Organic Field-effect Transistors Based on Vapor Deposited 2,9-Dialkylpentacene Films

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Organic field-effect transistors based on vapor deposited films of 2,9-diethylpentacene (C\textsubscript{2}-PEN), 2,9-dibutylpentacene (C\textsubscript{4}-PEN) and 2,9-dioctylpentacene (C\textsubscript{8}-PEN) were successfully fabricated. All the alkylpentacene based OFETs showed typical \textit{n}-channel FET characteristics, and the best field-effect mobility of 4.8×10^{-2} cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} with on/off current ratio of ~10\textsuperscript{4} was obtained for the C\textsubscript{2}-PEN based OFET. Interestingly, the filed-effect mobility decreased as alkyl-chain length becomes longer. According to the molecular orbital calculations, the 2,9-dialkylpentacenes form doubly bent molecular structures in which the all-anti alkyl groups are not lie on the same plane as that of the pentacene core. The alkyl-chains may hinder the intermolecular interactions and overlap, meaning the poor intermolecular charge transfer.

Keywords: organic field-effect transistor, alkylpentacene, molecular orbital calculation

1. Introduction

Organic field-effect transistors (OFETs) have been currently focused in the field of material sciences, because of their potential applications for flexible, large-area and low-cost electronic devices such as pliable displays, radio frequency identification tags and flexible sensors [1-3]. Recently, a number of newly developed organic semiconductors have been reported as high-performance organic transistor materials [4-10]. Among the organic semiconductors, pentacene is the most popular and promising material since it offers high field-effect mobility ($\mu_{\text{ET}}$) as high as 3.0 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} [11,12]. Pentacene derivatives are also promising materials, for example, perfluoropentacene [13] is a high-performance \textit{n}-channel material and 6,13-bis(triisopropyl-silylethynyl)pentacene [14] is a good solution processed material.

Recently, we have synthesized a series of 2,9-dialkyl-substituted pentacenes as shown in Figure 1, and investigated their liquid crystallinity [15]. For longer alkyl chain compounds, focal conic or baton texture was observed, indicating the

\begin{center}
\begin{tabular}{c}
\textbf{C\textsubscript{2}-PEN: R=C\textsubscript{2}H\textsubscript{5}} \\
\textbf{C\textsubscript{4}-PEN: R=C\textsubscript{4}H\textsubscript{9}} \\
\textbf{C\textsubscript{8}-PEN: R=C\textsubscript{8}H\textsubscript{17}}
\end{tabular}
\end{center}

Fig. 1. Chemical structures of 2,9-dialkylpentacenes.
existence of an ordered smectic phase. In this work, we investigate characteristics of the OFETs using alkyl-substituted pentacenes (C\textsubscript{n}-PEN; n=2, 4 and 8) as active layers.

2. Experimental

2.1. Materials

2,9-diethylpentacene (C\textsubscript{2}-PEN), 2,9-dibutylpentacene (C\textsubscript{4}-PEN), 2,9-dioctylpentacene (C\textsubscript{8}-PEN) were synthesized as the reported procedure [15]. The resulting alkyl-substituted pentacenes were purified by vacuum sublimation in several times before use.

2.2. Device fabrications

The “top contact” (top source and drain contact, bottom gate contact) type OFET devices (Figure 2) were fabricated as follows. Heavily doped n\textsuperscript{+}-Si (100) wafers with a thermally grown insulating SiO\textsubscript{2} layer (210 nm thick) were used as the substrates. After removing the bottom side of SiO\textsubscript{2} layer, gold electrode (50 nm thick) was deposited on the bare side of the SiO\textsubscript{2} substrate as a gate contact. A thin film (50 nm) of alkylpentacene as an active layer was vapor deposited on the Si/SiO\textsubscript{2} substrate maintained at various substrate temperatures (T\textsubscript{sub}) at a deposited rate of ca. 0.1 nm s\textsuperscript{-1} under a pressure of 1~2 x 10\textsuperscript{-3} Pa. Gold source and drain electrodes (800 nm thick) were deposited through a shadow mask on top of the organic thin film layer. For a typical device, the drain-source channel width (W) and length (L) are 1.5 mm and 50 \mu m, respectively.

2.3. Measurements and evaluations

X-ray diffractions (XRDs) of vapor deposited organic films on the Si/SiO\textsubscript{2} substrate were obtained with a Philips PW1830 diffractometer with a CuK\alpha source (\lambda = 1.541 Å) under ambient conditions. Atomic force microscope (AFM) images of the deposited films were obtained by “tapping mode” with Digital Instruments NanoScope IIIa in air.

The electrical properties of the OFET devices were measured by using an Agilent 4155C semiconductor parameter analyzer under vacuum at room temperature. Field-effect mobility (\mu\textsubscript{FE}) was calculated in the saturated regime (V\textsubscript{d} = -100 V) of the drain current (I\textsubscript{d}) using the following equation,

\[ I_d = \left( \frac{W C_i \mu_{FE}}{2L} \right) (V_g - V_{th})^2 \]  

(1)

where C\textsubscript{i} is capacitance of the SiO\textsubscript{2} insulator, V\textsubscript{d} and V\textsubscript{th} are the gate and threshold voltages, respectively. Current on/off ratio (I\textsubscript{on}/I\textsubscript{off}) was
determined from the maximum ($I_{on}$) and minimum ($I_{off}$) value of the $I_d$.

2.4. Molecular orbital calculations

Molecular orbital (MO) calculations were carried out by Density Functional Theory (DFT) methods at the B3LYP/6-31G(d) level using the Gaussian03 program [16].

3. Results and Discussion

Fig. 3(a) shows the linear $I_d$~$V_d$ characteristics at various $V_g$ and Figure 3(b) shows ($I_d$)$^{1/2}$~$V_g$ and log($I_d$)~$V_g$ characteristics for a C2-PEN based FET device fabricated at $T_{sub} = 100\, ^{\circ}C$. The device shows a typical output profile of a metal-oxide-semiconductor FET. As shown in Fig. 3(a), channel conductance increase as $V_g$ becomes more negative, meaning that the C2-PEN film behave as a $p$-type semiconductor. The field-effect mobility and the threshold voltage were calculated from the slope and intercept, respectively, for the linear portion of the ($I_d$)$^{1/2}$~$V_g$ plot (Fig. 3(b)). Field-effect characteristics for the C2-PEN based OFETs are summarized in Table 1.

<table>
<thead>
<tr>
<th>$T_{sub}$ / °C</th>
<th>$\mu_{FET}$ / cm$^2$V$^{-1}$s$^{-1}$</th>
<th>$V_{th}$ / V</th>
<th>$I_{on}$ / $I_{off}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>rt</td>
<td>$1.1 \times 10^{-2}$</td>
<td>-20</td>
<td>$10^3$</td>
</tr>
<tr>
<td>60</td>
<td>$3.3 \times 10^{-2}$</td>
<td>-30</td>
<td>$10^5$</td>
</tr>
<tr>
<td>100</td>
<td>$4.8 \times 10^{-2}$</td>
<td>-20</td>
<td>$10^4$</td>
</tr>
</tbody>
</table>

The mobilities depend on the deposition temperature of the films, while $V_{th}$ and $I_{on}$/$I_{off}$ was $-20 \sim -30$ V and $10^3 \sim 10^5$, respectively. The mobility for the C2-PEN film deposited at 100 °C was higher than that at room temperature (rt) and 60 °C. This is attributed to the difference in grain size for the C2-PEN films. Fig. 4 shows AFM images of the C2-PEN films (50 nm) deposited on Si/SiO$_2$ substrates at different substrate temperatures. The grain size for the C2-PEN film deposited at 100 °C was bigger than that at rt and 60 °C. Usually, carrier mobility in the crystal grain (intragnain mobility) is larger than that across the the grain-boundary (intergrain mobility), so that the overall mobility for the polycristalline film increases with the decrease of the number of grain-boundaries [17-19]. A similar consideration

Fig. 4. AFM images of the C2-PEN films (50 nm) deposited on Si/SiO$_2$ at (a) $T_{sub}$ = rt, (b) $T_{sub}$ = 60 °C and (c) $T_{sub}$ = 100 °C

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{FET}$ / cm$^2$V$^{-1}$s$^{-1}$</th>
<th>$V_{th}$ / V</th>
<th>$I_{on}$ / $I_{off}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2-PEN$^a$</td>
<td>$4.8 \times 10^{-2}$</td>
<td>-20</td>
<td>$10^3$</td>
</tr>
<tr>
<td>C2-PEN$^a$</td>
<td>$4.4 \times 10^{-3}$</td>
<td>-18</td>
<td>$10^4$</td>
</tr>
<tr>
<td>C2-PEN$^b$</td>
<td>$8.8 \times 10^{-4}$</td>
<td>-20</td>
<td>$10^3$</td>
</tr>
</tbody>
</table>

a) $T_{sub}$ = 100 °C, b) $T_{sub}$ = 60 °C.
Fig. 5. X-ray diffraction patterns of the C₈-PEN films (50 nm) deposited on Si/SiO₂.

is applicable to the present case. Namely, the charge transport is predominant by the intergrain transport.

Similar $T_{sat}$ dependence of the mobility was observed in C₄-PEN based OFET devices. The mobility was $8.8 \times 10^{-4}$ cm²V⁻¹s⁻¹ at $T_{sat} = 35$, and the maximum value ($4.4 \times 10^{-3}$ cm²V⁻¹s⁻¹) was obtained at $T_{sat} = 100$ °C. For the C₈-PEN based OFET devices, the highest mobility was obtained at $T_{sat} = 60$ °C. The best field-effect characteristics for C₂-PEN, C₄-PEN, and C₈-PEN based OFETs are summarized in Table 2. The field-effect mobility decrease as alkyl-chain length becomes longer.

Fig. 5 shows X-ray diffraction patterns of the alkylpentacene films (50 nm) deposited on Si/SiO₂ substrate at $T_{sat} = 100$ °C for C₂-PEN and C₄-PEN, and at $T_{sat} = 60$ °C for C₈-PEN. The values of $d$-spacing were independent of $T_{sat}$, and were 18.9, 23.0 and 31.8 Å for C₂-PEN, C₄-PEN, and C₈-PEN films, respectively. The $d$-spacings were increased with the elongation of the alkyl-chain, which may be qualitatively understood by considering that longer molecules form thicker layers.

In order to gain further insight into the relationship between molecular structure and FET characteristics, we examine the conformations of the alkylpentacenes by MO calculation. The most stable conformations of the alkylpentacenes obtained by DFT-MO calculation with B3LYP/6-31G(d) level are shown in Figure 6. The pentacene cores are almost flat in all conformations. The alkylpentacenes form doubly bent molecular structures in which the all-anti alkyl groups are not lie on the same plane as that of the pentacene core. Calculated molecular lengths of C₂-PEN, C₄-PEN and C₈-PEN were 18.9, 23.6 and 33.4 Å, respectively. By comparing the $d$-spacings with the calculated molecular lengths, all the C₈-PEN molecules orientate almost perpendicular to the Si/SiO₂ substrate in the thin
films, those are favorable for high performance OFETs. Usually, molecular packing in the grain is also much depend on the compounds and dominates the carrier transport properties of OFET devices. In this case, the field-effect mobility decrease as alkyl-chain length becomes longer. The alkyl groups of the doubly bent molecular structured C_{60}-PEN may hinder the intermolecular interactions, and the carrier transfer.

4. Conclusion

In summary, we have successfully fabricated the OFETs based on vapor deposited films of C_{20}-PEN, C_{40}-PEN and C_{60}-PEN as the active layer. All the C_{60}-PEN based OFETs showed typical p-channel FET characteristics, and the highest field-effect mobility of 4.8×10^{-2} cm^{2}V^{-1}s^{-1} with I_{on}/I_{off} = -10^{4} was obtained for C_{20}-PEN. The field-effect mobility decreased as alkyl-chain length becomes longer. According to the DFT-MO calculations, the alkylpentacenes form doubly bent molecular structures in which the all-anti alkyl groups are not lie on the same plane as that of the pentacene core. The alkyl-chains may hinder the intermolecular interactions and overlap, meaning the poor intermolecular charge transfer.

References