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Description
Endohedral metallofullerene field-effect transistor (FET) device was fabricated with thin films of $C_{3v}$ 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, $\mu$, was estimated to be $1.5 \times 10^{-4}$ 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 C₆₀ by Haddon et al [1], which showed n-channel properties and high field-effect mobility \( \mu \) of \( 0.08 - 0.30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \). Subsequently, Haddon developed the C₇₀ FET device with the \( \mu \) of \( 2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) [2]. The improvement of the C₆₀ FET device has been successively examined, and the \( \mu \) value recently reached to \( 0.56 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) [3]. This value was comparable to that reported for \( N,N'\text{-dialkyl-3,4,9,10-perylene tetracarboxylic diimide derivative (PTCDI-C8)} \) FET, namely the highest \( \mu \) value among the FETs with thin films of organic molecules (OFETs) exhibiting n-channel performance [11].

The highest \( \mu \) value among p-channel OFETs is \( 1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) in pentacene FET [12]. Therefore, the combination of C₆₀ 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 C₆₀/C₆₀ 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@C₈₂ and La₂@C₈₀ [5,8]. These FETs showed n-channel normally-on properties, being different from enhancement-type FETs with C₆₀ and C₇₀ [1,2]. The \( \mu \) values were lower than those of C₆₀ and C₇₀ 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 $\mu$ values were higher by one order of magnitude than those of endohedral metallofullerene 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 $\mu$ 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$_2$SO$_4$/H$_2$O$_2$. 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 x 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 $\mu$m, 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.
The plots show the n-channel normally-on FET properties, which are similar to those of Dy@C\textsubscript{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\textsubscript{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\textsubscript{82} FET [5]. The high $I_B$ originates from the small mobility gap energy, $E_{gM}$, of M@C\textsubscript{82}; the $E_{gM}$ of the $C_{2v}$ isomer of Pr@C\textsubscript{82} and Dy@C\textsubscript{82} were estimated to be 0.29 and 0.20 eV, respectively, from the $\rho$–$T$ plots [13,15]. Furthermore, the band gap energies, $E_{gB}$, of the $C_{2v}$ isomer of Pr@C\textsubscript{82} and Dy@C\textsubscript{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\textsubscript{60} (1.8 – 2.1 eV) and C\textsubscript{70} (2.2 eV) [17-19].

The intrinsic channel current, $I_C$, induced by applying $V_G$ in the Pr@C\textsubscript{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\textsubscript{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 $\mu$ and $V_T$ of the Pr@C$_{82}$ FET at 320 K were estimated to be $1.5 \times 10^{-4}$ 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 $\mu$ 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 $\mu$ 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 $\mu$. The large positive value of $V_{TI}$ shows clearly the normally-off enhancement character for the Pr@C$_{82}$ FET.

The $T$ dependence of $\mu$ is shown in Fig. 2(a). The $\mu$ 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 $\mu$ value at 350 K reached to $2.5 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, which was 50 times higher than that at 230 K. The $\ln \mu$ vs. $1/T$ plot is shown in the inset of Fig. 2(a), which shows a linear 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 $\mu$ 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 $\rho$ 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 $V_{T1}$ reflects only a channel conduction induced by field-effect. As seen from Fig. 2(c), the variation of $V_{T1}$ is fairly smaller than that of $V_T$; the $V_{T1}$ 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.

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Figure captions

FIG. 1. (a) Schematic representation of $C_{2v}$-$\text{Pr@C}_{82}$, and cross sectional view of $\text{Pr@C}_{82}$ 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 $\text{Pr@C}_{82}$ 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) $\mu$, (b) $I_B$, and (c) $V_T$ and $V_{TI}$ of the $\text{Pr@C}_{82}$ FET. In $\ln \mu - 1/T$ plot is shown in the inset of (a) together with fitted line (solid line). Closed circles refer to the points measured for $\mu$, $I_B$ and $V_T$, and closed squares refer to the points measured for $V_{TI}$. 
Fig. 1.
Fig. 2.