

## Solution-processed *n*-type organic thin-film transistors with high field-effect mobility

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We report the performance of solution-processed *n*-type organic thin-film transistors (OTFTs) based on C<sub>60</sub> derivatives. Long-chain alkyl-substituted C<sub>60</sub>, C<sub>60</sub>-fused *N*-methylpyrrolidine-*meta*-C12 phenyl (C60MC12), was used as a semiconducting layer. The C60MC12-thin-film transistor shows high electron mobility of 0.067 cm<sup>2</sup>/V s in saturation regime. From the result of x-ray diffraction analysis, the C60MC12 active layer forms highly ordered crystalline film. We found that self-assemble ability of long alkyl chains plays an important role for fabrication of highly ordered crystalline film, leading to achievement of high electron mobility in solution-processed *n*-type OTFTs. © 2005 American Institute of Physics. [DOI: 10.1063/1.2130712]

Organic semiconductors have received much attention for the application of organic thin-film transistors (OTFTs) and *p-n* junction devices, such as organic light-emitting devices and photovoltaic cells, since organic electronics have been expected to realize low-cost, large-area, and flexible devices.<sup>1,2</sup> In the case of *p*-type materials, the highest field-effect mobility has already reached the level of hydrogenated amorphous silicon. In addition, because of recent progress in the development of *n*-type materials,<sup>3-7</sup> the highest mobility in *n*-type OTFTs has also caught up with the level of *p*-type OTFTs. However, there are few reports concerning solution-processed *n*-type OTFTs with high electron mobility,<sup>8-10</sup> whereas a number of promising solution-processed *p*-type OTFTs have been reported, such as polythiophenes,<sup>11-14</sup> oligothiophenes,<sup>15,16</sup> pentacenes,<sup>17,18</sup> and functionalized acenes.<sup>19</sup> For application of printable organic complementary metal-oxide semiconductor circuit, development of solution-processable *n*-type materials is needed.

Recently, it has been reported that solution-processable C<sub>60</sub>, [6,6]-phenyl C61-butyric acid methyl ester (PCBM), shows high field-effect electron mobility (0.004–0.01 cm<sup>2</sup>/V s).<sup>9,10</sup> However, the spin-coated PCBM film takes disordered structure.<sup>20</sup> Aiming at higher mobility of solution-processable C<sub>60</sub>-thin-film transistor (TFT) by improving the molecular order in the film, we have focused on long-chain alkyl substituted C<sub>60</sub>.<sup>21,22</sup> An advantage of this compound is not only high solubility for organic solvent but also easy fabrication of highly ordered film by using the self-assemble ability of a long alkyl chain. Therefore, an improvement in electron mobility is expected by employing long-chain alkyl substituted C<sub>60</sub> as an active layer in a solution-processed *n*-type OTFT.

In this letter, we report the TFT performance of C<sub>60</sub>-fused *N*-methylpyrrolidine-*meta*-C12 phenyl [C60MC12, see Fig. 1(a)]. The electron mobility in the saturation regime was as high as 0.067 cm<sup>2</sup>/V s. The molecular order in the film,

i.e., crystallinity of the active layer was investigated in relation to the TFT performance.

C60MC12 was synthesized according to a similar route in the previous report.<sup>22,23</sup> [6,6]-PCBM [see Fig. 1(a)] was purchased from Frontier Carbon Corporation. The electronic state of the C<sub>60</sub> portion in C60MC12 and [6,6]-PCBM is almost similar, since the functional group in C60MC12 adds to a 6:6 ring juncture of C<sub>60</sub>. We fabricated TFTs of C60MC12 and PCBM with top-contact configuration [Fig.

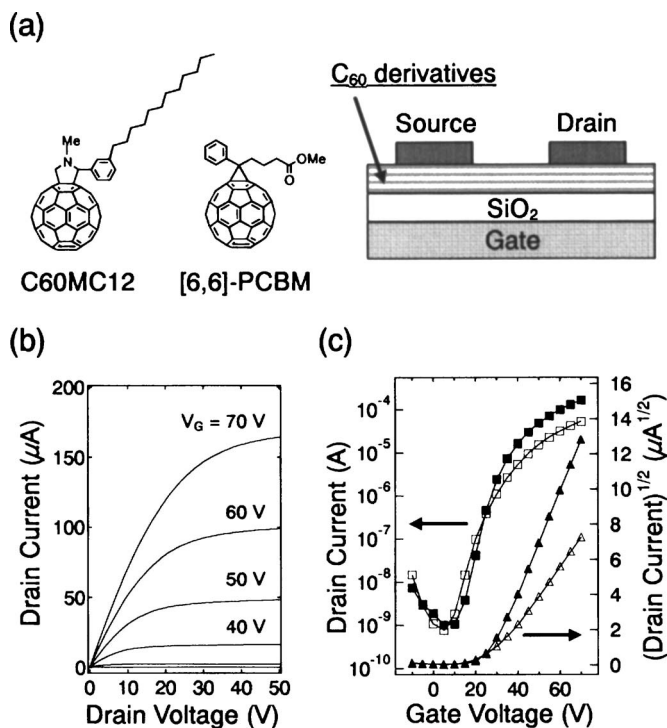


FIG. 1. (a) Molecular structures of C60MC12 and [6,6]-PCBM (left) and schematic structure of a top-contact TFT (right). (b)  $I_D$ - $V_D$  characteristics of C60MC12-TFT at room temperature (293 K). (c)  $I_D$ - $V_G$  (squares) and  $I_D^{1/2}$ - $V_G$  (triangles) plots of PCBM-(open) and C60MC12-(solid) TFTs at  $V_D=50$  V.

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1(a)]. The devices were constructed on a highly doped *p*-type silicon wafer covered with 300-nm-thick SiO<sub>2</sub> (a capacitance per unit area of 10 nF/cm<sup>2</sup>). The SiO<sub>2</sub> surface was treated with hexamethyldisilazane. Each film of C60MC12 and PCBM was fabricated on the SiO<sub>2</sub> by spin coating from 10 mg/ml chloroform solution under ambient condition. Spin-coating condition was 500 rpm for 5 s, then 2000 rpm for 60 s. The thickness of each film is about 100 nm. Finally, gold source and drain electrodes were deposited on the films by using resistive heating evaporation source. A nickel thin plate, which was patterned with channel lengths (*L*) of 20 μm and channel widths (*W*) of 5 mm, was used as a metal shadow mask. For the measurement of the TFT characteristics, Au wires were connected to the device electrodes using silver paste. The TFT characteristics were measured with Keithley 6430 and 2400 source measurement units in a vacuum (10<sup>-6</sup>–10<sup>-7</sup> Torr) after annealing at 373 K for 12 h.

Figure 1(b) shows drain current-drain voltage (*I<sub>D</sub>*-*V<sub>D</sub>*) characteristics of C60MC12-TFT at room temperature (293 K). The device showed excellent *n*-channel characteristics. Figure 1(c) shows the transfer characteristics of the C60MC12-TFT at *V<sub>D</sub>*=50 V. For comparison with the C60MC12-TFT, the characteristics of PCBM-TFT are shown in Fig. 1(c). The on/off current ratios (*I<sub>on</sub>*/*I<sub>off</sub>*) of the C60MC12- and PCBM-TFT are 1.6 × 10<sup>5</sup> and 7 × 10<sup>4</sup>, respectively. The *I<sub>on</sub>*/*I<sub>off</sub>* of the C60MC12-TFT is about two times higher than that of the PCBM-TFT. The field-effect mobility  $\mu$  and the threshold voltage *V<sub>T</sub>* were estimated from the square root of drain current-gate voltage (*I<sub>D</sub>*<sup>1/2</sup>-*V<sub>G</sub>*) plots of Fig. 1(c), according to the standard equation in the saturation regime,<sup>1</sup>  $I_D = (W/2L) \mu C_i (V_G - V_T)^2$ , where *I<sub>D</sub>* is the drain current, *W* and *L* are the conduction channel width and length, respectively, *C<sub>i</sub>* is the capacitance per unit area of gate dielectric, and *V<sub>G</sub>* is the gate voltage.

In the case of the C60MC12-TFT,  $\mu$  and *V<sub>T</sub>* were 0.067 cm<sup>2</sup>/V s and 26.1 V, respectively. On the contrary, the PCBM-TFT exhibited  $\mu$  of 0.023 cm<sup>2</sup>/V s and *V<sub>T</sub>* of 27.3 V. To confirm reproducibility, we measured each transistor of PCBM and C60MC12 by several samples. The mean values of  $\mu$  for the C60MC12- and PCBM-TFT are 0.06 cm<sup>2</sup>/V s and 0.02 cm<sup>2</sup>/V s, respectively. From these results, the  $\mu$  and *I<sub>on</sub>*/*I<sub>off</sub>* of the C60MC12-TFT are found to exhibit excellent performance compared with these of the PCBM-TFT. In particular, the  $\mu$  of C60MC12-TFT is about three times higher than that of PCBM-TFT. Moreover, this value is higher than the  $\mu$  of the poly(benzobisimidazobenzophenanthroline)-TFTs in the saturation regime (0.03–0.05 cm<sup>2</sup>/V s).<sup>8</sup>

After the TFT measurement, the C60MC12 and PCBM active layers were subjected to out-of-plane x-ray diffraction (XRD) measurement and atomic force microscope (AFM) observation (Fig. 2). Film crystallinity and morphology are quite different in the two films. In the case of the C60MC12 film, 00*l* reflections were observed up to the sixth and no other reflection was observed within 25° in 2 theta. These result indicates that the C60MC12 film take the well-ordered layer structure, that is, the crystallites are preferentially oriented with the (001) plane parallel to the substrate. The AFM image demonstrates that the C60MC12 film consists of large grains with size of ~1 μm. On the contrary, no diffraction peak was observed in the PCBM film from the XRD measurement. The AFM image of the PCBM film demonstrates a

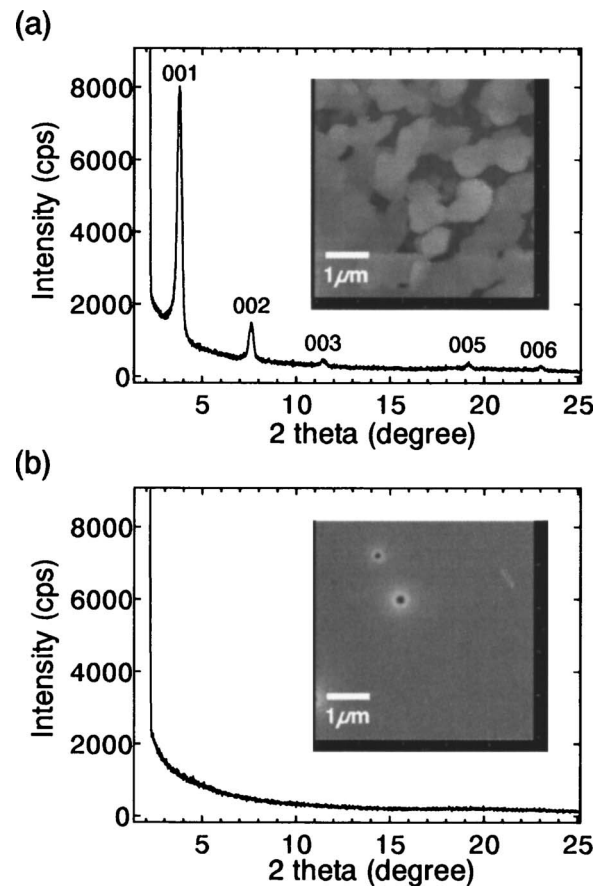


FIG. 2. Out-of-plane XRD patterns of spin-coated C60MC12 (a) and PCBM (b) films. Insets show AFM images of C60MC12 (a) and PCBM (b) films.

homogeneous morphology without large crystalline domains. These results indicate that the PCBM film takes an amorphouslike structure or is composed of homogeneously distributed small nanocrystals. These findings agree with the results of transmission electron microscopy observation and electron diffraction measurement of spin-coated PCBM film reported by Yang *et al.*<sup>20</sup>

The spacing of the (001) plane in the C60MC12 film calculated by Bragg's equation is 2.32 nm. The XRD peak patterns and the spacing of C60MC12 spin-coated film agree with these of the previously reported cast film.<sup>22</sup> We also characterized the in-plane structure of the C60MC12 cast film by using grazing incidence XRD measurement. The result indicated that C<sub>60</sub> moieties form a two-dimensional arrangement of the square lattice (*a*=10.1 Å,  $\gamma$ =90°). Since the C<sub>60</sub> diameter is 10.0 Å in the closed-packed single crystal,<sup>24</sup> it is considered that  $\pi$ - $\pi$  intermolecular overlaps between C<sub>60</sub> moieties are strong in the C60MC12 film. From the results of XRD analysis and the minimum energy conformation of C60MC12 examined by a MM2 calculation, we illustrate the schematic film structures in the active layer, where the C60MC12 film takes 2.32-nm-period bilayer structures with interdigitated dodecyl chains [Fig. 3(a)].<sup>22</sup> High electron mobility of the C60MC12-TFT is considered to be due to smooth electron conduction in crystalline domain with ordered C<sub>60</sub> layer.

Figure 3(b) shows the temperature dependence of field-effect electron mobility between 100 K and 300 K. The mobilities of C60MC12- and PCBM-TFT decreased with decreasing temperature. At 100 K, the mobility of the PCBM-

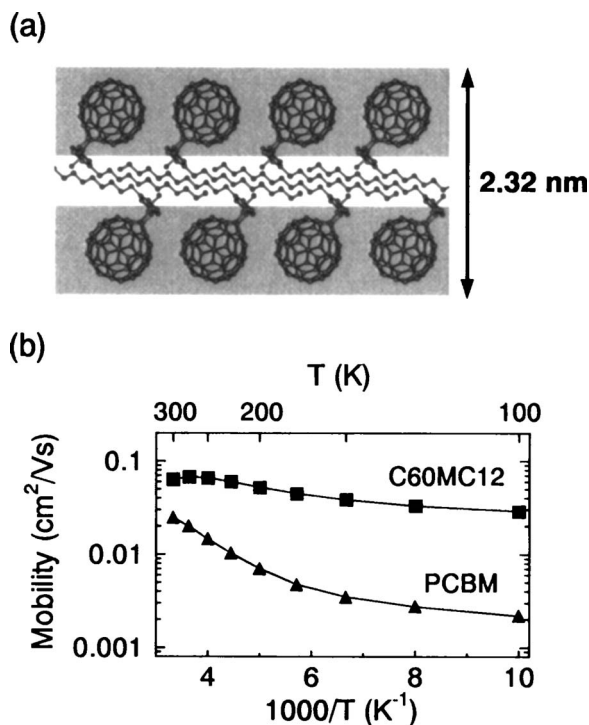


FIG. 3. (a) Illustration of schematic film structure of C60MC12 active layer. (b) Temperature dependence of the field-effect mobility extracted from the characteristics of C60MC12- (squares) and PCBM-TFT (triangles) in the saturation regime ( $V_D=50$  V).

TFT reached down to  $0.002 \text{ cm}^2/\text{V s}$ , which is one order of magnitude lower than the mobility at 300 K ( $0.025 \text{ cm}^2/\text{V s}$ ). On the contrary, temperature dependence of the mobility of the C60MC12-TFT is more moderate: The mobility at 100 K ( $0.029 \text{ cm}^2/\text{V s}$ ) maintained the value about half as much as that at 300 K ( $0.064 \text{ cm}^2/\text{V s}$ ). The activation energy ( $E_a$ ) of the C60MC12-TFT given by  $\mu \propto \exp(-E_a/kT)$  is 20 meV in the range 200–250 K, which is small compared with that of the PCBM-TFT (63 meV). The result indicates that electron traps between grain boundaries are very shallow in the C60MC12 film.

In summary, we have demonstrated the performance of solution-processed *n*-type OTFTs based on  $C_{60}$  derivatives. The C60MC12-TFT shows high electron mobility of  $0.067 \text{ cm}^2/\text{V s}$  in the saturation regime at room temperature (293 K). We found that the self-assemble ability of long alkyl chains plays an important role for the fabrication of highly ordered crystalline film, leading to achievement of high electron mobility in solution-processed *n*-type OTFT. Our result has demonstrated the importance of molecular

order in the film, and has shown the possibility of further improvement of the OTFT performance.

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