to obtain crystals in different shapes, sizes, morphologies and qualities [28].

Crystals of C12-BTBT formed from solvents of different boiling point and solubility (Table 1) exhibit distinct morphologies. Drying from a low boiling point solvent, chloroform (4 mg/ml), leads to precipitation of scaly crystal clusters (Fig. 1a). When drying from another low boiling point solvent but with poor solubility, hexane (1.1 mg/ml), small regular-shaped crystals are formed (Fig. 1b). When a higher-boiling point solvent toluene is used instead (1 mg/ml, Fig. 1c), some plate-like crystals are precipitated at the substrate edge, implying that slower evaporation rate combined with a local high supersaturation degree can assist the formation of plate-like crystals. To lower the solubility, ethanol, which hardly dissolves C12-BTBT ( $<0.1 \text{ mg/ml}$ ), is mixed with toluene solution (toluene:ethanol = 1:1, 1 mg/ml). Also, ethanol is dropped around the substrates to form a saturated atmosphere, lowering the evaporating rate of solvents and allowing ethanol molecules to diffuse gradually into the solution [29,30]. Some of the precipitated crystals exhibit sharp characteristic edges (Fig. 1d), but most are in small sizes ( $<100 \mu\text{m}$ ) and show non-uniform colors, indicating relatively low quality. The above results suggest that dispersed large crystals of C12-BTBT may be expected to be obtained from drying a single solvent with poor solubility and high boiling point. It turns out that when drying anisole solution (1 mg/ml) in a tightly covered Petri-dish, isolated crystals exhibiting clear facets are formed, reaching  $400 \mu\text{m}$  in size (Fig. 1e). When observed under a cross-polarizer, these crystals exhibit strong birefringence (Fig. 1f) that proves high crystallinity.

Besides the choice of solvents, the concentration of solution is also an important factor in crystallization control. When the concentration of anisole solution is reduced from 1 mg/ml to 0.5 mg/ml, the driving force of crystallization becomes much smaller. Consequently, thin crystalline domains in the size of several hundreds of microns are formed (Fig. 2b), distinct from the crystals obtained from the 1 mg/ml solution (Fig. 2a). Despite having irregular shapes, the domains feature visible terraces under optical microscopes. In general, these crystals have much smaller thicknesses (30–200 nm) than those crystals shown in Figs. 1e and 2a ( $>500 \text{ nm}$ ), and thus are probably more favorable for transistor in the staggering configuration for the sake of carrier injection [31]. Whether these irregular domains are in high crystalline degree will be investigated in the next section.



Scheme 1. Molecular structure of C12-BTBT and the method of crystallization.

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