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Description	

## Field-effect transistors with thin films of perylene on SiO<sub>2</sub> and polyimide gate insulators

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Field-effect transistor (FET) devices have been fabricated with thin films of perylene on SiO<sub>2</sub> and polyimide gate insulators, and *p*-channel FET properties have been found in both FET devices. The perylene FET devices with SiO<sub>2</sub> and polyimide gate insulators exhibited field-effect mobility,  $\mu$ , values of  $7.0 \times 10^{-3}$  and  $3.7 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, at 300 K under vacuum of 10<sup>-6</sup> Torr. These FET devices were found to operate under atmospheric condition after exposure to air. The  $\mu$  value increased with increasing temperature from 160 to 280 K, showing a hopping carrier transport. © 2006 American Institute of Physics. [DOI: 10.1063/1.2182024]

A number of field-effect transistor (FET) devices have been fabricated with thin films of organic molecules because of the next-generation electronics.<sup>1,2</sup> The values of field-effect mobility,  $\mu$ , of the FETs with organic molecules (organic FETs) are generally lower than those,  $\sim 1000$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, of the conventional FETs with inorganic materials. However, the organic FETs are well known to have many advantages such as large-area coverage, structural flexibility, shock resistance, and low-temperature/low-cost processing, in comparison with conventional FETs. The highest  $\mu$  value in *p*-channel organic thin-film FET devices was 1.5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for the pentacene thin-film FET.<sup>3</sup> Recently, the  $\mu$  value reached 8–20 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in the rubrene single-crystal FET devices exhibiting *p*-channel behavior.<sup>4–6</sup> On the other hand, the highest  $\mu$  value in *n*-channel organic FET devices was  $\sim 0.6$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for the *N,N'*-dialkyl-3,4,9,10-perylene tetracarboxylic diimide derivative and C<sub>60</sub> FET devices.<sup>7,8</sup> These  $\mu$  values are comparable to those of the recent amorphous Si FETs.<sup>1,2</sup>

New organic materials have been extensively studied for the purpose of the realization of FET devices with high  $\mu$  value and low threshold voltage,  $V_T$ .<sup>1,2</sup> In particular, discovery of new organic materials except for pentacene, which can operate as high-performance *p*-channel FET, are indispensable for a breakaway from pentacene-dependent electronics. Recent progress of *p*-channel FET devices with rubrene and tetracene single crystals can lead to the breakaway from the pentacene based FET devices.<sup>4–6,9</sup> However, FET devices with thin films as the active layer are preferable in comparison with the single crystal FET, from the viewpoint of future applications in flexible and portable electronics. The recent approaches to new organic materials for thin-film FET devices are based mainly on the utilizations of functionalized pentacene and other  $\pi$ -conjugated organic acene molecules such as tetracene.<sup>1,2,10–13</sup>

In the present study, we have fabricated the organic FET devices with thin films of perylene, which is an aphenic molecule, on SiO<sub>2</sub>/Si and polyimide/poly(ethylene terephtha-

late) (PET) substrates, and we have clarified their FET properties in order to search for new  $\pi$ -conjugated organic materials available to the FET device and to investigate the possibilities of applications in flexible devices. The  $\mu$  value in the FET device increased by four orders of magnitude in comparison with that of the perylene FET reported previously.<sup>14</sup> The FET properties have also been studied by exposure to air. The atomic force microscope (AFM) and x-ray diffraction have been used in order to clarify the relationship between the morphology of the thin films and the electric transport. Furthermore, the temperature dependence of the  $\mu$  value has been studied in a temperature region from 160 to 300 K.

The cross-sectional views of the perylene FET devices are shown in Fig. 1(a); the device structure is top-contact type. The perylene sample (Tokyo Kasei Co.; GR) was used without further purification. The commercially available SiO<sub>2</sub>/Si(100) wafer was used as a substrate after washing with acetone, methanol, H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>, and ultrapure water. The SiO<sub>2</sub>/Si substrate was treated with hexamethyldisilazane (HMDS) to form a hydrophobic surface. The thickness and capacitance,  $C_0$ , of SiO<sub>2</sub> were 420 nm and  $8.2 \times 10^{-9}$  F cm<sup>-2</sup>, respectively. The films of polyimide gate insulator were formed by spin coating a high-purity polyimide precursor (KEMITITE CT4112, Kyocera Chemical) on the Au/PET substrate at 2000 rpm for 5 s and 4000 rpm for 20 s. The films were heated at 100 °C for 10 min and at 180 °C for 1 h. The surface of polyimide films was treated to be hydrophobic with HMDS. The  $C_0$  of the polyimide films was estimated to be  $1.9 \times 10^{-9}$  F cm<sup>-2</sup> from the capacitance  $C(=C_0S)$  determined by LCR meter, where the  $S$  is the area of electrode.

One hundred nm thick perylene thin films were formed by  $\sim 2.0$  nm/s deposition rate of thermal deposition under a vacuum of 10<sup>-8</sup> Torr, and 50 nm thick Au electrodes were formed on the thin films of perylene. The channel length,  $L$ , and the channel width,  $W$ , of this device were 30 and 6000  $\mu$ m, respectively. The FET properties of the perylene FET device were measured under vacuum of 10<sup>-6</sup> Torr. After

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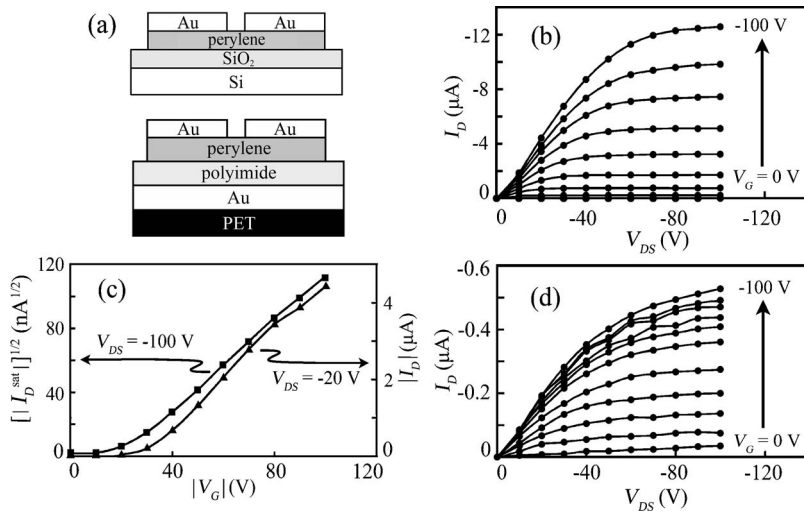


FIG. 1. (a) Device structures of the perylene thin-film FETs. (b)  $I_D$ - $V_{DS}$  plots for the perylene FET with SiO<sub>2</sub> insulator at 300 K. (c) ( $\blacktriangle$ ):  $|I_D|-|V_G|$  plot at  $V_{DS}=-20$  V, and ( $\blacksquare$ ):  $|I_D^{\text{sat}}|^{1/2}-|V_G|$  plot for the perylene FET with SiO<sub>2</sub> insulator. (d)  $I_D$ - $V_{DS}$  plots for the perylene FET with polyimide insulator at 300 K.

exposure to air, the FET properties were measured under atmospheric condition.

The drain current,  $I_D$ , versus drain-source voltage,  $V_{DS}$ , plots for the perylene FET formed on the SiO<sub>2</sub>/Si substrate at 300 K are shown in Fig. 1(b), and the plots show  $p$ -channel normally off FET properties. The  $I_D$ - $V_{DS}$  plots were measured in  $p$ -channel measurement mode, i.e.,  $I_D < 0$ ,  $V_G < 0$ , and  $V_{DS} < 0$ . The  $|I_D|-|V_G|$  plot at  $V_{DS}=-20$  V is also shown in Fig. 1(c). The  $|I_D|$  increases with an increase in  $|V_G|$  from 0 to 100 V. The  $\mu$  value for the perylene FET was estimated to be  $1.8 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at 300 K from the  $|I_D|-|V_G|$  plot above  $|V_G|=50$  V [Fig. 1(c)] with the relation,  $|I_D| \sim (\mu WC_0/L)(|V_G|-|V_T|)|V_{DS}|$  for  $|V_{DS}| \ll |V_G|-|V_T|$ .<sup>15</sup> This  $\mu$  value is higher by four orders of magnitude than that,  $3 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , of the perylene thin-film FET device fabricated previously.<sup>14</sup>

Here, it should be noted that the vacuum level of  $10^{-8}$  Torr in the present study is better than that of  $10^{-6}$  Torr in the previous study, and that the surface of the SiO<sub>2</sub>/Si substrate is changed to hydrophobic by HMDS treatment in the present study. The  $V_T$  was estimated to be  $-23$  V from the  $|I_D|-|V_G|$  plot [Fig. 1(c)]. The current on-off ratio was estimated to be  $\sim 10^4$  from the  $|I_D|$  at  $|V_G|=100$  V and the  $|I_D|$  at  $|V_G|=0$  V in the plots shown in Fig. 1(b). Furthermore, the  $\mu$  and  $V_T$  values for perylene thin-film FET were estimated to be  $2.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $-20$  V, respectively, from the  $|I_D^{\text{sat}}|^{1/2}-|V_G|$  plot [Fig. 1(c)] above  $|V_G|$  of 30 V with the relation,  $|I_D^{\text{sat}}|^{1/2} = (\mu WC_0/2L)^{1/2}(|V_G|-|V_T|)$  for  $|V_{DS}| > |V_G|-|V_T|$ ,<sup>14</sup> where  $|I_D^{\text{sat}}|$  refers to the saturation value of  $|I_D|$ . The  $|I_D^{\text{sat}}|^{1/2}-V_G$  plot was obtained at  $V_{DS}=-100$  V. The device also operated as  $p$ -channel FET under atmospheric condition, and it showed the  $\mu$  value of  $2.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  whose value was estimated from the  $|I_D^{\text{sat}}|^{1/2}-V_G$  plot. The  $\mu$  value of  $2.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  estimated under atmospheric condition is lower by 1 order of magnitude than that,  $2.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , estimated under  $10^{-6}$  Torr.

Most of the 70 perylene FET devices with SiO<sub>2</sub> gate insulator fabricated in the present study showed higher  $\mu$  values than  $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  under  $10^{-6}$  Torr, and the highest  $\mu$  value was  $7.0 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ; this value was estimated from the saturation region at  $V_{DS}=-100$  V. Thus, in the present study, the  $\mu$  value increases by four orders of magnitude from  $3 \times 10^{-7}$  to  $7.0 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

The  $I_D$ , versus  $V_{DS}$  plots for the perylene FET formed on the polyimide/PET substrate at 300 K are shown in Fig. 1(d), and the plots show  $p$ -channel normally on FET properties; the slight drain current flows even at  $V_G$  of 0 V. The  $\mu$  value for the perylene FET was estimated to be  $3.9 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at 300 K from the  $|I_D|-|V_G|$  plot above  $|V_G|=20$  V with the relationship in the linear region ( $V_{DS}=-20$  V). The  $V_T$  value was estimated to be 8 V, showing normally on FET properties. This is the flexible FET device with perylene thin films. Furthermore, this device also operated under atmospheric conditions, and the  $\mu$  value under atmospheric conditions,  $5.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , was higher than that,  $3.9 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , estimated under  $10^{-6}$  Torr. The  $\mu$  values estimated from the  $|I_D^{\text{sat}}|^{1/2}-|V_G|$  plot were  $3.7 \times 10^{-4}$  and  $6.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively, under  $10^{-6}$  Torr and atmospheric conditions.

The AFM image for the surface of perylene thin films is shown in Fig. 2(a). The very large grains are observed in this image. The grain size of perylene thin films can be evaluated

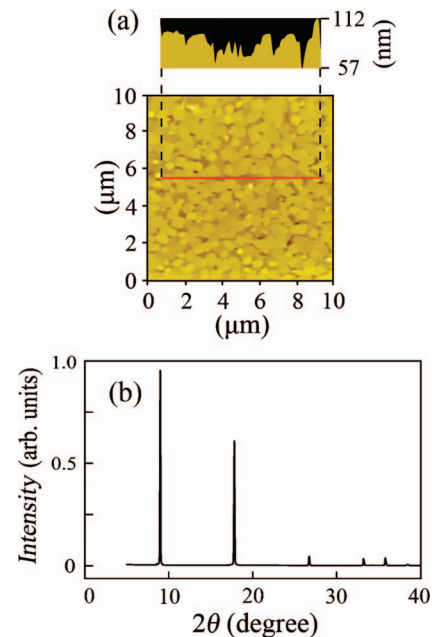


FIG. 2. (Color) (a) AFM image and (b) x-ray diffraction pattern for the thin films of perylene; In (a) the cross sectional image (top) along the red line and the surface image (bottom). In (b) the wavelength of x-ray is 1.5418 Å.

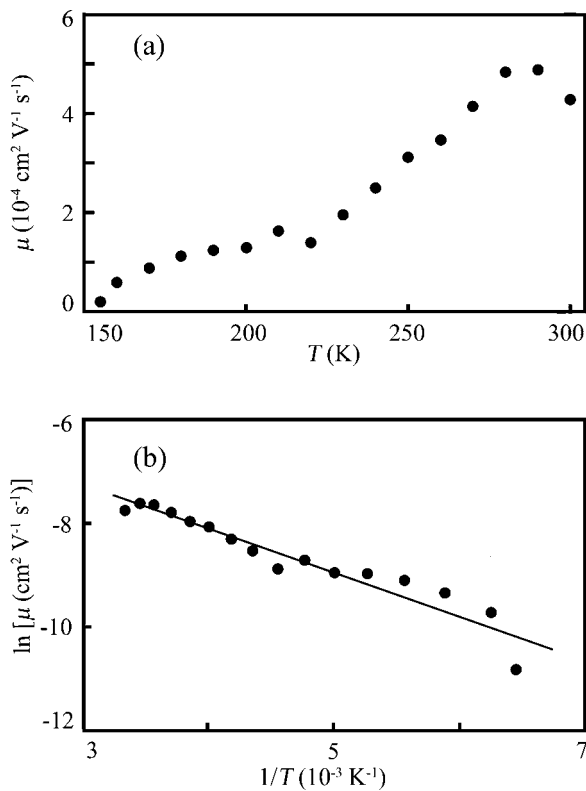


FIG. 3. (a)  $\mu$ - $T$  and (b)  $\ln \mu$ - $1/T$  plots for the perylene FET with  $\text{SiO}_2$  insulator. In (b) the solid line refers to the line fit with the relationship,  $\ln \mu = E_a/(k_B T) + C$ , where  $C$  is constant.

to be 400–1000 nm from the contrast of the AFM image. The maximum roughness of the surface was  $\sim 60$  nm. This implies the existence of large grain boundaries. The x-ray diffraction pattern of the thin films showed Bragg reflections (Fig. 2(b)). This implies that the thin films consist of crystallites. The size of crystallite was estimated to be  $\sim 70$  nm from the Bragg reflection peaks. It should be noted that the grain (500–1000 nm) of perylene thin films consists of some crystallites. The size of crystallite is larger than that (24–44 nm) of the thin films fabricated previously.<sup>14</sup> Thus, it can be concluded that the improvement of crystallinity in the thin films of perylene produces the rapid increase in  $\mu$  from  $3 \times 10^{-7}$  to  $7.0 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>14</sup> This improvement is caused by high vacuum level and hydrophobic treatment of the surfaces.

The temperature dependence of  $\mu$  value in the perylene FET device is shown in Fig. 3(a); it was measured with the device exhibiting the  $\mu$  value of  $4.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at 300 K. The  $\mu$  increased exponentially with an increase in temperature up to 280 K. The plot of  $\mu$ - $T$  shows that the channel conduction of the perylene FET device follows a thermally activated hopping-transport model ( $\mu \sim \exp(-E_a/k_B T)$ ), where the  $E_a$ ,  $k_B$ , and  $T$  refer to activation energy, Boltzmann constant, and temperature. The  $E_a$  value was estimated to be 0.07 eV from the  $\ln \mu$ - $1/T$  plot shown in Fig. 3(b). This value is the same order as that, 0.038 eV, for the pentacene thin-film FET exhibiting the  $\mu$

value of  $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,<sup>16</sup> and the  $E_a$  value of 0.07 eV is smaller than that, 0.29 eV, of the  $\text{C}_{60}$  thin-film FET.<sup>17</sup> This result suggests that the connectivity between grains is better than that in the thin films of  $\text{C}_{60}$ , because the  $E_a$  value can be closely associated with the hopping barrier in the intergrains.

In the present study, we have succeeded in fabrication of FET devices with thin films of perylene on  $\text{SiO}_2$  and polyimide gate insulators, and the  $\mu$  value in the perylene/ $\text{SiO}_2$ /Si FET device reached  $\sim 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The FET properties have been investigated in connection with the morphology of thin films determined by AFM image and x-ray diffraction. This study shows that the morphology of the active layer plays a conclusive role in the improvement of the FET properties in the organic FET devices. The success in the fabrication of perylene FET device with polyimide gate insulator will open the way for the flexible FET device with organic phene molecules. The improvement of the FET properties of perylene FET device and the fabrication of flexible FET device with perylene thin films will lead to the breakaway from pentacene-dependent electronics and should produce diversity of materials for organic electronics.

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