Characteristics of Thin-Film Transistors Based on 2,8-Disubstituted Chrysene Derivatives with Polymer-Treated SiO₂ Dielectric Layers

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ABSTRACT

We investigated the characteristics of organic thin-film transistors based on 2,8-disubstituted chrysene derivatives with a polymer treated SiO₂ dielectric layer to examine the effect of polymer coating. Field-effect characteristics were strongly influenced by the applied polymer insulators, and the best field-effect mobility ($2.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was obtained for the CYTOP-treated device incorporating 2,8-diphenyl chrysene.

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1. Introduction

During the past few decades, organic semiconductors have attracted significant attention as a new class of electronic materials for organic field-effect transistors (OFETs), organic light-emitting diodes and organic solar cells.^{1–3} Particularly, OFETs have been intensively investigated for applications in organic integrated circuits for flexible active-matrix displays, radio frequency identification tags, and chemical and biological sensors, because of the merits of organic materials, such as low cost, flexibility, and easy fabrication.^{4–8} A typical OFET comprises an organic semiconductor, a gate dielectric (insulator), and three electrodes (source, drain, and gate). When voltage is applied between the source and drain electrodes, a channel current flows through the organic semiconductor layer associated with the charge carrier transport. The charge carrier mobility is strongly influenced by the organic semiconductor layer, and therefore, great efforts have been made toward the development of various semiconducting small molecules and polymers. Among these, fused π -conjugated semiconductors such as acene-, thienoacene-, and thienothiophene-based compounds are promising materials for high-performance OFETs.^{9–12}

Recently, we synthesized a series of 2,8-disubstituted chrysene derivatives as novel fused π -conjugated semiconductors, and applied them to organic thin-film¹³ and single-crystal¹⁴ transistors. These transistors based on 2,8-disubstituted chrysene derivatives showed typical *p*-channel FET characteristics, and field-effect mobilities of 0.04 and $1.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were obtained for the 2,8-diphenyl chrysene (Ph-CR) based thin-film and single crystal transistors, respectively. It is well known that the field-effect characteristics are strongly influenced by the surface features of the gate dielectric.¹⁵ The control of the gate dielectric surface can efficiently increase the field-effect mobility of OFETs because the surface characteristics of the gate dielectric can determine the growth pattern of the first few monolayers of an organic semiconductor on the gate dielectric. To control the gate dielectric surface properties to achieve favorable ordering of organic semiconductors, a common practice is surface treatment of the SiO₂ gate dielectric by a thin polymeric layer¹⁶ or a self-assembled monolayer (SAM), such as octadecyltrichlorosilane¹⁷ and hexamethyldisilazane.¹⁸ However, most of the organosilane-based SAM treatments require handling under inert conditions because of the high reactivity of the organosilane-coupling reagents to moisture.

Figure 1. Chemical structures of Ph-CR and Nap-CR.

In this study, we investigate the characteristics of organic thin-film transistors based on 2,8-disubstituted chrysene derivatives (Fig. 1) with a polymer-treated SiO₂ dielectric layer to examine the effect of polymer coating. Polymer coating of the SiO₂ gate dielectric can be easily accomplished by a spin-coating technique under ambient conditions.

2. Experimental

Ph-CR and 2,8-bis(2-naphthyl)chrysene (Nap-CR) were synthesized by a procedure analogous to reported methods.^{14,19} The resulting 2,8-disubstituted chrysene derivatives were purified by vacuum sublimation before use. Other chemicals were reagent grade or better and were used as received.

Thin-film transistors were fabricated in a top-contact configuration as follows. Heavily doped n^+ -Si (100) wafers with a thermally grown insulating SiO₂ layer (thickness 210 nm) were used as substrates. After removing the bottom of the SiO₂ layer, a gold electrode (thickness 50 nm) was deposited on the bare side of the Si/SiO₂ substrate as a gate contact. The insulating SiO₂ layer was treated with a thin film (ca. 30 nm) of a polymer insulator such as poly(methyl methacrylate) (PMMA) or CYTOP (Asahi Glass Corp.) (Fig. 2). 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 under an N₂ atmosphere.^{20,21} A thin film (thickness 50 nm) of the chrysene derivative, as an active layer, was vapor deposited on the polymer-treated Si/SiO₂ substrate maintained at various substrate temperatures (T_{sub}) at a deposition rate of approximately 0.1 nm s^{-1} under a pressure of $1\text{--}2 \times 10^{-3} \text{ Pa}$. Gold films (thickness 80 nm) as drain and source electrodes were deposited on the organic semiconductor

Figure 2. Chemical structures of PMMA and CYTOP. **Figure 3.** Output characteristics of the Ph-CR based OFET device deposited on the CYTOP-treated SiO₂ insulator at $T_{\text{sub}} = 60^\circ\text{C}$.

layer through a shadow mask. The drain-source channel width (W) and length (L) were 1.5 mm and 50 μm , respectively. The electrical properties of the resulting devices were measured 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 $I_{\text{d}} = (WC_i/2L)\mu_{\text{FET}}(V_{\text{g}} - V_{\text{th}})^2$, where C_i is the insulator capacitance, and V_{g} 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 I_{d} .

X-ray diffractions (XRDs) of the vapor-deposited chrysene derivative films on the polymer treated Si/SiO₂ substrate were obtained with a Philips PW1830 diffractometer using a CuK α source ($\lambda = 0.1541\text{ nm}$) under ambient conditions. Atomic force microscopy (AFM) images of the organic films on the substrate were obtained in the “tapping mode” with Digital Instruments NanoScopeIIIa in air.

3. Results and Discussion

Figure 3 shows a typical drain current as a function of the applied drain voltage at various gate voltages for OFETs based on Ph-CR thin films with CYTOP-treated SiO₂ insulators. The devices show a typical output profile of a metal-oxide-semiconductor FET, and the channel conductance increases as V_{g} becomes more negative, indicating that the Ph-CR film behaves as a p -type semiconductor. The field-effect mobility was calculated from the slope of the linear portion of the $(-I_{\text{d}})^{1/2} - V_{\text{g}}$ plot. The field-effect characteristics were strongly influenced by T_{sub} . For example, the mobilities of the Ph-CR based devices with a bare SiO₂ insulator were 1.5×10^{-3} , 4.1×10^{-2} , and $4.1 \times 10^{-3}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ for the $T_{\text{sub}} = \text{rt}$, 60, and 100°C , respectively.¹³ The best results were obtained for $T_{\text{sub}} = 60^\circ\text{C}$ (Ph-CR) and $T_{\text{sub}} = 100^\circ\text{C}$ (Nap-CR). The field-effect

Table 1. Field-effect characteristics of OFETs based on Ph-CR and Nap-CR films deposited on polymer-treated SiO₂ insulators.

Compound	Polymer insulator	$T_{\text{sub}}/^\circ\text{C}$	$\mu_{\text{FET}}/\text{cm}^2\text{ V}^{-1}\text{ s}^{-1}$	$I_{\text{on}}/I_{\text{off}}$
Ph-CR ¹³	—	60	0.04	10^5
Ph-CR	PMMA	60	0.65	10^6
Ph-CR	CYTOP	60	2.8	10^4
Nap-CR ¹³	—	100	0.02	10^5
Nap-CR	PMMA	100	0.26	10^6
Nap-CR	CYTOP	100	0.76	10^6

Figure 4. (Color online) AFM images of the Ph-CR film (thickness 50 nm) deposited on (a) bare, and (b) PMMA- and (c) CYTOP-treated Si/SiO₂ at $T_{\text{sub}} = 60^\circ\text{C}$.

characteristics of chrysene-based thin-film transistors with various polymer insulator treatments at the optimal T_{sub} are summarized in Table 1.

The field-effect characteristics also strongly correlated with the applied polymer insulator, and the best field-effect mobility ($2.8\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) was obtained for the CYTOP-treated device incorporating Ph-CR. The reported contact angles with water for SiO₂, PMMA, and CYTOP are 20, 68, and 108° , respectively.^{22,23} It is known that hydrophobic insulators are favorable for high-performance organic thin-film transistors. To obtain further information on the effect of the polymer insulator, we obtained XRD and AFM images of the vapor-deposited films.

According to the primary XRD peak, the interlayer distances were 19.7 and 23.9 $\text{\AA}$ for Ph-CR (PMMA, $T_{\text{sub}} = 60^\circ\text{C}$) and Nap-CR (PMMA, $T_{\text{sub}} = 100^\circ\text{C}$), respectively. These values were not significantly influenced by the applied polymer insulator, and indicated that the molecules are oriented with nearly upright structures on the substrate.^{13,14} Figure 4 shows AFM images of the Ph-CR films deposited on bare and polymer-treated Si/SiO₂ substrates. Needle-like grains were observed for bare and PMMA-treated composites, while the films on CYTOP exhibited round shapes and larger grains, which are suitable morphology for electrical transport between source and drain electrodes. Similar AFM images were obtained for the Nap-CR films. Furthermore, the applied polymer insulator may reduce charge trapping states at the interface by covering the hydrophilic SiO₂ surfaces.²⁴ At this time the effect of polymer treating on the field-effect mobilities cannot be understood sufficiently and is under investigation.

4. Conclusions

In summary, chrysene-based thin-film transistors with polymer-treated insulators show a typical p -type output profile of a metal-oxide-semiconductor FET. Field-effect characteristics were strongly influenced by the applied polymer insulators, and high field-effect mobilities of 2.8 and $0.76\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ were obtained for the CYTOP-treated devices incorporating Ph-CR and Nap-CR, respectively.

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