Single Crystal Organic Field-effect Transistors Based on 2,8-Diphenyl and Dinaphthyl Chrysenes

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1. Introduction

Organic semiconductors have attracted significant attention in materials science because of their potential application in large-area, low-cost and flexible electronic devices such as optical displays, chemical and physical sensors and radio frequency identification tags [1-5]. In particular, organic field-effect transistors (OFETs), the fundamental building blocks of organic-based circuits, are one of the most important topics. Low-cost production via a printing process and large area coverage are among the attractive research topics. However, disorder and grain boundaries in organic thin films are intrinsic properties of organic semiconductors and degrade device performance. Therefore, to study the

intrinsic charge transport properties of organic semiconductors and conduct correlation studies of crystal structure and FET performance, single crystal devices are needed. Single crystal OFETs perform better than thin film transistors, because of high molecular ordering and the absence of boundaries in the crystal. Great effort has been devoted to the development of newly fused π -conjugated organic semiconductors for high-performance organic single crystal transistors [6-11].

We recently synthesized a series of 2,8-disubstituted chrysene derivatives and applied them to organic thin film transistors [12]. Chrysene derivatives based thin film transistors showed typical *p*-channel FET characteristics, and their performance in devices was strongly affected by the molecular ordering and grain size of the organic thin films. The best field-effect mobility of $4.1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a current on/off ratio of 10^5 was obtained for 2,8-diphenyl chrysene (Ph-CR) based transistors. In this study, we fabricated and measured chrysene based single crystal OFETs to examine the intrinsic properties of chrysene derivatives.

Figure 1. Molecular structures of chrysene derivatives.

2. Experimental

Ph-CR and 2,8-bis(2-naphthyl)chrysene (Nap-CR) were synthesized by a previously reported procedure [12, 13]. All compounds were

Figure 2. Schematic illustration of the single crystal OFET device.

characterized by a combination of ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), IR and MS spectroscopy. The resulting chrysene derivatives were purified by vacuum sublimation before use. Other materials were reagent grade or better and were used as received.

Organic single crystals were grown by horizontal physical vapor transport in an argon gas flow [14]. The evaporating material was heated to 280 °C in the hot zone of a two-zone furnace. The second zone of the furnace was maintained at 230 °C. The crystals grew spontaneously on the wall of a glass tube in the colder zone of the furnace.

Top-contact type single crystal OFET devices were prepared by crystal lamination (Figure 2) [9–11]. As substrates for the lamination, we used an n^+ -doped Si wafer with 210 nm thick thermally grown SiO_2 , which was treated with a thin film (ca. 30 nm) of a polymer insulator such as poly(methyl methacrylate) (PMMA) or CYTOP (Asahi Glass Corp.). The polymer insulators were spin-coated at 2000 rpm and then dried at 70 °C and annealed at 100 °C for 3 h (PMMA) or dried at 90 °C and baked at 200 °C for 1 h (CYTOP) on a hot plate in N_2 atmosphere [15, 16]. Shiny, thin and detected-free chrysene single crystals were carefully selected and laminated on top of the substrates. Source and drain electrodes were applied with a colloidal graphite paste.

The electrical properties of the OFET devices were measured by using an Agilent 4155C semiconductor parameter analyzer under vacuum at room temperature. The field-effect mobility (μ_{FET}) was extracted from the saturated regime of the drain current (I_d) using the equation $I_d = (WC_i/2L) \mu_{\text{FET}} (V_g - V_{\text{th}})^2$, where C_i is capacitance of the insulator, V_d and V_{th} are the gate and threshold voltages, respectively. The current on/off ratio ($I_{\text{on}}/I_{\text{off}}$) was determined from the maximum (I_{on}) and minimum (I_{off}) values of the I_d .

Figure 3. (a) Molecular and (b) packing structures of Ph-CR.

The X-ray crystal structure analysis was performed on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated $\text{Mo-K}\alpha$ ($\lambda = 0.71069$ Å) radiation at -180 °C. Molecular orbital (MO) calculations were carried out by Density Functional Theory (DFT) methods at the B3LYP/6-31G(d) level using the Gaussian03 program [17].

3. Results and discussion

Very thin and planar crystals of Ph-CR and Nap-CR were obtained by horizontal physical vapor transportation. To investigate the molecular conformation and stacking of the molecules in the crystal state, X-ray single-crystal analysis was performed. Figure 3 shows molecular and packing structures for single crystal of Ph-CR. The phenyl substituents of Ph-CR are tilted 26.4° from the chrysene plane, and the crystal structure of Ph-CR exhibits a herringbone pattern that is favorable for high performance organic transistors [18, 19]. The packing structure of Nap-CR is not solved completely here because of poor crystal thickness.

Figure 4 shows the typical drain current as a function of the applied drain voltage at various gate voltages for OFETs based on Ph-CR and Nap-CR single crystals whose SiO_2 insulator was treated with CYTOP. The devices show a typical p -channel output profile of a metal-oxide-semiconductor FET. The field-effect mobility and the threshold voltage were calculated from the slope and intercept, respectively, of the linear portion of the $(-I_d)^{1/2} - V_g$ plot. The field-effect characteristics of chrysene based single crystal OFETs with various polymer insulator treatments are summarized in Table 1. The field-effect characteristics were strongly affected by the applied polymer insulator. The reported

Figure 4. I_d vs. V_d characteristics at various gate biases for OFET devices based on (a) Ph-CR and (b) Nap-CR single crystals whose SiO_2 insulator was treated with CYTOP.

contact angles with water for SiO_2 , PMMA and CYTOP are 20° , 68° and 108° , respectively [20, 21]. Hydrophobic insulators are known to be favorable for high performance thin-film and single crystal OFETs [8, 21, 22]. The best FET characteristics of $\mu_{\text{FET}} = 2.2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $I_{\text{on}}/I_{\text{off}} = 10^6$ were obtained in the CYTOP treated device for the Nap-CR single crystal.

To obtain further information on the relationship between molecular structure and FET characteristics, we examined the energy levels of

Figure 5. Calculated energy diagram and frontier orbitals of (a) Ph-CR [12] and (b) Nap-CR.

the chrysene derivatives by MO calculations. The electronic properties of unsubstituted chrysene, Ph-CR and Nap-CR were calculated with the DFT MO calculation [B3LYP/6-31G(d)] embedded in the Gaussian 03 software package. The resulting molecular orbitals and energy diagrams are shown in Figure 5 [12]. The HOMO energy levels of Ph-CR and Nap-CR are slightly higher than that of unsubstituted chrysene (-5.50 eV), and the LUMO energy levels of Ph-CR and Nap-CR are slightly lower than that of the unsubstituted chrysene (-1.25 eV). The band gap energy for the Nap-CR (3.87 eV) are slightly narrower than that for Ph-CR (4.03 eV), which is favorable for charge transport between molecules.

4. Conclusion

We successfully fabricated single crystal OFETs based on chrysene derivatives Ph-CR and Nap-CR. The single crystal chrysene based OFETs showed typical *p*-channel FET characteristics, and the highest field-effect mobility of $2.2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with an on/off current ratio of 10^6 was obtained for Nap-CR.

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Table 1. Field-effect characteristics of chrysene based single crystal OFETs with various polymer insulator treatments.

Compound	Polymer insulator	$\mu_{\text{FET}} / \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	$I_{\text{on}}/I_{\text{off}}$	V_{th} / V
Ph-CR	-	0.29	10^4	-20
Ph-CR	PMMA	0.37	10^4	-22
Ph-CR	CYTOP	1.6	10^3	-35
Nap-CR	-	0.54	10^3	-18
Nap-CR	PMMA	0.96	10^5	-17
Nap-CR	CYTOP	2.2	10^6	-33

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