High mobility n-type thin-film transistors based on 3,4,9,10-perylenetetracarboxylic diimide with thermal treatments

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The authors demonstrated that N,N'-ditridecyl-3,4,9,10-perylenetetracarboxylic diimide (PTCDI-C13) thin-film transistors (TFTs) exhibited high field-effect electron mobility of 2.1 cm²/V s by just annealing at an adequate temperature (140 °C) after the TFT fabrications. While PTCDI-C13 formed c-axis oriented thin films, the thermal treatments improved crystallinity of the thin films as revealed by x-ray diffraction. The thermal treatment also affected thin-film morphologies; the morphologies changed from oval ball-like grains to flat and large tilelike grains, which had molecular height steps and whose size reached several micrometers. © 2006 American Institute of Physics. [DOI: 10.1063/1.2349290]

Organic thin-film transistors (TFTs) have attracted considerable interests in recent years because of their many potential applications such as flexible, large-area, and low-cost electronic devices. Among many organic semiconductors investigated, pentacene has been shown to possess the highest mobility in thin-film states, and the mobility is favorably compared with that of hydrogenated amorphous silicon. Most materials with high mobility in thin-film state such as pentacene and thiophene derivatives are p-type semiconductor whose main carrier is hole. However, there have been few reports on high performance n-type organic TFTs. To move ahead with organic electronics, it is more desirable to use complementary metal-oxide semiconductor (CMOS)-like logic circuits that call for both p- and n-type TFTs due to their low power consumptions and simple circuit designs. Thus, improvements of n-type organic TFT performance are prior to this end.

3,4,9,10-perylenetetracarboxylic diimide (PTCDI) is one of the most important n-type materials with high field-effect electron mobility due to the large π-electron system and strong electron affinity. For example, N,N'-diphenyl PTCDI is one of the first n-type organic TFT materials reported by Horowitz et al. Recently, Malenfant et al. reported that N,N'-dioctyl PTCDI exhibited high field-effect electron mobility of ~0.6 cm²/V s, and then Chesterfield et al. also showed the highest field-effect electron mobility in organic semiconducting materials of up to 1.7 cm²/V s by finely controlling deposition conditions (substrate temperature and deposition rate) to attain well organized thin films of the material. It is well known that alkyl chains with π-electron cores are effective for self-assembling. By extension of this research stream, incorporating longer alkyl chains to PTCDI as N substituents will be an effective way to get higher electron mobility in PTCDI systems. In addition, since long alkyl chains have higher mobile natures than rigid π-electron systems, repairing molecular alignments and crystal disorders probably occurs with thermal treatments of the thin films at rather low temperatures. In this letter, we report that mobility of TFT using PTCDI with tridecyl as a long alkyl chain is dramatically improved by simple thermal treatments after device fabrications.

Figure 1 shows the structural formula of ditridecyl PTCDI abbreviated as PTCDI-C13. Figure 1 also shows the schematic structure of top-contact PTCDI-C13 TFTs fabricated. The devices were prepared on heavily doped p-type silicon wafers with 200-nm-thick thermally grown SiO₂, which were utilized as a gate electrode and a gate dielectric (specific capacitance of 15 nF/cm²), respectively. PTCDI-C13 (purchased from Aldrich) was thermally evaporated at the rate of 0.3 A/s onto the substrates whose temperature is a room temperature. Finally, Au was thermally evaporated onto the PTCDI-C13 film through a shadow mask to form source-drain electrodes. The channel length and width were 100 μm and 2 mm, respectively. TFT characteristics were measured in a vacuum (below 5 × 10⁻⁴ Pa) at room temperature using an Advantest R6245 two-channel source-measure unit. After the first measurement the device was thermally treated in a vacuum for 1 h and then slowly cooled down to room temperature with keeping the vacuum. The devices were exposed to the atmosphere before and after the thermal treatment. After the treatment, another TFT characteristic measurement was carried out again under the same condition. X-ray diffraction (XRD) was measured with Phillips EDAX-9100 using Cu Kα radiation under the 0/2θ geometry. Surface morphologies of thin films were evaluated with a Seiko SPA-400 atomic force microscope (AFM) with a

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![](image) FIG. 1. Chemical structure of PTCDI-C13 and schematic of TFT structure.
organic TFTs. As shown in Fig. 2, threshold voltage of 44 V were determined from a gate voltage above 0.5 cm²/V s. Moreover, we have demonstrated that drain currents are much larger than those of the same device after a thermal treatment at 140 °C, the same as the case of the TFTs. The crystal structure of PTCDI-C13 was analyzed with a Bruker SMART APEX II ULTRA.

The drain current-drain voltage ($I_D$-$V_D$) plots of an as-prepared PTCDI-C13 TFT (before thermal treatment) were shown in Fig. 2(a). The device showed typical n-type characteristics. The n-type behavior was just obtained in vacuum. When devices were exposed to the atmosphere, the TFTs did not work. However, the TFTs exhibited closely the same n-type behavior again by putting the device in vacuum again. Field-effect electron mobility of $5.4 \times 10^{-3}$ cm²/V s and threshold voltage of 44 V were determined from a gate voltage above 0.5 cm²/V s. Moreover, we have demonstrated that drain currents are much larger than those of the same device after a thermal treatment at 140 °C, the same as the case of the TFTs. The crystal structure of PTCDI-C13 was analyzed with a Bruker SMART APEX II ULTRA.

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supposed that the orientation works in favor of carrier transports due to strong intermolecular interactions. In addition, the larger gains also have a beneficial effect on the transports because grain boundaries interfere with the transports. The results of the XRD measurements and the AFM observations also supported enhancing electron mobility mentioned above. On the other hand, although PTCDI-C13 films treated at 200 °C had high crystallinity and larger grains, the mobility was 0.54 cm²/V s, smaller than that treated at 140 °C. Some cracks observed in Fig. 4(c) probably cause the small improvement of electron mobility. However, when the cracks vanish in the thin film at such high temperature annealing, PTCDI-C13 TFTs probably attain much higher mobility because quite larger tilelike grains appeared as shown in Fig. 4(c). Note that some self-assembling nature of PTCDI-C13 probably caused the surprisingly large gains segmentalized with the cracks.

In conclusion, we showed that electron mobility in PTCDI-C13 TFTs stood at 2.1 cm²/V s with just annealing at the adequate temperature (140 °C) after the TFT fabrications. While PTCDI-C13 formed c-axis oriented thin films, crystallinity of the thin films was improved by the thermal treatment. The thin-film morphologies changed from oval ball-like grains to flat and large tilelike grains with molecular height steps by the thermal treatment. We expect that higher mobility will be achieved with simple thermal treatments at lower temperatures by optimizing alkyl-chain length of PTCDI. Moreover, decreasing of threshold voltages is a prior issue to build CMOS-like organic logic circuits. Now such researches are in progress.

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