Organic Field-Effect Transistor Using Oligoselenophene as an Active Layer

Yoshihito Kunugi,*[,†] Kazuo Takimiya,[‡]
Kiwamu Yamane,[‡] Kazuo Yamashita,[†]
Yoshio Aso,[‡] and Tetsuo Otsubo[‡]

Faculty of Integrated Arts and Sciences,
Hiroshima University, 1-7-1 Kagamiyama,
Higashi-Hiroshima 739-8521, Japan, and
Graduated School of Engineering,
Hiroshima University, 1-4-1 Kagamiyama,
Higashi-Hiroshima 739-8527, Japan

Received September 20, 2002
Revised Manuscript Received October 30, 2002

Thiophene oligomers and polymers are promising compounds applicable to organic field-effect transistors[1] (OFETs), photodiodes,[2] light-emitting diodes,[3] and their integrated devices.[4] Selenophene is a homologue of the chalcogenophenes and the chemical and physical properties are similar to those of thiophene. To our knowledge, however, there has been no report on organic devices made with oligo- or polyselenophenes. This may be ascribable to the poor electrical properties of the polyselenophenes reported in early studies of the system. For example, the conductivities of doped polyselenophene films[5] are in the range of 10^{-4}−10^{-2} S cm^{-1}, which are fairly small compared with those (10−100 S cm^{-1}) of doped polythiophenes.[6] Recently, we have synthesized structurally well-characterized oligoselenophenes and found that the iodine-doped oligoselenophenes exhibit the conductivities of 10^{-2} S cm^{-1}, which are comparable with those of the analogous doped oligothiophenes.[7] This result encourages us in the studies of electronic devices based on organic functionality materials. The present work is the first report of an OFET made with oligoselenophene, showing good FET behavior.

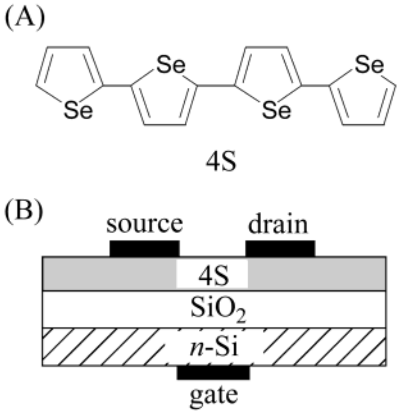

Figure 1. (A) The chemical structure of 4S and (B) the device structure of the OFET.

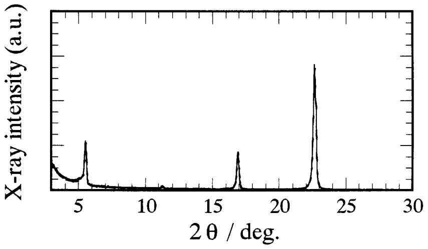

Figure 2. X-ray diffraction pattern of the 4S film (50 nm) deposited on Si/SiO$_2$ at T_s = 20 °C.

2,2′:5′,2″:5″,2‴-Quaterselenophene (4S) was synthesized by the Stille coupling reaction between dibromobiselenophene and 2-fold of 2-tributylstanyl selenophene[7] and purified twice by sublimation prior to use.[8] OFETs were fabricated on heavily doped n^+-Si (100) wafers with a 220-nm thermally grown SiO$_2$ (Figure 1). The 4S film (50-nm thick) was vacuum-deposited onto the Si/SiO$_2$ substrate, and succeedingly Au films (100 nm) as drain and source electrodes were deposited on the organic layer through a shadow mask. 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 under vacuum with an ADVANTEST R6245 power supply. The field-effect mobilities were calculated in the saturation regime of the i_d as shown in a previous paper.[9] X-ray diffractions (Cu, $\lambda_{K\alpha}$ = 1.541 Å) of the organic thin films on Si/SiO$_2$ substrate were measured with a Maxscience M18XHF diffractometer. AFM images of the organic thin films were obtained by using a Shimadzu SPM-9500 microscope. All the measurements were conducted at room temperature (RT).

The sublimed film of 4S is orange and shiny. X-ray diffraction of the 4S film on Si/SiO$_2$ shows a series of the peaks, indicating the order of the molecular repeat with 15.7 Å (Figure 2). This value was independent of the substrate temperature (T_s) and consistent with the *b*-axis of the single-crystal unit cell (a = 7.94 Å, b = 15.93 Å, c = 6.07 Å), corresponding to the direction of

---

* To whom correspondence should be addressed.

[†] Faculty of Integrated Arts and Sciences, Hiroshima University.

[‡] Graduated School of Engineering, Hiroshima University.

(1) (a) Katz, H. E.; Lovinger, A. J.; Laquindanum, J. G. *Chem. Mater.* **1998**, *10*, 457. (b) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741.

(2) (a) Yu, G.; Heeger, A. J. *Appl. Phys. Lett.* **1994**, *64*, 3422. (b) Kunugi, Y.; Harima, Y.; Yamashita, K. *J. Chem. Soc., Chem. Commun.* **1995**, 787. (c) Kunugi, Y.; Miller, L. L.; Maki, T.; Canavesi, A. *Chem. Mater.* **1997**, *9*, 1061.

(3) (a) Berggren, M.; Inganas, O.; Gustafsson, G.; Rasmusson, J.; Andersson, M. R.; Hjertberg, T.; Wennerstrom, O. *Nature* **1994**, *372*, 444. (b) Geiger, F.; Stoldt, M.; Schweizer, H.; Bauerle, P.; Umbach, E. *Adv. Mater.* **1993**, *12*, 922. (c) Kunugi, Y.; Tabakovic, I.; Canavesi, A.; Miller, L. L. *Synth. Met.* **1997**, *89*, 227.

(4) Crone, B.; Dodabalapur, A.; Lin, Y.-Y.; Filas, R. W.; Bao, Z.; LaDuca, A.; Sarpeshkar, R.; Katz, H. E.; Li, W. *Nature* **2000**, *403*, 521.

(5) (a) Yoshino, K.; Kohno, Y.; Shiraishi, T.; Kaneto, K.; Inoue S.; Tsukagoshi, K. *Synth. Met.* **1985**, *10*, 319. (b) Glenis, S.; Ginley, D. S.; Frank, A. J. *J. Appl. Phys.* **1987**, *62*, 190. (c) Bourahla, A.; Saiter, J. M.; Vautier, C. *Mater. Chem. Phys.* **2001**, *69*, 163.

(6) (a) Chorro, C.; Moukala, B.; Lere-Porte, J.-P.; Petrissans, J. *Mol. Cryst. Liq. Cryst.* **1990**, *187*, 199. (b) Kunugi, Y.; Harima, Y.; Yamashita, K.; Ohta, N.; Ito, S. *J. Mater. Chem.* **2000**, *10*, 2673. (c) Zotti, G. *Synth. Met.* **1998**, *97*, 267.

(7) (a) Nakanishi, H.; Inoue, S.; Otsubo, T. *Mol. Cryst. Liq. Cryst.* **1997**, *296*, 335. (b) Inoue, S.; Nakanishi, H.; Takimiya, K.; Aso, Y.; Otsubo, T. *Synth. Met.* **1997**, *84*, 341.

(8) Toxicities of the oligoselenophene compounds are not well-known. The synthesis must be carefully performed in an efficient hood. Disposable vinyl or latex gloves and chemical-resistant safety goggles should be worn.

(9) Kunugi, Y.; Takimiya, K.; Yamashita, K.; Aso, Y.; Otsubo, T. *Chem. Lett.* **2002**, 958.

10.1021/cm020949f CCC: $25.00

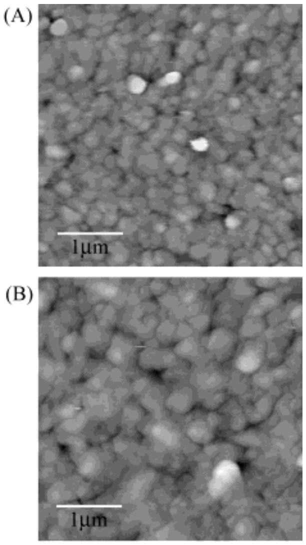

Figure 3. AFM images of the 4S films (50 nm) deposited on Si/SiO_2 at (A) $T_s = 20$ °C and (B) $T_s = 60$ °C.

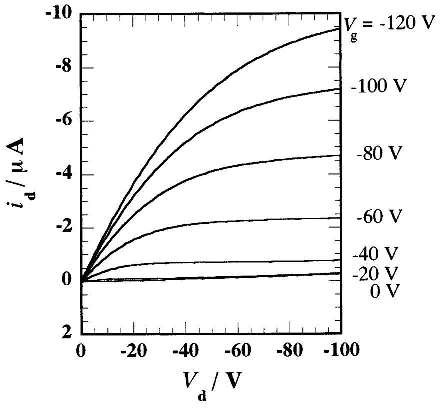

Figure 4. i_d vs V_d curves at different gate biases for the OFET device using the 4S film ($T_s = 60$ °C) as an active layer.

the molecular long axis.[10] In other words, the molecule arrangement is essentially normal to the substrate. It is well-known that this type of orientation is particularly useful in achieving high carrier mobility because the direction of $\pi-\pi$ stacking is in the plane of the current-flow direction.

In general, the field-effect mobility of an organic semiconductor depends on the grain size of the crystal as well as the orientation of the molecules. Figure 3 shows AFM images of the 4S films deposited on Si/SiO_2 at different substrate temperatures. The grain size is 0.04−0.1 μm^2 at $T_s = 20$ °C and increases to 0.1−0.3 μm^2 at $T_s = 60$ °C. However, further T_s elevation did not affect the grain size anymore.

Table 1. Field-Effect Mobilities of the 4S and 4T Films Prepared at Different Substrate Temperatures

compound	T_s (°C)	mobility ($cm^2 V^{-1} s^{-1}$)	grain size (μm^2)
4S	20	1.3×10^{-3}	0.04−0.1
4S	60	3.6×10^{-3}	0.1−0.3
4S	100	0.8×10^{-3}	0.1−0.3
4T	RT	$1-2.5 \times 10^{-3}$ [a,b]	
4T	65	$5-8 \times 10^{-3}$ [b]	3−8[b]

[a] Reference 11. [b] Reference 12.

Figure 4 represents a typical plot of the i_d versus V_d at various gate voltages for the OFET based on 4S. The channel conductance increases as the V_g becomes more negative, meaning that the 4S film behaves as a *p*-type semiconductor. The field-effect mobilities estimated for the 4S were summarized in Table 1, together with those of quaterthiophene (4T) for comparison. The mobilities depend strongly on the deposition temperature. The mobility of the 4S deposited at 60 °C was higher than that at 20 °C. This is attributed to the difference in grain size between the films prepared at 20 and 60 °C (see Figure 3). It is worthy of note that the mobility of the 4S deposited at 100 °C is small compared with that at 60 °C. Similar trends have been reported for oligothiophenes and the derivatives,[13] but the reason for the decrease of motilities has not been explained clearly yet. Thus, the largest mobility of 3.6×10^{-3} $cm^2 V^{-1} s^{-1}$ was obtained for the 4S film deposited at $T_s = 60$ °C. It is noted that the mobilities of the 4S film deposited at 60 °C and 4T film at 65 °C are almost the same, although the grain sizes are different.

In summary, the OFET using the oligoselenophene as an active layer has been first successfully fabricated. The 4S OFET shows *p*-channel characteristics. The best mobility of 3.6×10^{-3} $cm^2 V^{-1} s^{-1}$ was obtained for the 4S film prepared at a substrate temperature of 60 °C, which is comparable with that for the 4T films deposited at 65 °C. Oligoselenophenes modified with more selenophene rings or alkyl chains are expected to yield higher mobilities. Further studies are in progress to prove this hypothesis.

Acknowledgment. This work was supported by an Industrial Technology Research Grant Program in 2001 from NEDO of Japan (01A26005a) and Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan (13750761). We are grateful to Professors S. Yamanaka, K. Inumaru, and H. Fukuoka (Hiroshima University) for the measurements of X-ray diffractions. We also thank Mr. H. Murakami (Hiroshima University) for experimental assistance with the Si-wafer treatments.

CM020949F

---

(10) Nakanishi, H.; Inoue, S.; Aso, Y.; Otsubo, T. *Synth. Met.* **1999**, *101*, 639.

(11) Hajlaoui, R.; Horowitz, G.; Garnier, F.; Arce-Brouchet, A.; Laigre, L.; Kassmi, A. E.; Demanze, F.; Kouki, F. *Adv. Mater.* **1997**, *9*, 389.

(12) Videlot, C.; Ackermann, J.; Brisset, H.; Raynal, P.; Rebout, C.; Kassimi, A. E. *Fifth International Symposium on Functional π-Electron Systems*, Neu-ulm, Germany, 2002; pp 5541−0371.

(13) (a) Katz, H. E.; Lovinger, A. J.; Laquindanum, J. G. *Chem. Mater.* **1998**, *10*, 457. (b) Meng, H.; Bao, Z.; Lovinger, A. J.; Wang, B.-C.; Mujsce, A. M. *J. Am. Chem. Soc.* **2001**, *123*, 9214.