Transport properties of field-effect transistors with thin films of C<sub>76</sub> and its electronic structure

Sugiyama, Hiroyuki; Nagano, Takayuki; Nouchi, Ryo; Kawasaki, Naoko; Ohta, Yohei; Imai, Kumiko; Tsutsui, Michiko; Kubozono, Yoshihiro; Fujiwara, Akihiko

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The C\textsubscript{76} field-effect transistor (FET) showed n-channel normally-off like behavior with n-channel field-effect mobility, $\mu_n$, of $3.9 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and the highest on-off ratio, 125, among higher fullerenes FETs. The carrier transport in the C\textsubscript{76} FET followed a thermally-activated hopping transport model. The normally-off like properties of C\textsubscript{76} FET could be reasonably explained based on the electronic structure of thin films determined from photoemission spectroscopy.
1. Introduction

Much effort has been directed to development of new field-effect transistors (FETs) with thin films of organic molecules because of application in plastic electronics such as electronic papers and flexible displays, and their properties have been rapidly improved during the past 10 years [1,2]. The \( n \)-channel field-effect mobility, \( \mu_n \), of the FETs with thin films of organic molecules reaches the value of 4.9 cm\(^2\) V\(^{-1}\) s\(^{-1}\) [3], which is higher than those of the amorphous Si FET devices [1,2].

We have so far fabricated the FET devices with thin films of a series of higher fullerenes and endohedral metallofullerenes in order to realize high-performance organic FET devices [4-8]. These devices showed \( n \)-channel normally-on FET properties which originated from high bulk currents. The properties are different from the normally-off properties in C\(_{60}\) and C\(_{70}\) FETs [3-11]. However, the observed normally-on FET properties seem to be inconsistent with the characters of intrinsic semiconductor expected for higher fullerenes, \textit{i.e.}, the normally-on properties of higher fullerenes may originate from extrinsic factors such as impurity doping into their thin films and defects formed in the thin films. Therefore, we need to clarify electronic properties of thin films of higher fullerenes and to pursue the normally-off FET properties as well as high \( \mu_n \) value. In this study, we have succeeded in fabrication of new FET devices with thin films of C\(_{76}\) which showed normally-off behavior, and investigated its transport properties. The normally-off like properties realized in the C\(_{76}\) thin film FET have been discussed on the basis of the electronic structure of thin films of C\(_{76}\), and the electronic structures were compared with those of C\(_{78}\) exhibiting normally-on properties and C\(_{60}\) exhibiting normally-off.
2. Experimental

The purified C76 was obtained by using high performance liquid chromatography (HPLC) with toluene as eluent from the soot containing fullerenes produced by arc-discharge of graphite rods containing Eu2O3. The time-of-flight (TOF) mass spectra of the sample showed a single peak due to C76 (Fig. 1(a)). The molecular symmetry of C76 is exactly \( D_2 \), because only \( D_2 \)-C76 can be experimentally obtained [12]. The molecular structure is schematically shown in Fig. 1(b). Further, the C78 sample used for the comparison with the C76 possesses \( D_3 \) symmetry and the sample was synthesized by the same procedure as that described above. The commercially available sample was used for the formation of C60 thin films.

The commercially available SiO2/Si(100) wafer was used as a substrate after washing with acetone, methanol and \( \text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 \), and the SiO2/Si substrate was treated with hexamethyldisilazane (HMDS) to form a hydrophobic surface. The thickness and capacitance, \( C_0 \), of SiO2 were 400 nm and \( 8.6 \times 10^{-9} \text{ F cm}^{-2} \), respectively. The source and drain electrodes were formed by a thermal deposition of Au under \( 10^{-8} \text{ Torr} \), and the thickness of electrodes was 50 nm. The thin films of C76 were formed on the source/drain electrodes by a thermal deposition under a vacuum of \( 10^{-8} \text{ Torr} \); the device structure is bottom-contact type. The thickness of C76 was concluded to be 10 nm judging from the amounts of samples used and the experimental condition in thermal deposition. The channel length, \( L \), and the channel width, \( W \), of these devices were 30 and 3000 \( \mu \text{m} \), respectively. The FET properties of the devices fabricated in this study were measured under \( 10^{-6} \text{ Torr} \) after annealing for >12 h at 120°C under \( 10^{-6} \text{ Torr} \). The crystallinity of thin films of C76 was investigated by X-ray diffraction.

Photoemission (PE) spectra of C76, C78 and C60 thin films on Au surfaces were measured in
the energy $E$ region of 4.3 – 6.2 eV under atmospheric condition with PE spectrometer (RIKEN AC-2). Furthermore, for the energy calibration, the PE spectrum of Au thin films was also measured.

3. Results and Discussion

3.1. Transport properties of C$_{76}$ FET

The drain current, $I_D$, vs. drain-source voltage, $V_{DS}$, plots for the C$_{76}$ FET at 300 K are shown in Fig. 2(a). The plots show $n$-channel normally-off like FET properties. The $I_D - V_G$ plot at $V_{DS} = 10$ V is also shown in Fig. 2(b). The $I_D$ increases with an increase in $V_G$ from -30 to 100 V, and the small $I_D$ is observed at $V_G$ of 0 V. The $n$-channel field-effect mobility, $\mu_n$, and the $V_T$ at 300 K for the C$_{76}$ FET were determined to be $3.9 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ and -5 V, respectively, from the $I_D - V_G$ plot (Fig. 2(b)) with general formula for MOS FET in the linear region [13].

As seen from Fig. 2(b), the application of $V_G$ can substantially control the $I_D$ in the C$_{76}$ FET device. As the bulk current $I_B$, which flows in the whole region of thin films, cannot be controlled by the application of $V_G$, the observed $I_D$ is not associated with the $I_B$ but channel current, which flow in the interface region between C$_{76}$ and SiO$_2$. The maximum on-off ratio was estimated to be 125 from the ratio of $I_D$ at $V_G = 100$ V to that at $V_G = -30$ V. Thus, the properties of C$_{76}$ FET are close to normally-off as in C$_{60}$ FET [4,9,11]. The on-off ratio of 125 is much higher than those of normally-on type higher fullerene FET devices: ~2 for C$_{82}$, ~6 for C$_{84}$, and ~7 for C$_{88}$ [5,6,8]. Here, it is important to note that the C$_{76}$ device fabricated in the early stage of this study showed normally-on FET properties with the low on-off ratio of 3.4. However, subsequent trials of FET-device fabrication with some different batches of C$_{76}$
samples produced normally-off like behavior, as shown in Figs. 2(a) and (b). In the section 3.2, the PE spectrum of the C76 thin films is reported and its energy band diagram is drawn and discussed in order to clarify the correlation between the electronic structure and the normally-off FET properties.

The $\mu_n$ value of the C76 FET ($10^{-4} - 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$) is lower than that of C60 FET ($0.1 - 4.9$ cm$^2$ V$^{-1}$ s$^{-1}$) [3,4,9,11]. We stress that a critical factor for the low $\mu_n$ values in fullerene FET devices is crystallinity of the thin films. In fact, a recent remarkable increase in $\mu_n$ in the C60 FET is due to an improvement of crystallinity of thin films by a use of pentacene buffer layer [3]. No Bragg peaks were observed in the X-ray diffraction of the thin films of C76, showing that these thin films are amorphous, i.e., the crystallite size is quite small in thin films of C76. This small crystallite size and large number of grain boundaries may suppress the $\mu_n$ value of C76.

The $\mu_n$ value of C76 FET increases exponentially with an increase in temperature from 240 to 300 K (Fig. 2(c)). The plot of $\mu_n - T$ shows that the channel conduction of the C76 FET device follows a thermally-activated hopping-transport model ($\mu_n \sim \exp[-E_a/k_B T]$). The $E_a$ value was determined to be 0.20 eV, from the $\ln \mu - 1/T$ plot with the above equation, whose value is almost the same as those, 0.13 – 0.14 eV, of C82 – C88 FETs [5,6,8]. The $E_a$ value of 0.20 eV is also close to that, 0.17 eV, of C78 FET determined from $\mu_n - T$ plot (not shown); this plot was obtained in the FET device with the C78 thin films in which PE spectrum was measured for the comparison of the electronic structures, as described in the section 3.2. These results mean that the hopping barrier height between grains of C76 is almost the same as those for thin films of C78, C82, C84 and C88.
3.2. Electronic structure of thin films of C$_{76}$

We raise a question why high bulk current is observed for the most of higher fullerenes [5,6,8] because the higher fullerenes are expected to be intrinsic semiconductors, contrary to endohedral metallofullerenes. The band gap energy, $E_{\text{band}}$, of C$_{76}$ is reported to be 1.30 eV from the photoemission [14] and electron energy loss spectra [15]. We measured the PE spectrum of thin films of C$_{76}$ on Au surface in order to determine the ionization potential (IP), which can be related to the highest occupied molecular orbital (HOMO). The PE spectrum of the C$_{76}$ thin films of the device exhibiting normally-off like FET properties is shown in Fig. 3(a). From the onset of PE spectrum, the IP value was determined to be 5.69 eV for the C$_{76}$ thin films on Au surface. The PE spectrum for the Au films was measured (not shown) for the comparison, and the IP value was 4.89 eV. The PE from Au is observed in the low $E$ region of PE spectra for the thin films of C$_{76}$, C$_{78}$ and C$_{60}$ (Figs. 3(a) – (c)).

The energy diagram of C$_{76}$ thin films exhibiting normally-off like FET properties, determined based on the $E_{\text{band}}$ value (1.30 eV) described above and the IP value (5.69 eV) determined from the PE spectrum (Fig. 3(a)), is shown in Fig. 4. The electronic structure of C$_{76}$ is an intrinsic semiconductor-type because the Fermi level, $E_F$, of Au is located in the midpoint of the band gap. Here the $E_F$ value of C$_{76}$ is assumed to align to that of Au owing to the contact of C$_{76}$ and Au. This energy diagram explains reasonably the normally-off like behavior in C$_{76}$ FET device because the diagram implies that the lowest unoccupied molecular orbital (LUMO) level are not doped owing to the large energy difference, $\Delta E$ (= 0.50 eV), between the $E_F$ and the LUMO level.

The PE spectrum of the thin films of the C$_{78}$ FET device exhibiting $n$-channel normally-on
FET properties (not shown) is shown in Fig. 3(b). From the transfer curve the $\mu_n$, $V_T$ and on-off ratio were estimated to be $4.6 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, 35 V and 4.5, respectively. The positive $V_T$ observed for the C$_{78}$ device exhibiting normally-on properties is due to high bulk current. From the onset of PE spectrum, the IP value can be estimated to be 5.59 eV for the C$_{78}$ thin films on Au surface. As seen from Fig. 4, the LUMO of C$_{78}$ is extremely close to the $E_F$, i.e., the $\Delta E$ is 0.08 eV because the $E_{\text{band}}$ value of C$_{78}$ thin films is estimated to be 0.78 eV from the onset of the electronic absorption spectrum (Fig. 3(d)). This small $\Delta E$ indicates the existence of impurity levels which should produce many thermally-activated electrons in LUMO. This can explain reasonably the normally-on behavior in C$_{78}$ FET.

Furthermore, the PE spectrum of C$_{60}$ thin films was measured to confirm the validity of the energy diagram determined from the PE spectrum and the correlation between the electronic structure and the FET properties; the PE spectrum is shown in Fig. 3(c). Since the IP value is estimated to be 5.79 eV from the onset of the PE spectrum (Fig. 3(c)) and the $E_{\text{band}}$ value is reported to be 2.6 eV [16], the $\Delta E$ is expected to be very large value of 1.7 eV; the IP value of 5.79 eV is the same as that reported previously [16]. The large $\Delta E$ of 1.7 eV should produce intrinsic semiconductor-like behavior or normally-off FET properties in C$_{60}$ FET device. These results show clearly that the energy band diagram of the thin films determined from the PE spectrum is effective for the prediction of the FET properties.

4. Concluding remarks

In this study, the normally-off like FET properties have been realized in C$_{76}$ FET, although all fullerenes except for C$_{60}$ and C$_{70}$ showed only $n$-channel normally-on properties up to
now [3-11]. The normally-off like properties could be reasonably explained on the basis of the energy band diagram determined from the PE spectrum of C\textsubscript{76} thin films. Here, it should be noted that the $E_{\text{band}}$ value in fullerene decreases substantially with an increase in the number of C, although the individual fullerene symmetry affects $E_{\text{band}}$ to some extent. Therefore, the realization of normally-off properties should become difficult gradually with an increase in the number of C because of difficulty in keeping the large $\Delta E$. This implies that to locate the $E_F$ at the exact midpoint between LUMO and HOMO is more important in higher fullerenes than C\textsubscript{60} and C\textsubscript{70} with large $E_{\text{band}}$, i.e., to form non-doped thin films by use of pure samples is definitive for normally-off properties in higher fullerenes.

This study successfully realized normally-off like properties in the smallest higher fullerene C\textsubscript{76} owing to the formation of intrinsic semiconductor-like thin films based on the improvement of sample purity. The next possible target for normally-off higher fullerene FET device may be C\textsubscript{84} because the $E_{\text{band}}$ is 1.1 eV [17] whose value is in the midpoint between C\textsubscript{76} (1.3 eV) and C\textsubscript{78} (0.78 eV), although the previous study reported normally-on FET properties [6].

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Figure captions

Fig. 1. (a) Time-of-flight (TOF) mass spectrum of the purified sample of C\textsubscript{76} and (b) molecular structures of D\textsubscript{2}-C\textsubscript{76}.

Fig. 2. (a) \textit{I\textsubscript{D} - V\textsubscript{DS}} and (b) \textit{I\textsubscript{D} - V\textsubscript{G}} plots for C\textsubscript{76} FET at 300 K. (c) \(\mu\textsubscript{e} - T\) plot for C\textsubscript{76} FET. Inset of (c), ln \(\mu\textsubscript{e} - 1/T\) plot.

Fig. 3. PE spectra of thin films of (a) C\textsubscript{76}, (b) C\textsubscript{78} and (c) C\textsubscript{60}. The fullerene thin films are formed on Au surfaces. (d) Electronic absorption spectrum of thin films of C\textsubscript{78}.

Fig. 4. Energy diagrams of thin films of C\textsubscript{60}, C\textsubscript{76} and C\textsubscript{78}. 
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