Fabrication and characterization of field-effect transistor device with C_{2v} isomer of Pr@C_{82}

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Endohedral metallofullerene field-effect transistor (FET) device was fabricated with thin films of C_{2v} isomer of $Pr@C_{82}$. This device showed n-channel normally-on type FET properties, where high bulk current of $Pr@C_{82}$ was observed at gate voltage of 0 V. The mobility, μ, was estimated to be 1.5×10^{-4} cm^{2} V^{-1} s^{-1} at 320 K, which is comparable to those of other endohedral metallofullerene FET devices. The normally-on properties have been found to originate from the high bulk current caused by the small energy gap of $Pr@C_{82}$.

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Field-effect transistors (FETs) with thin films of fullerenes have been extensively studied by many investigators [1-10]. The potential applications of fullerene FETs in next-generation electronic devices have been discussed based on their good FET performance. The first fullerene FET device was fabricated with thin films of C_{60} by Haddon *et al* [1], which showed n-channel properties and high field-effect mobility μ of $0.08 - 0.30$ cm^2 V^{-1} s^{-1}. Subsequently, Haddon developed the C_{70} FET device with the μ of 2×10^{-3} cm^2 V^{-1} s^{-1} [2]. The improvement of the C_{60} FET device has been successively examined, and the μ value recently reached to 0.56 cm^2 V^{-1} s^{-1} [3]. This value was comparable to that reported for *N,N'*-dialkyl-3,4,9,10-perylene tetracalboxylic diimide derivative (PTCDI-C8) FET, namely the highest μ value among the FETs with thin films of organic molecules (OFETs) exhibiting n-channel performance [11].

The highest μ value among p-channel OFETs is 1.5 cm^2 V^{-1} s^{-1} in pentacene FET [12]. Therefore, the combination of C_{60} and pentacene led to high performance ambipolar FET device and CMOS logic gate circuit [4,5]; the CMOS circuits have been extensively used to fabricate various types of chips such as memories and microprocessor owing to low-power consumption, good-noise margin, and ease of design. Furthermore, the ambipolar devices and CMOS circuits were fabricated with C_{60}/C_{60} related materials as n-channel conductor and organic molecules/organic polymers as p-channel conductor [6,7].

The endohedral metallofullerene FETs have been first fabricated with Dy@C_{82} and La_2@C_{80} [5,8]. These FETs showed n-channel normally-on properties, being different from enhancement-type FETs with C_{60} and C_{70} [1,2]. The μ values were lower than those of C_{60} and C_{70} FETs [1,2]. Subsequently, the higher fullerene FETs were fabricated with thin films of C_{82} and C_{84} [9,10], which also showed normally-on properties, and the μ values were higher by one order of magnitude than those of endohedral mertallofullerene FETs [5,8]. In the present study, we have fabricated a new endohedral metallofullerene FET device with thin films of C_{2v} isomer of $Pr@C_{82}$, which showed the μ value comparable to those of endohedral metallofullerene FETs reported so far [5,8]. The FET properties in the $Pr@C_{82}$ FET device have been investigated above 150 K, and the clear FET properties were observed above 230 K, which corresponds to the semiconductor-semiconductor transition suggested from temperature (T) dependence of resistivity [13]. The typical normally-off enhancement-type FET properties have been found by subtracting the bulk current I_B from the drain current I_D.

Schematic representation of C_{2v} isomer of $Pr@C_{82}$ and a cross-sectional view of the FET device are shown in Fig. 1(a). The purified sample of the C_{2v} isomer of $Pr@C_{82}$ was obtained based on the procedure reported previously [14]. The purity was estimated to be higher than 99% by time-of-flight (TOF) mass spectrum. Commercially available $SiO_2/Si(100)$ wafer was used as substrates after cleaning with acetone, methanol and H_2SO_4/H_2O_2. The surface of $SiO_2/Si(100)$ wafer was treated to be hydrophobic with hexamethyldisilazane (HMDS). The capacitance of SiO_2, C_0, was 8.2×10^{-9} F cm^2. The thin film of the C_{2v} isomer of $Pr@C_{82}$ was formed by a thermal deposition under a vacuum of 10^{-8} Torr. The channel length L and the channel width W of this device were 30 and 2000 μm, respectively. The characteristics of the $Pr@C_{82}$ FET device were measured under 10^{-6} Torr after annealing for 24 h at 403 K under 10^{-6} Torr.

The I_D *vs*. drain-source voltage V_{DS} plots for the $Pr@C_{82}$ FET at 320 K are shown in Fig.

1(b). The plots show the n-channel normally-on FET properties, which are similar to those of Dy@C_{82} FET reported previously [5]. As shown in Fig. 1(b), the high I_D is observed at the gate voltage, V_G, of 0 V. In the inset of Fig. 1(b) the I_D-V_{DS} plots are shown at $V_G \geq -40$ V, and the I_D is not vanishing even at $V_G = -40$ V. The I_D vs. V_G plot at $V_{DS} = 20$ V is shown in Fig. 1(c). The I_D increases with increasing V_G to positive, but the decrease in I_D is not clearly observed when applying negative V_G (Fig. 1(c)). This fact implies that the FET property is not normal depletion-type. The high I_D, which is not reduced by applying negative V_G, can be attributed to the existence of high I_B characteristic of Pr@C_{82}. The I_B, which flows the broad region of the thin films, cannot completely be disappeared because the negative V_G exclusively produces the depletion of the limited region near the interface between the thin films and the dielectric gate insulator. The high I_B is also observed in the Dy@C_{82} FET [5]. The high I_B originates from the small mobility gap energy, E_{gM}, of M@C_{82}; the E_{gM}s of the C_{2v} isomer of Pr@C_{82} and Dy@C_{82} were estimated to be 0.29 and 0.20 eV, respectively, from the $\rho - T$ plots [13,15]. Furthermore, the band gap energies, E_{gB}s, of the C_{2v} isomer of Pr@C_{82} and Dy@C_{82} were determined to be 0.7 and 0.6 eV, respectively, from scanning tunneling spectroscopy [13,16], which were smaller than those of C_{60} (1.8 – 2.1 eV) and C_{70} (2.2 eV) [17-19].

The intrinsic channel current, I_C, induced by applying V_G in the Pr@C_{82} FET device can be obtained by subtracting the I_B from the I_D observed, *i.e.*, $I_C = I_D - I_B$, where the I_B refers to the I_D at $V_G = 0$ V. The plots of I_C *vs.* V_{DS} at 320 K are shown in Fig. 1(d). The plots exhibit typical normally-off enhancement-type FET properties. This result clearly shows that the Pr@C_{82} FET possesses essentially normally-off enhancement-type characters and the high bulk current apparently produces normally-on properties. The ratio of the I_C at V_G = 120 V to the I_C at V_G = 30 V obtained at V_{DS} = 20 V, which essentially corresponds to the on-off ratio of this FET device, was 41. The V_G of 30 V is below the threshold voltage intrinsic to channel conduction, V_{TI}, of 51 V estimated from the $I_C – V_G$ plot, as described in the subsequent section. The ratio of 41 is larger by 11 factors of magnitudes than the ratio, 3.7, of the I_D at V_G = 120 V to the I_D at V_G = 30 V, which corresponds to the apparent on-off ratio of this FET device; the V_G of 30 V is below the threshold voltage, V_T, of 37 V estimated from the $I_D – V_G$ plot. Consequently, it can be concluded that the channel conduction induced by V_G in this FET device is hidden in the high bulk current of thin films of Pr@C_{82}.

The μ and V_T of the Pr@C_{82} FET at 320 K were estimated to be 1.5 x 10^{-4} cm^2 V^{-1} s^{-1} and 37 V, respectively, from the I_D- V_G plot (Fig. 1(c)) at V_{DS} of 20 V with the relation, $I_D = (\mu W C_0 / L)(V_G - V_T)V_{DS}$ [20]. The μ value of the Pr@C_{82} FET is comparable to those of endohedral metallofullerene FETs fabricated so far [5,8]. Furthermore, the V_{TI} was estimated to be 51 V from the $I_C – V_G$ plot with the above equation, and the V_{TI} can be directly associated with the channel conduction. Here it should be noted that the μ estimated from $I_C – V_G$ plot is the same as that from $I_D – V_G$ plot because the slope of the plot is associated with the μ. The large positive value of V_{TI} shows clearly the normally-off enhancement character for the Pr@C_{82} FET.

The T dependence of μ is shown in Fig. 2(a). The μ increases exponentially with increasing T above 230 K. The FET properties could not be observed below 230 K owing to very low I_D of this device. Consequently, the FET properties found in the present study reflect the nature of the high-T (HT) phase of the C_{2v}-Pr@C_{82} with small E_{gM} and E_{gB} above 230 K [13]. The μ value at 350 K reached to 2.5 x 10^{-4} cm^2 V^{-1} s^{-1}, which was 50 times higher than that at 230 K. The lnμ *vs*. 1/T plot is shown in the inset of Fig. 2(a), which shows a liner relationship as in the C_{82} and C_{84} FETs [9,10]. The activation energy, E_a, was estimated to be 0.22 eV from the equation, $\ln\mu = -E_a/(k_BT) + C$, where k_B refers to Boltzmann constant, and C is a constant. The E_a value corresponds to the E_{gM} of 0.44 eV because $E_{gM} = 2E_a$. The fact that the μ value follows the above equation suggests that the conduction in the Pr@C_{82} FET is dominated by the electron hopping between the bands originating from localized lowest unoccupied molecular orbital (LUMO).

The T dependence of I_B observed at V_{DS} = 20 V and V_G = 0 V is shown in Fig. 2(b). The I_B increases exponentially with increasing T. The E_{gM} of C_{2v}-Pr@C_{82} was estimated to be 0.32 eV from the I_B – T plot at 240 – 300 K, where the I_B is measured with two-probe method. This E_{gM} value is consistent with that, 0.29 eV, determined from ρ at 240 – 300 V measured with four-probe method [13]. Therefore, the T dependence of I_B reflects intrinsic nature of the HT phase of the C_{2v}-Pr@C_{82}, though the contribution of contact resistance may be contained in the absolute value of I_B. The I_B of 67 nA at 350 K is ~30 times higher than that of 2 nA at 230 K.

The V_T decreases considerably from 57 V at 240 K to 23 V at 350 K with increasing T, as shown in Fig. 2(c); the small V_T at 230 K may be due to the error caused by very low I_D. The V_T involves the contributions from bulk conduction as well as channel conduction induced by applying V_g. The remarkable decrease in V_T (Fig. 2(c)) seems to be caused by the increase in I_B shown in Fig. 2(b). The T dependence of V_{TI} is plotted in Fig. 2(c) to verify the effect of the I_B on the V_T, where the V_{TI} reflects only a channel conduction induced by field-effect. As seen from Fig. 2(c), the variation of V_{TI} is fairly smaller than that of V_T; the V_{TI} at 240 and 350 K are 71 and 47 V, respectively. Therefore, the remarkable decrease in V_T does not imply the variation of channel conduction but the increase in the bulk conduction.

In the present study, the FET properties affected by the high bulk current have been studied in the C_{2v}-Pr@C_{82} FET device in a wide T region. This is the first study on T dependence of FET properties of endohedral metallofullerene. The FET properties were observed for the HT phase of C_{2v}-Pr@C_{82}, but could not be observed for the low-T (LT) phase owing to the small I_D below 230 K. The fabrication of the Pr@C_{82} FET shows that various types of fullerenes are available as materials of electronic devices, and that the FET properties reflect directly the intrinsic natures of fullerenes.

This work was partly supported by Mitsubishi foundation, and a Grant-in-Aid (15350089) of Ministry of Education, Culture, Sports, Science and Technology, Japan.

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Figure captions

FIG. 1. (a) Schematic representation of C_{2v}-Pr@C$_{82}$, and cross sectional view of Pr@C$_{82}$ together with measurement circuit of n-channel mode. Plots of (b) I_D -V_{DS}, (c) I_D –V_G and (d) I_C -V_{DS} for the Pr@C$_{82}$ FET at 320 K. Plots of I_D -V_{DS} at $V_G \geq$ -40 V are shown in the inset of (b). Closed circles refer to the points measured.

FIG. 2. T dependences of (a) μ, (b) I_B, and (c)V_T and V_{TI} of the Pr@C$_{82}$ FET. ln μ – 1/T plot is shown in the inset of (a) together with fitted line (solid line). Closed circles refer to the points measured for μ, I_B and V_T, and closed squares refer to the points measured for V_{TI}.

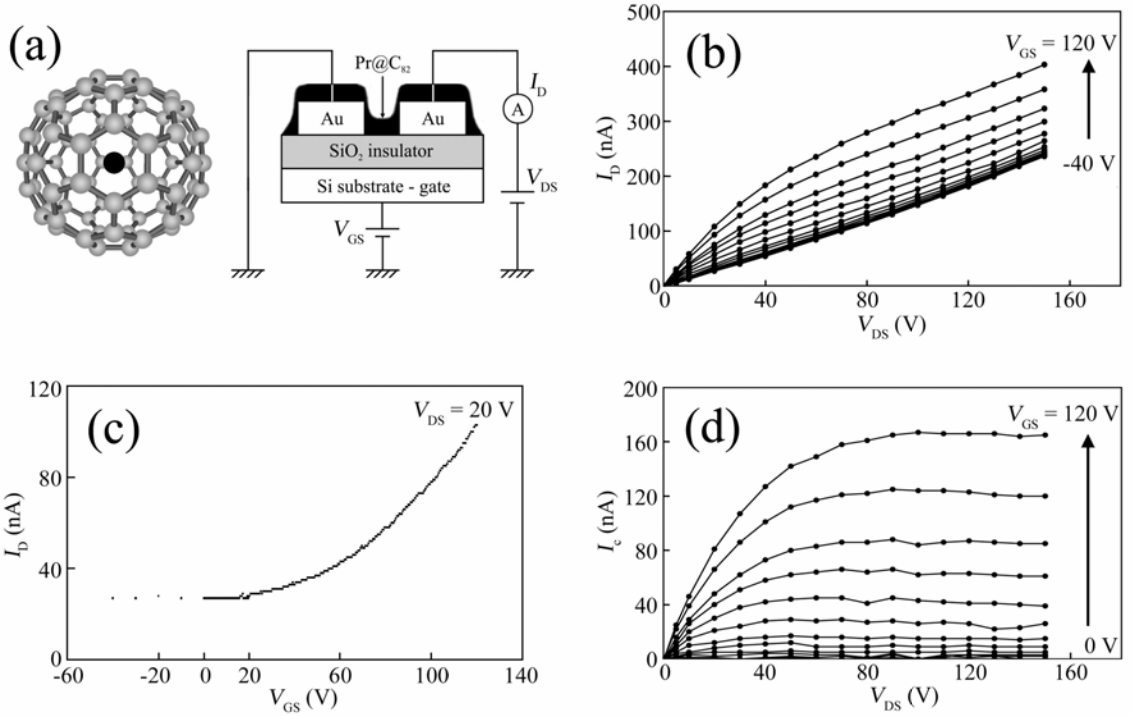
(a)
Pr@C$_{82}$
Au
Au
SiO$_2$ insulator
Si substrate - gate
V_{GS}
V_{DS}
I_D
A
(b)
I_D (nA)
V_{DS} (V)
V_{GS} = 120 V
-40 V
0
100
200
300
400
500
0
40
80
120
160
(c)
I_D (nA)
V_{GS} (V)
V_{DS} = 20 V
0
40
80
120
-60
-20
0
20
60
100
140
(d)
I_c (nA)
V_{DS} (V)
V_{GS} = 120 V
0 V
0
40
80
120
160
200
0
40
80
120
160

Fig. 1.

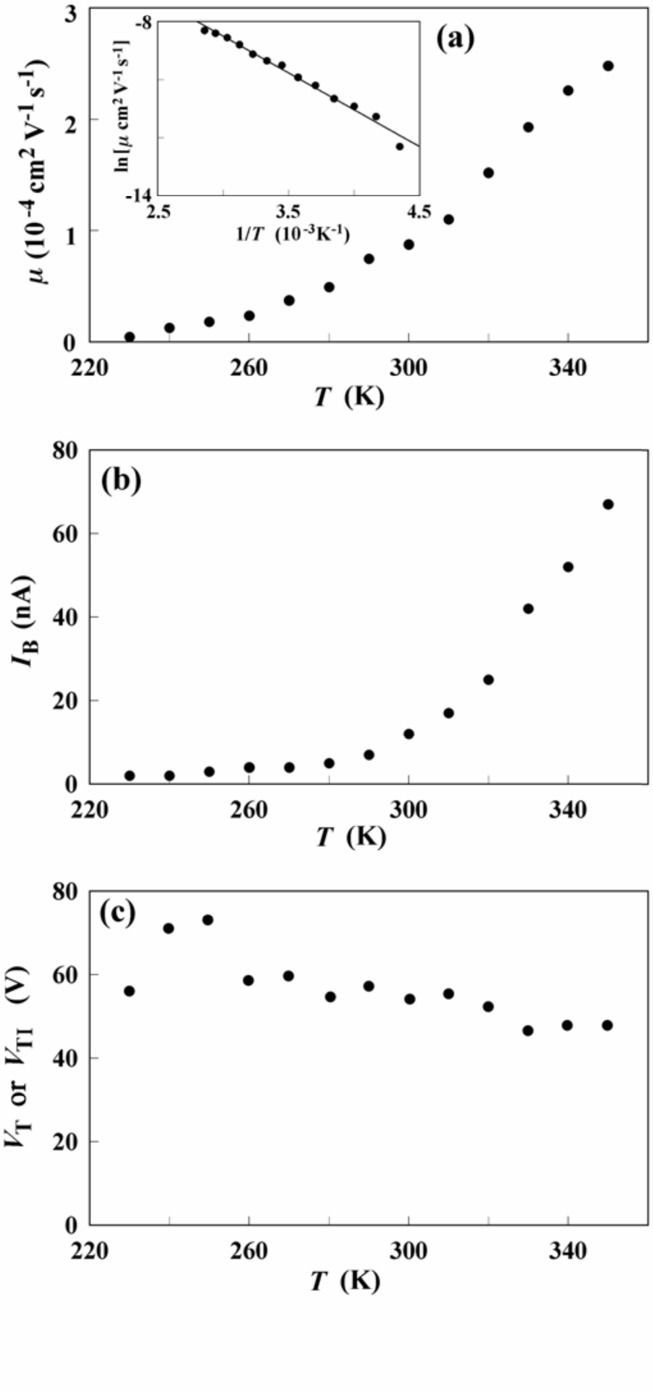
(a)
μ (10⁻⁴ cm² V⁻¹ s⁻¹)
0
1
2
3
220
260
300
340
T (K)
ln [μ cm² V⁻¹ s⁻¹]
-8
-14
2.5
3.5
4.5
1/T (10⁻³ K⁻¹)
(b)
I_B (nA)
0
20
40
60
80
220
260
300
340
T (K)
(c)
V_T or V_TI (V)
0
20
40
60
80
220
260
300
340
T (K)

Fig. 2.