

High mobility *n*-type thin-film transistors based on *N,N'*-ditridecyl perylene 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.^{1,2} 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.³⁻⁵ Most materials with high mobility in thin-film state such as pentacene and thiophene derivatives are *p*-type semiconductor whose main carrier is hole.⁶⁻⁸ However, there have been few reports on high performance *n*-type organic TFTs.⁹⁻¹⁵ 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.*¹⁶ Recently, Malenfant *et al.* reported that *N,N'*-dioctyl PTCDI exhibited high field-effect electron mobility of ~ 0.6 cm²/V s,¹² 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.¹⁷ 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 Å/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 μ m 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 devices were 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 *K* α radiation under the $\theta/2\theta$ geometry. Surface morphologies of thin films were evaluated with a Seiko SPA-400 atomic force microscope (AFM) with a

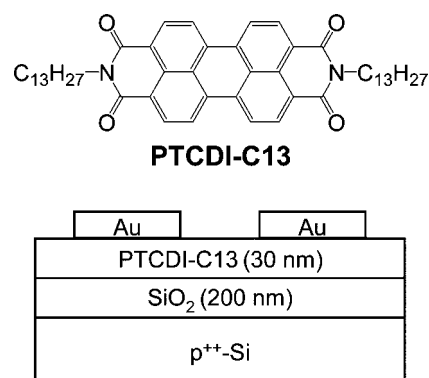


FIG. 1. Chemical structure of PTCDI-C13 and schematic of TFT structure.

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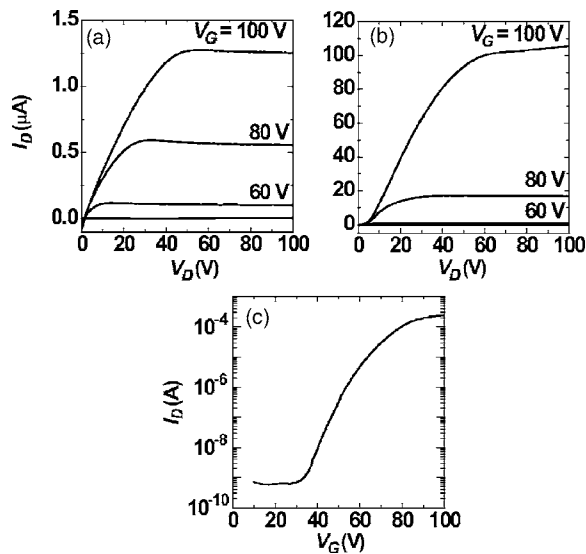


FIG. 2. I_D - V_D characteristics of PTCDI-C13 TFTs (a) before any thermal treatment (as fabricated) and (b) after the thermal treatment at 140 °C. (c) I_D - V_G characteristic of the 140 °C-treated TFT at the drain voltage of 100 V.

dynamic force mode. Sample thin films for the XRD and AFM were also prepared onto Si substrates with SiO₂ layers 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 5.4×10^{-3} cm²/V s and threshold voltage of 44 V were determined from a gate voltage (V_G) dependence of the saturated drain currents. On the other hand, as Fig. 2(b) shows the other I_D - V_D characteristics of the same device after a thermal treatment at 140 °C, the drain currents are much larger than those of the same device before the treatment. After thermal treatments at 100–220 °C, all test TFT devices showed field-effect mobility above 0.5 cm²/V s. Moreover, we have demonstrated high electron mobility of 2.1 cm²/V s when the TFT was treated at 140 °C. This is the highest mobility in n -channel organic TFTs. As shown in Fig. 2(c), the device exhibited enough high on/off ratio of 4.2×10^5 . However, the threshold voltage of the device somewhat increased, and then became 60 V.

Figure 3(a) shows XRD patterns of PTCDI-C13 thin

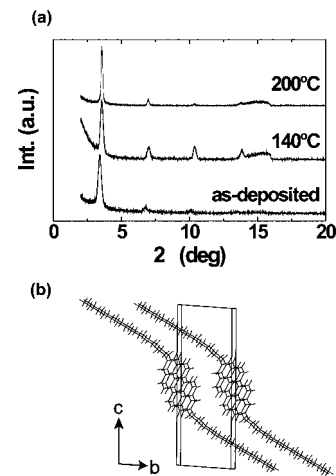


FIG. 3. (a) XRD patterns of as-deposited and thermally treated PTCDI-C13 thin films. (b) Side view of the PTCDI-C13 crystals. Crystallographic parameters of PTCDI-C13: crystal class is triclinic (P1) and the cell constants are $a=4.661(5)$ Å, $b=8.592(9)$ Å, $c=25.31(3)$ Å, $\alpha=86.380(12)^\circ$, $\beta=85.786(13)^\circ$, $\gamma=82.473(11)^\circ$, and $Z=2$.

films thermally treated at 140 and 200 °C, together with that of an as-prepared thin film. Since several diffraction peaks were observed from both as-deposited and thermally treated films, PTCDI-C13 forms oriented thin films even in as-deposited films. In the as-deposited film, three reflection peaks appeared at 3.43°, 6.77°, and 10.11° which correspond to d spacing of 25.7, 13.1, and 8.77 Å, respectively. These peaks were assigned to (001), (002), and (003) based on the crystal structure of PTCDI-C13 as shown in Fig. 3(b). Thus, the c axis was perpendicularly ordered on the substrate in thin-film state. After the thermal treatment at 140 °C, a new reflection peak of (004) appeared and each peak became narrower, so crystallinity of thin films improved. Thermal treatments at higher temperature attained higher crystallinity because of more narrowing as shown in Fig. 3(a). Note that reflection peaks slightly shifted after any thermal treatments above 100 °C and corresponded to those of the lattice constant of PTCDI-C13.

Figure 4 shows the AFM topography images of PTCDI-C13 thin films thermally treated at 140 and 200 °C together with that of an as-deposited film. As shown in Fig. 4(a), PTCDI-C13 formed ellipsoidal-ball-like grains in the as-prepared film. On the contrary, the grain style dramatically changed from ball-like to tilelike in the film treated at 140 °C. The height (25 Å) of each tiles corresponded to the length of the c axis of PTCDI-C13 crystal; thus the thermally treated PTCDI-C13 thin films have high crystallinity. The size of the grains stood at a few micrometers. The crystal-like cofacial molecular orientation shown in Fig. 3(b) probably appears in the thermally treated thin films, and then it is

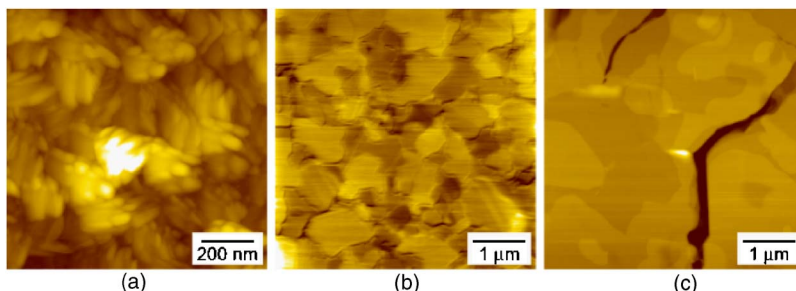


FIG. 4. (Color online) AFM topographs of PTCDI-C13 thin films with (a) no thermal treatment (as prepared) and annealing at (b) 140 °C and (c) 200 °C.

supposed that the orientation works in favor of carrier transports due to strong intermolecular interactions. In addition, the larger grains 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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