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Solution-Processed Organic Field Effect Transistor Using a Liquid Crystalline Semiconductor, 8TNAT8

HIROSATO MONOBE,^{1,*} MASAOMI KIMOTO,²
AND YO SHIMIZU¹

¹Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST) Midorigaoka, Ikeda, Osaka, Japan

²Okuno Chemical industries Co., Ltd., Jyoutou-ku, Osaka, Japan

In this study, we used a liquid crystalline (LC) semiconductor, 8TNAT8, solutions (e.g. 0.1 wt% in toluene) for forming an organic semiconductor layer by solution casting method, and fabricated field effect transistors (FETs) with top-contact/bottom-gate (TCBG) and bottom-contact/bottom-gate (BCBG) geometries. These LC semiconductors show FET characteristic properties and have high carrier mobilities of 0.08 and 0.01 cm² V⁻¹ s⁻¹ for TCBG and BCBG type FETs, respectively. We have also investigated the influence of electrode surface modification for a BCBG type FET. These results imply 8TNAT8 is a candidate for solution-processed FETs.

Keywords Calamitic liquid crystals; mesophase semiconductor; field effect transistor; charge carrier transport; printed electronics

1. Introduction

In the field of organic electronics, solution-processed organic semiconductors for large and flexible electronic devices which are fabricated by low temperature process, in particular field effect transistors (FETs) have gotten much attention in these years [1–3]. Numerous of the characteristic properties of liquid crystalline (LC) semiconductors, such as their self-assembling nature, electrically inactive domain boundaries, and good solubility in ordinary organic solvents, make them attractive candidates for application in FET devices [4–16].

Calamitic LC semiconductors have the advantage of achieving the 2D hopping conduction required for lateral type thin film transistors such as FETs, in contrast to the 1D hopping conduction shown by disc-shaped molecules. Recently, we reported that a calamitic LC semiconductor, 2,6-di(5'-n-octyl-2'-thienyl)naphthalene (8TNAT8) showed a drift hole mobility of 0.1 cm² V⁻¹ s⁻¹ in a 3D mesophase and a p-type FET mobility of 0.14 cm² V⁻¹ s⁻¹ in a polycrystalline thin film which was vapor deposited for a top-contact/bottom-gate (TCBG) geometry devices [17].

In this study, we used a LC semiconductor, 8TNAT8, solutions (e.g. 0.1 wt% in toluene) for forming an organic semiconductor layer by solution casting method, and fabricated TCBG and bottom-contact/bottom-gate (BCBG) type FETs. BCBG type of FET devices

*Address correspondence to Hirosato Monobe, Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST) Midorigaoka, Ikeda, Osaka 563-8577, Japan. E-mail: monobe-hirosato@aist.go.jp

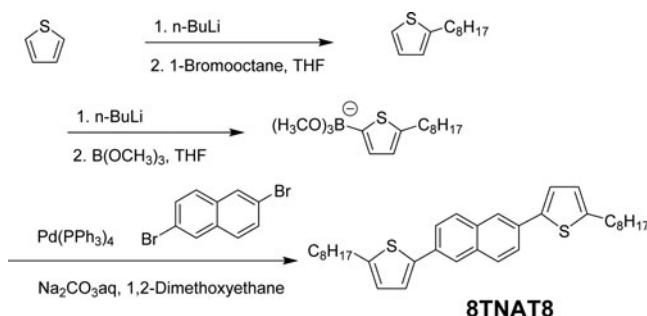


Figure 1. Synthetic Route of 2,6-di(5'-n-octyl-2'-thienyl)naphthalene (8TNAT8).

is more suitable for printing processes. These LC semiconductors show FET characteristic properties and have high carrier mobilities of 0.08 and 0.01 cm² V⁻¹ s⁻¹ for TCBG and BCBG type FETs at room temperature, respectively. We have also investigated the influence of surface modification of metal electrodes for BCBG type FETs.

2. Experimental Methods

A LC semiconductor, 8TNAT8, has been synthesized through three steps and a synthetic route is shown in Figure 1. The product was purified by column chromatography (silicagel, hexane and CHCl₃) and further purification by several repetition of recrystallization from the mixture of ethanol and toluene. The final procedure of purification was different from previous case which was sublimation in vacuo [17]. Its mesomorphic characterization (melting and clearing points are 93 and 182°C, respectively) has been presented and discussed previously [18]. The LC organic semiconductor film was deposited by solution casting method onto the non-pretreated thermally oxidized, highly n-doped silicon substrates from a 0.1 wt% 8TNAT8 toluene solution and dried under the atmosphere at room temperature.

FET devices were fabricated in TCBG and BCBG geometry. The thickness of SiO₂ gate dielectric was 300 nm. Gold source and drain electrodes with 50 nm-thick were evaporated on the top of the films through shadow masks under 5 × 10⁻⁴ Pa, producing the channel length/width (W/L) of 56/2000 μm. For BCBG geometry devices, a 3 nm-thick chromium layer was also evaporated on the dielectric layer prior to depositing gold electrodes through the same mask as an adhesive layer. The metal electrodes of BCBG type of FETs were modified with pentafluorobenzenethiol (PFBT) by immersed into 10 mM ethanol solution at 30 minutes to improve potential matching between electrodes and an

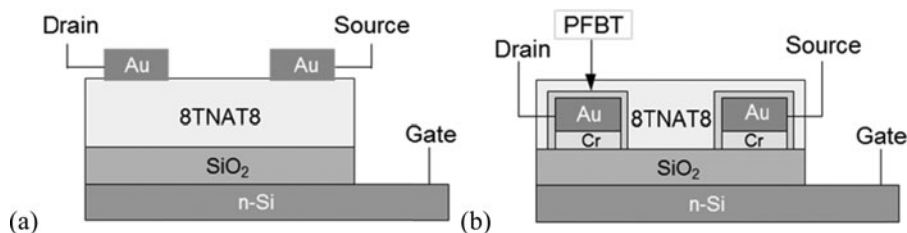


Figure 2. Schematic representations of the FET device configuration for (a) TCBG and (b) BCBG geometries.

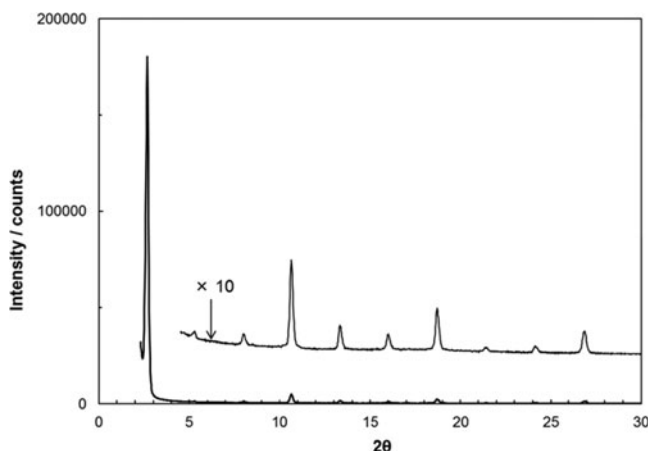


Figure 3. XRD pattern of solution casted 8TNAT8 film on FET devices at room temperature.

organic semiconductor [19]. Schematic representations of device geometries of FETs are shown in Figure 2.

A film structure of LC semiconductor layer of FET devices was investigated by XRD (Rigaku, Rint2000 with $\text{CuK}\alpha$). Work function and ionization potential of metal electrodes and a LC semiconductor film were measured by a photoelectron yield spectrometer (Riken, AC-2). All electric measurements were carried out at room temperature in vacuo using a combination of a sourcemeter (Keithley, 2400) and a picoammeter (Keithley, 6487). FET mobilities (μ_{FET}) were calculated in the saturation regime by using the relationship: $\mu_{\text{FET}} = (2I_{\text{DS}}^{\text{sat}}L) / (WC(V_{\text{G}} - V_{\text{th}})^2)$, where $I_{\text{DS}}^{\text{sat}}$ is the source-drain saturation current, C (1.15×10^5 nF) is the dielectric capacitance, V_{G} is the gate voltage, and V_{th} is the threshold voltage. The latter can be estimated as the intercept of the linear section of the plot of V_{G} vs. $(I_{\text{DS}})^{1/2}$ (at $V_{\text{DS}} = -50$ V).

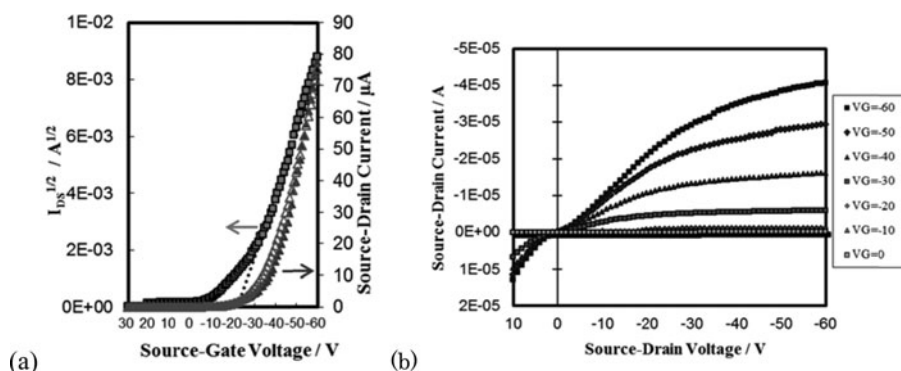


Figure 4. (a) Typical output and (b) transfer characteristics of solution casted 8TNAT8 film of TCBG type of FETs.

3. Results and Discussion

3.1. Film Properties of Solution-Processed LC Semiconductor

The XRD pattern for an 8TNAT8 semiconductor film of FET devices shows very clear several reflection peaks on non-treated oxide surface of Si substrate as shown in Fig. 3. In the small-angle region, a very strong (001) and systematic reflections comes up corresponding to the layer spacing of the molecular of the 2D sheets. This indicates the almost same order of high quality film with layered structure was obtained by solution casting method as well as vapor deposited film [17].

3.2. FET Characteristics

Figure 4 shows the typical FET characteristics of the solution casted 8TNAT8 semiconductor film of TCBG type devices. FET mobility was calculated to be $0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, whereas those of the vapor deposited and spin-coated devices were calculated to be 0.03 and $0.0001 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively [17]. The improvement of FET mobility of solution casted film compared to that of spin-coated one could be attributed the higher quality of the semiconductor thin film.

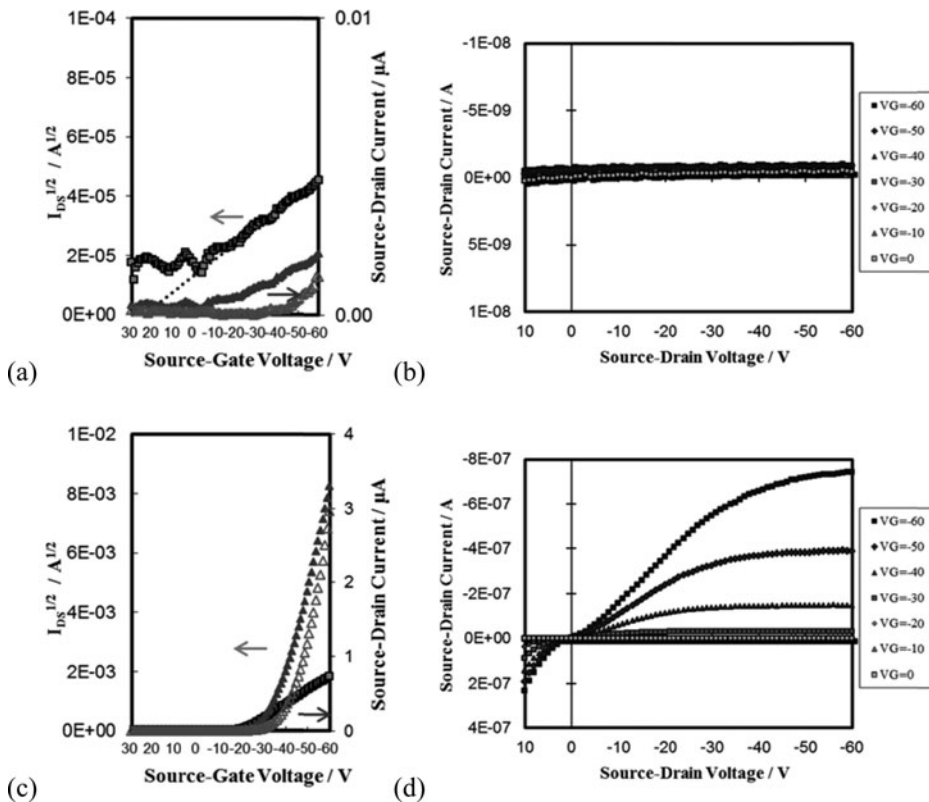


Figure 5. Typical output and transfer characteristics of BCBG type of FETs (a) (b) with and (c) (d) without PFBT treatment of metal electrodes, respectively.

Table 1. FET characteristics of 8TNAT8 TCBG and BCBG type devices fabricated on bare Si/SiO₂ substrates (measured under vacuo)

Geometry Type	LC Semiconductor Film	μ_{FET} (cm ² /Vs)	On/off ratio	V_{th} (V)
BCBG	Casting on SiO ₂	4.7×10^{-7}	2×10^1	23.1
BCBG	Casting on SiO ₂ (PFBT treated electrodes)	0.01	7×10^4	−19.1
TCBG	Casting on SiO ₂	0.08	1×10^6	−12.0
TCBG	Vacuum deposited on SiO ₂	0.03 ^a	3×10^{3a}	−21.6 ^a
TCBG	Vacuum deposited on HMDS	0.14 ^a	2×10^{3a}	−27.4 ^a

^asee ref. 17.**Table 2.** Work function and ionization potential of electrodes and 8TNAT8

Sample	w/wo PFBT	Work function / IP (eV)
Au	with PFBT	5.4
	without	4.9
Cr	with PFBT	4.9
	without	4.7
8TNAT8	—	−5.3

Figure 5 shows the FET characteristics of BCBG type devices with/without PFBT modifications of metal electrodes. FET mobility was calculated to be 0.01 cm² V^{−1} s^{−1} for PFBT modified electrodes, where that was less than 10^{−6} cm² V^{−1} s^{−1} for devices without PFBT treatment. The FET mobilities of TCBG and BCBG geometry devices are summarized in Table 1.

Table 2 summarized the work function of metal electrodes of BCBG type FETs and the ionization potential of an 8TNAT8 thin film measured by a photoelectron yield spectrometer (Rikenkeiki, AC-2) in air. High source contact resistance is common in organic FETs and can cause a current reduction of I_{DS} for small V_{DS} and high V_{G} . The HOMO energy level of 8TNAT8 was found to be −5.3 eV, indicating a slight difference in the hole-injection barrier from Au (−4.9 eV) and Cr (−4.7 eV). Charge-injection limited by space charges near the source electrodes may also result in a nonlinear reduction of drain current. The HOMO energy level of PFBT treated Au and Cr electrodes were −5.4 and −4.9 eV, respectively, and their easier charge-injections to 8TNAT8 lead to showing high FET mobility.

4. Conclusions

We fabricated TCBG and BCBG types of FETs by solution casting from a LC semiconductor, 8TNAT8, solution (e.g. 0.1 wt% in toluene). The solution-processed FETs show FET characteristics and mobility was 0.08 and 0.01 cm² V^{−1} s^{−1} for TCBG type FETs and BCBG type FETs with PFBT modified electrodes, respectively. Potential matching between the electrodes and the organic semiconductor is important for performance for LC FETs with BCBG geometry. Numerous characteristic properties of LC semiconductors, such as their self-assembling nature, fast charge transport, electrically inactive domain boundaries,

and good solubility in ordinary solvents, make them attractive candidates for application in printed FET devices.

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