Organic Field-Effect Transistors Using Di(2-thienyl)naphthodithiophenes as Active Layers

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Two isomeric di(2-thienyl)naphthodithiophenes, *anti*- and *syn*-DThNDTs, have been investigated as active materials of organic field-effect transistors (FETs). Field-effect mobilities of $2–3 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$ were obtained for the *anti*-DThNDT film, while no obvious FET function was observed with the *syn*-DThNDT film.

Recently, organic field-effect transistors (OFETs) are receiving much attention because of their potential applications to flexible, light and small electronic devices.[1,2] A large number of small organic molecules and conjugated polymers such as pentacene,[3] oligothiophene[4] and poly(alkylthiophene)[5] can be used as active layers of the OFETs. It is worthy of note that the field-effect mobilities of $1.5–3.1\,cm^2\,V^{-1}\,s^{-1}$ reported for the single crystal p-type pentacenes are greater than those ($0.1–1\,cm^2\,V^{-1}\,s^{-1}$) for a-Si.[1,3]

We have recently synthesized naphthodithiophene derivatives, which are new types of heteroarene isoelectronic with pyrene.[6–8] In this work, isomeric 2,6-di(2-thienyl)-naphtho[1,8-bc : 5,4-b′c′]dithiophene (*anti*-DThNDT) and 2,5-di(2-thienyl)naphtha [1,8-bc : 5,4-b′c′]dithiophene (*syn*-DThNDT) were studied as active materials of the OFETs. The *anti*-DThNDT is a linear and plane molecule which has a C_2 symmetry axis, while the *syn*-DThNDT is a bent molecule though there is a C_2 axis as well as a symmetry plane. Electronic absorption maxima of the *anti*- and *syn*-DThNDT in tetrahydrofuran are 519 and 444 nm, respectively, indicating that the *anti*-DThNDT has narrow HOMO-LUMO energy-gap compared with the *syn*-DThNDT.[8]

The *anti*- and *syn*-DThNDTs were synthesized as described already.[8] OFETs were fabricated on heavily doped n^+-Si (100) wafers with a 220 nm thermally grown SiO_2. The DThNDTs (50–100 nm thick) were thermally deposited onto the SiO_2/Si substrate, and succeedingly Au films (100 nm) as drain and source electrodes were deposited on the organic layer through a shadow mask (Figure 1). For a typical device, the drain-source channel length and width are 50 μm and 2 mm, respectively. Characteristics of a drain current (i_d) versus drain voltage (V_d) of the OFET devices were measured with an ADVANTEST R6245 power supply under dry N_2 atmosphere. The field-effect mobilities (μ_{FET}) were calculated in the saturation regime using the equation (1).

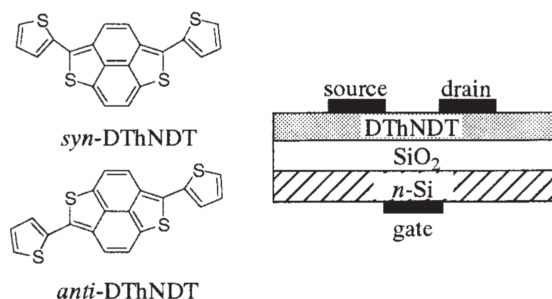

Figure 1. Chemical structures of organic materials used and the device structure of the OFET.

$$i_d = \frac{WC_i}{2L}\mu_{FET}(V_g - V_t)^2 \qquad (1)$$

where W and L are the channel width and length, respectively. C_i is the capacitance per unit area of the SiO_2, V_g the gate voltage and V_t the threshold voltage which can be calculated from a plot of $(i_d)^{1/2}$ vs V_g. X-ray diffraction (XRD) of the organic thin films on SiO_2/Si substrate was measured with a Maxscience M18XHF diffractometer. UV-Vis spectra and AFM images of the organic thin films were obtained by using a Shimadzu UV-3101PC spectrometer and Shimadzu SPM-9500 microscope, respectively. All the measurements were conducted at room temperature.

The thin film of the *anti*-DThNDT is shiny and red-purple, while the *syn*-DThNDT film is rough and yellow. The optical absorption maxima of *anti*- and *syn*-DThNDT films are 480 nm and 412 nm, respectively. XRD of the *anti*-DThNDT film on SiO_2/Si substrate exhibited a d spacing of 13.40 Å. This value is consistent with the *a* axis of the single-crystal unit-cell (*a*: 13.33 Å, *b*: 3.93 Å, *c*: 15.26 Å).[8] On the other hand, any significant peak was not observed with the *syn*-DThNDT film, indicating that the film is amorphous.

Figure 2 shows AFM images of the (a) *syn*- and (b) *anti*-DThNDT films (100 nm) on SiO_2/Si substrate. For the *syn*-DThNDT film, large grain (about 1–2 μm length) consists of cohered small grain (diameter = 0.1–0.2 μm) and SiO_2/Si substrate is not wholly covered with *syn*-DThNDT. In the case of the *anti*-DThNDT film, SiO_2/Si substrate is fully covered with needle-like crystals (diameter = 0.2–0.3 μm).

Figure 3 shows a typical plot of the i_d vs V_d at various V_g for the OFET based on *anti*-DThNDT. The channel conductance increases as V_g becomes more negative, meaning that the *anti*-DThNDT film behaves as a p-type semiconductor. The μ_{FET} estimated for the *anti*-DThNDT film was $2–3\times 10^{-4}\,cm^{-2}\,V^{-1}\,s^{-1}$. On the other hand, no obvious FET function was observed with the *syn*-DThNDT film. The i_d observed was less than 1 nA when the V_d and V_g were varied in the range from 0 to −100 V, respectively. This is consistent with the AFM image descrived above, indicating the formation of the island-like film for *syn*-DThNDT.

The effective carrier mobility (μ_{eff}) across two grains in the polycrystalline film is given by the equation (2).

$$\frac{1}{\mu_{eff}} = \frac{1}{\mu_c} + \frac{1}{\mu_{gb}} \qquad (2)$$

where, μ_c and μ_{gb} are carrier mobilities in the crystal grain

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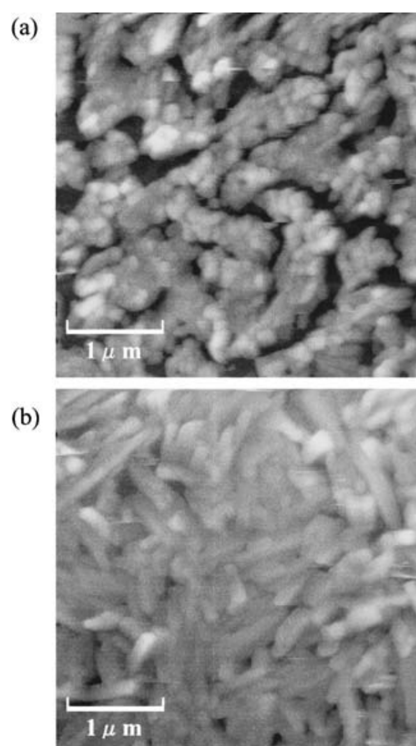

Figure 2. AFM images of the (a) *syn*- and (b) *anti*-DThNDT films (100 nm) on SiO_2/Si.

(intragrain mobility) and across the grain-boundary, respectively. Usually, μ_c is larger than μ_{gb}, so that the overall mobility for the polycrystalline film increases with the decrease of the number of grain-boundaries and the distance between the grains. A similar consideration is applicable to the present case. Namely, the charge transport is predominated by the intergrain transport. Further studies are in progress to improve the μ_{FET} by molecular design.

In summary, the sublimed *anti*-DThNDT film behaves as a p-channel semiconductor in the OFET and the μ_{FET} calculated in the saturation regime is 2–3 × 10^{-4} cm^{-2} V^{-1} s^{-1}. The FET based on *syn*-DThNDT did not work sufficiently. The results are attributed to the difference in morphology between the *anti*- and *syn*-DThNDT films. The XRD and AFM indicate that *anti*-DThNDT forms a highly packed film, but *syn*-DThNDT forms a porous film having grain-gaps (0.1–0.2 μm). The plane and symmetric molecules such as *anti*-DThNDT are suitable for the active materials in the OFETs.

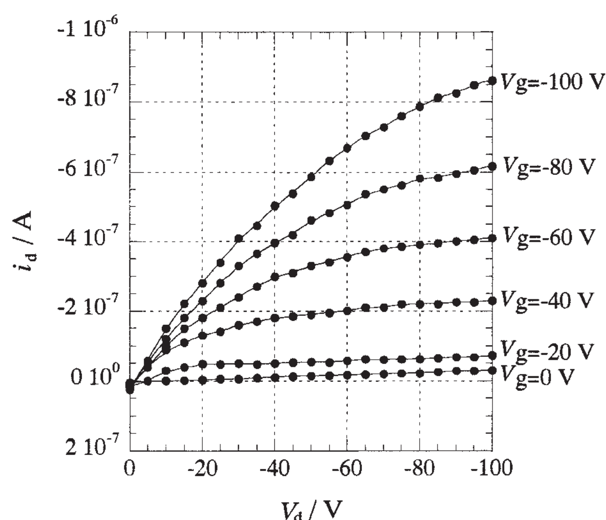

Figure 3. i_d vs V_d curves at different gate biases for the OFET device using the *anti*-DThNDT film as an active layer.

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