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Fabrication of field-effect transistor devices with fullerodendron by solution process

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n-channel field-effect transistor (FET) devices have been fabricated with thin films of fullerodendron on SiO_2/Si, polyimide/Au/poly(ethylene terephthalate), and polyvinyl alcohol/Au/poly(ethylene terephthalate) substrates by using solution processes. The value of field-effect mobility μ of the fullerodendron FET reaches 1.7×10^{-3} cm^2 V^{-1} s^{-1} at 300 K. The mobility gap and optical gap have been estimated to be 0.15 and 1.4 eV, respectively. The channel conduction in the FET device follows thermally activated hopping-transport mechanism below 300 K. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2198098]

Organic thin film field-effect transistor (OFET) devices have many advantages such as large-area coverage, structural flexibility, shock resistance, and low-cost processing, although the values of μ for the OFETs are generally lower than those, ~ 1000 cm^2 V^{-1} s^{-1}, for the conventional FETs with inorganic materials.[1,2] The highest μ value in *p*-channel OFET devices was 1.5 cm^2 V^{-1} s^{-1} for the pentacene thin-film FET,[3] and the μ value reached 8–20 cm^2 V^{-1} s^{-1} in *p*-channel rubrene single-crystal FETs.[4–6] The highest μ values in *n*-channel OFETs were ~0.6 cm^2 V^{-1} s^{-1} for the N,N'-dialkyl-3,4,9,10-perylene tetracalboxylic diimide derivative (PTCDI-C8) (Ref. 7) and C_{60} thin-film FET devices;[8] the C_{60} FET was first fabricated by Haddon *et al.*[9] These FETs were fabricated with either thin films formed by thermal deposition or single crystals on the SiO_2/Si substrates.

The flexible OFETs with thin films of pentacene and C_{60} were fabricated by formation of active layers on polymer gate insulators by thermal deposition.[10,11] Especially, the polyimide films showed good properties for gate insulators of the OFET devices.[10,11] Furthermore, the solution-processed OFET devices attracted special attention because they can be easily fabricated by low-temperature processes. Recently, various types of FET devices with [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM), which was the derivative of C_{60}, and rubrene were fabricated by using solution processes.[12–14] The high μ value of 0.09 cm^2 V^{-1} s^{-1} was realized in the PCBM FET with the gate insulator of polyvinyl alcohol (PVA).[13]

The PCBM and fullerodendron have similar structures, and the fullerodendron are soluble in organic solvents such as chloroform and chlorobenzene, as in PCBM. Furthermore, the fullerodendron can be expected to form the structurally ordered thin films because it has the highly dense and functional terminal groups of dendron.[15,16] Therefore, the fullerodendron can be a good candidate to develop solution-processed FET devices. In this letter, we report the solution-processed FET devices with fullerodendron. The FET devices were fabricated on SiO_2/Si, polyimide/poly(ethylene terephthalate) (PET) and PVA/PET substrates by using solution processes.

The molecular structure of fullerodendron used in the present study is shown in Fig. 1(a). The route of synthesis is described elsewhere.[17] Commercially available $SiO_2/Si(100)$ wafer was used as a substrate after washing with acetone, methanol, H_2SO_4/H_2O_2, and ultrapure water. The thickness and capacitance per unit area C_0 are 400 nm and 8.6×10^{-9} F cm^{-2}, respectively. Commercially available PET was used as a substrate after washing with acetone, 2-propanol, and ultrapure water, and it was dried at 190 °C. The Au gate electrodes with a thickness of 50 nm were formed on the PET substrate by the thermal deposition under 10^{-8} Torr. The films of PVA were formed on the Au/PET substrate by spin-coating of aqueous solution (10 wt %) of high-purity PVA (99% purity, Aldrich) at 500 rpm for 5 s and 2000 rpm for 20 s, while the polyimide films were formed on the Au/PET substrate by spin coating of polyimide precursor (Kemitite CT4112, KYOCERA Chemical) at 2000 rpm for 3 s and 5000 rpm for 7 s. The PVA films were heated at 90 °C for 10 min for drying, and the polyimide films were heated at 100 °C for 10 min and at 180 °C for 1 h. The C_0 values of PVA and polyimide insulators were determined to be 5.0×10^{-9} and 1.4×10^{-9} F cm^{-2}, respec-

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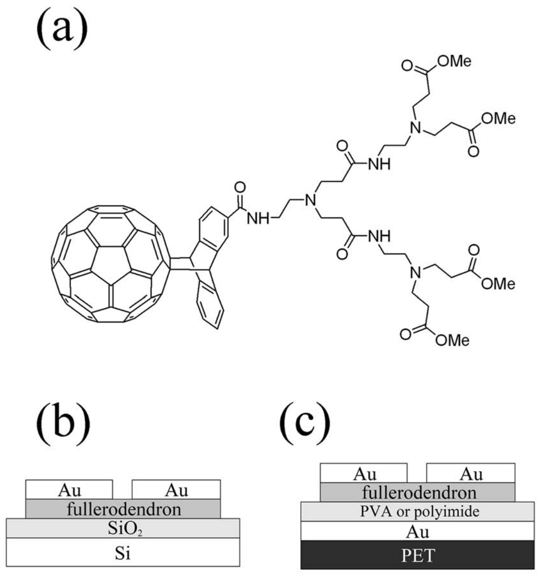

FIG. 1. (a) Molecular structure of fullerodendron. Device structures of (b) fullerodendron/SiO_2/Si FET and (c) fullerodendron/polyimide or PVA/PET FET.

tively, by measuring the capacitance C values with *LCR* meter.

The fullerodendron thin films with a thickness of ~350 nm were spin coated with a chlorobenzene solution (1.0×10^{-2} mol l^{-1}) of fullerodendron on the SiO_2/Si, PVA/Au/PET, and polyimide/Au/PET substrates under atmospheric condition. The source and drain Au electrodes with a thickness of 50 nm were formed on the thin films of fullerodendron by thermal deposition under ~10^{-8} Torr. The channel length L and the channel width W for these FET devices were 30 and 3000 μm, respectively. The device structures fabricated in this study are shown in Figs. 1(b) and 1(c).

Figure 2(a) shows the drain current I_D, versus drain-source voltage V_{DS} plots for fullerodendron FET formed on the SiO_2/Si substrate at 300 K. The I_D-V_{DS} plots were measured after annealing of the FET device at 40 °C for 19 h under vacuum of 10^{-6} Torr. The plots reveal *n*-channel normally-off FET properties; very small I_D is observed at the gate voltage V_G of 0 V. The I_D increases with an increase in V_G from 0 to 150 V, as shown in Figs. 2(a) and 2(b). The values of μ were estimated to be 6.6×10^{-4} cm^2 V^{-1} s^{-1} from a linear region at V_{DS}=10 V and 5.3×10^{-4} cm^2 V^{-1} s^{-1} from a saturation region at V_{DS}=150 V [Fig. 2(b)]. The values of threshold voltages $V_{\rm th}$ were estimated to be 12 and −1 V from the linear and saturation regions respectively. The highest μ value among the FET devices with the SiO_2 gate insulators fabricated in this study was 1.4×10^{-3} cm^2 V^{-1} s^{-1}, while the highest on-off ratio reached 10^4.

Figure 3(a) shows the I_D vs V_{DS} plots for the fullerodendron FET formed on the PVA/Au/PET substrate at 300 K. The I_D-V_{DS} plots were measured under vacuum of 10^{-6} Torr without annealing. The plots reveal *n*-channel normally-on FET properties; the I_D is not vanishing at the gate voltage V_G of 0 V. The I_D increases with an increase in V_G from 0 to 70 V, as shown in Fig. 3(a). The values of μ and $V_{\rm th}$ were estimated to be 3.0×10^{-4} cm^2 V^{-1} s^{-1} and −26 V, respectively, from a linear region at V_{DS}=10 V. The highest μ value among FET devices formed on the PVA/Au/PET substrate in this study was 1.7×10^{-3} cm^2 V^{-1} s^{-1}. The *n*-channel normally-on FET properties have also been observed in the fullerodendron/polyimid/PET FET device. The highest μ value realized in the devices with polyimide gate insulator was 2.1×10^{-4} cm^2 V^{-1} s^{-1}.

The temperature dependence of μ value in the fullerodendron FET formed on the SiO_2/Si substrate is shown in Fig. 2(c). The μ value increases exponentially with an increase in temperature up to 300 K, and the μ value reached 1.4×10^{-3} cm^2 V^{-1} s^{-1} at 300 K. The μ value decreased rapidly above 300 K, and the value recovered when decreasing temperature from 330 to 300 K. The reason why the rapid decrease occurs above 300 K is not clear at the present stage. The plot of μ-T shows that the channel conduction of the fullerodendron FET follows a thermally activated hopping transport model $[\mu\sim\exp(-E_a/k_{\rm B}T)]$ up to 300 K. The activation energy E_a was estimated to be 0.21 eV from the $\ln\mu-1/T$ plot shown in the inset of Fig. 2(c). The E_a value is larger than those, 0.13–0.14 eV, for the FETs with higher fullerenes, C_{82}, C_{84}, and C_{88},[18–20] while the value is consistent with those, 0.22–0.29 eV, for the FETs with C_{60} and Pr@C_{82}.[21,22] The temperature dependence of resistance R is shown in Fig. 2(d). The value of R was measured with the FET device by two-probe method; R was estimated from the

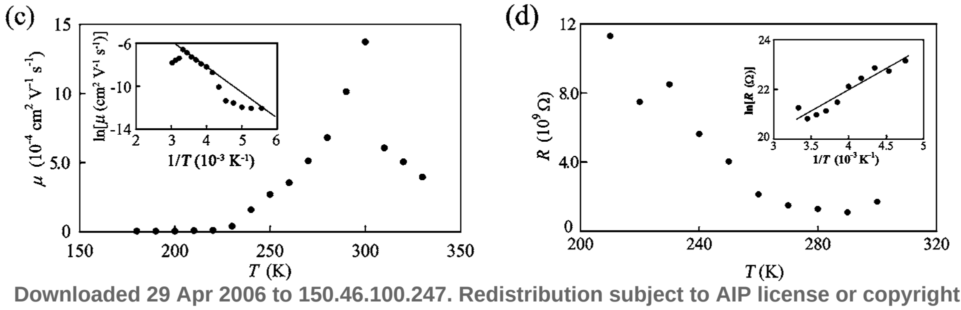

FIG. 2. (a) I_D-V_{DS} plots of fullerodendron/SiO_2/Si FET. (b) I_D-V_G plot at V_{DS}=10 V (○) and $I_D^{1/2}$-V_G plot (▲) at V_{DS}=150 V for fullerodendron/SiO_2/Si FET together with linear relationship (solid lines). (c) Temperature dependence of μ value for fullerodendron/SiO_2/Si FET. In the inset of (c) $\ln\mu$-$1/T$ plot is drawn with the linear relationship (solid line). (d) Temperature dependence of R value for fullerodendron thin films. In the inset of (d) $\ln R$-$1/T$ plot is drawn with the linear relationship (solid line).

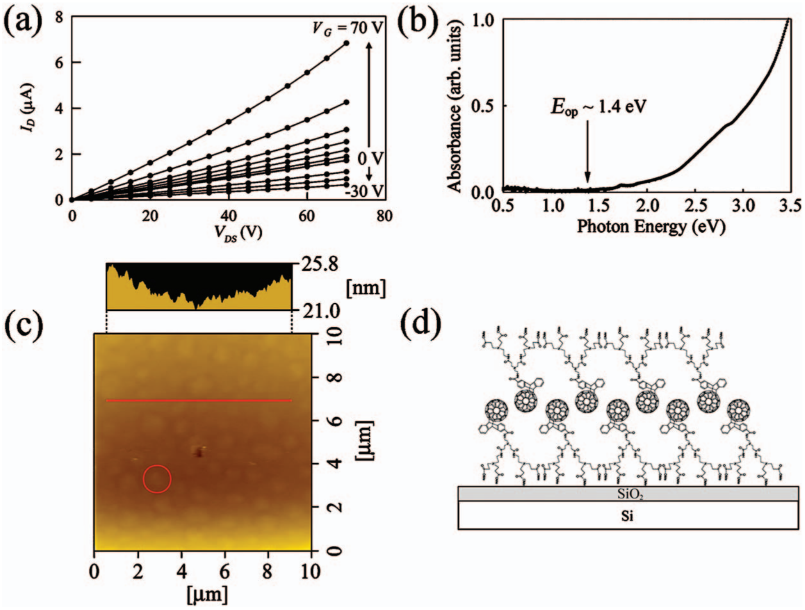

FIG. 3. (Color) (a) I_D-V_{DS} plots of fullerodendron/PVA/PET FET. (b) Optical absorption spectrum and (c) AFM image for the thin films of fullerodendron. The red circle refers to the single grain. Cross sectional view (top) along red line. (d) Schematic representation of fullerodendron assembly.

I_D value at $V_{DS}=50$ V and $V_G=0$ V. The gap energy E_g was estimated to be 0.30 eV from the ln $R-1/T$ plot shown in the inset of Fig. 2(d).

The optical gap E_{op} of fullerodendron was estimated to be 1.4 eV from the onset of the absorption spectrum of thin films of fullerodendron [Fig. 3(b)]. The E_{op} value is much larger than the E_g value, 0.30 eV. Therefore, the E_g value cannot be attributed to the band gap but two times of mobility gap, as suggested for C_{60} and C_{84} by Shiraishi *et al.*[23] Both x-ray diffraction patterns of the spin-coated fullerodendron thin films without annealing and the thin films annealed at 313 K exhibit no Bragg reflections, showing that the thin films of fullerodendron are not crystalline. The atomic force microscopy (AFM) image of the thin films of fullerodendron at 300 K is shown in Fig. 3(c); the thin films are not annealed. The grain size of the fullerodendron was 500–1000 nm from the AFM image. Very flat surface is observed in the cross sectional profile of AFM [Fig. 3(c)] roughness is within 5 nm in the region of 8600 nm.

Figure 3(d) shows the schematic representation drawn based on the x-ray reflectometry of the Langmuir-Blodgett (LB) films of fullerodendron reported by Hirano *et al.*[24] If the structure of spin-coated thin films of fullerodendron is similar to that of LB films, the fullerodendron molecules are expected to form the ordered structure suitable for device applications because electric conduction between fullerodendron molecules should occur through overlap of π orbitals between the C_{60} moieties. Therefore, the design of fullerodendron molecules exhibiting ordered structure is indispensable for the development of the high-performance flexible FET devices.

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