Transport properties of field-effect transistors with thin films of C_{76} and its electronic structure

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

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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, μ_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, *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 μ_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 C_{76} 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 Eu_2O_3. The time-of-flight (TOF) mass spectra of the sample showed a single peak due to C_{76} (Fig. 1(a)). The molecular symmetry of C_{76} is exactly D_2, because only D_2-C_{76} can be experimentally obtained [12]. The molecular structure is schematically shown in Fig. 1(b). Further, the C_{78} sample used for the comparison with the C_{76} 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 C_{60} thin films.

The commercially available SiO_2/Si(100) wafer was used as a substrate after washing with acetone, methanol and H_2SO_4/H_2O_2, and the SiO_2/Si substrate was treated with hexamethyldisilazane (HMDS) to form a hydrophobic surface. The thickness and capacitance, C_0, of SiO_2 were 400 nm and 8.6 x 10^{-9} F cm^{-2}, respectively. The source and drain electrodes were formed by a thermal deposition of Au under 10^{-8} Torr, and the thickness of electrodes was 50 nm. The thin films of C_{76} were formed on the source/drain electrodes by a thermal deposition under a vacuum of 10^{-8} Torr; the device structure is bottom-contact type. The thickness of C_{76} 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 μm, respectively. The FET properties of the devices fabricated in this study were measured under 10^{-6} Torr after annealing for >12 h at 120˚C under 10^{-6} Torr. The crystallinity of thin films of C_{76} was investigated by X-ray diffraction.

Photoemission (PE) spectra of C_{76}, C_{78} and C_{60} 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, μ_n, and the V_T at 300 K for the C_{76} FET were determined to be 3.9 x 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 C_{76} 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 μ_n value of the C_{76} FET ($10^{-4} – 10^{-3}$ cm^2 V^{-1} s^{-1}) is lower than that of C_{60} FET (0.1 – 4.9 cm^2 V^{-1} s^{-1}) [3,4,9,11]. We stress that a critical factor for the low μ_n values in fullerene FET devices is crystallinity of the thin films. In fact, a recent remarkable increase in μ_n in the C_{60} 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 C_{76}, showing that these thin films are amorphous, *i.e.*, the crystallite size is quite small in thin films of C_{76}. This small crystallite size and large number of grain boundaries may suppress the μ_n value of C_{76}.

The μ_n value of C_{76} 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 C_{76} FET device follows a thermally-activated hopping-transport model ($\mu_n \sim \exp[-E_a/k_BT]$). 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 $C_{82} – C_{88}$ FETs [5,6,8]. The E_a value of 0.20 eV is also close to that, 0.17 eV, of C_{78} FET determined from $\mu_n - T$ plot (not shown); this plot was obtained in the FET device with the C_{78} 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 C_{76} is almost the same as those for thin films of C_{78}, C_{82}, C_{84} and C_{88}.

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_{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_{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, ΔE (= 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 μ_n, V_T and on-off ratio were estimated to be 4.6 x 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 ΔE is 0.08 eV because the E_{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 ΔE 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_{band} value is reported to be 2.6 eV [16], the ΔE 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 ΔE 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_{76} thin films. Here, it should be noted that the E_{band} value in fullerene decreases substantially with an increase in the number of C, although the individual fullerene symmetry affects E_{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 ΔE. This implies that to locate the E_F at the exact midpoint between LUMO and HOMO is more important in higher fullerenes than C_{60} and C_{70} with large E_{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_{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_{84} because the E_{band} is 1.1 eV [17] whose value is in the midpoint between C_{76} (1.3 eV) and C_{78} (0.78 eV), although the previous study reported normally-on FET properties [6].

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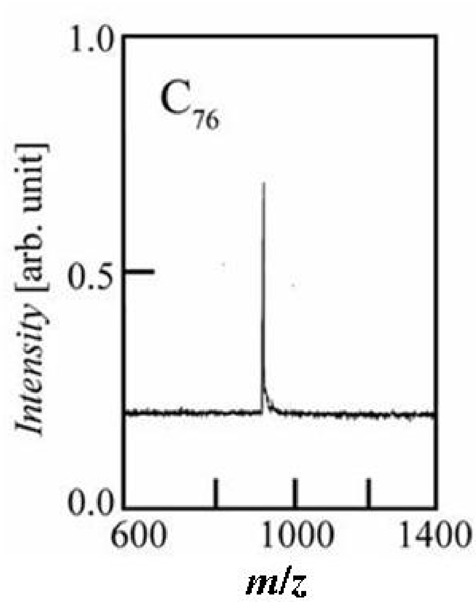
Figure captions

Fig. 1. (a) Time-of-flight (TOF) mass spectrum of the purified sample of C_{76} and (b) molecular structures of D_2-C_{76}.

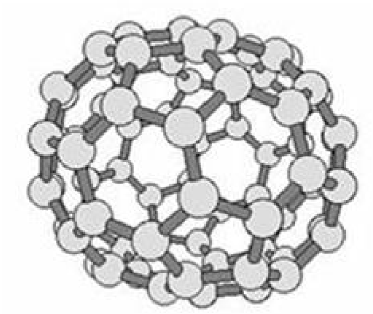
Fig. 2. (a) I_D - V_{DS} and (b) I_D - V_G plots for C_{76} FET at 300 K. (c) μ_n- T plot for C_{76} FET. Inset of (c), ln μ_n– $1/T$ plot.

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

Fig. 4. Energy diagrams of thin films of C_{60}, C_{76} and C_{78}.



(b) D_2-C_{76}



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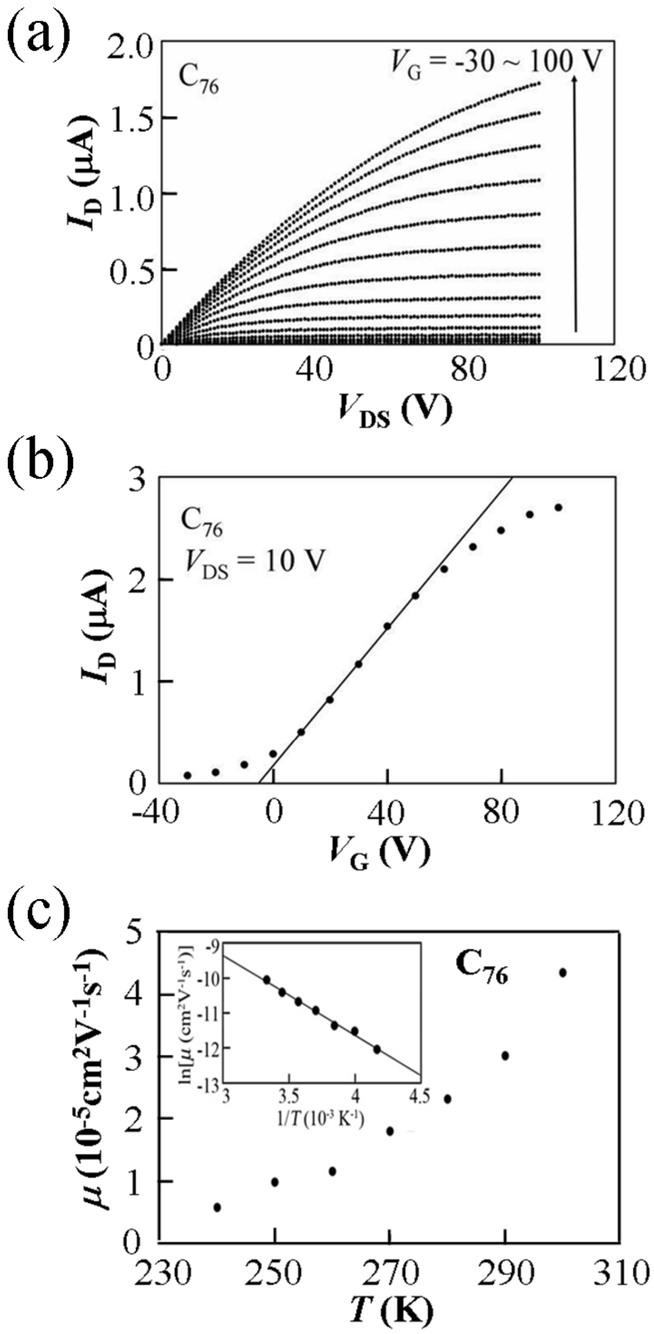

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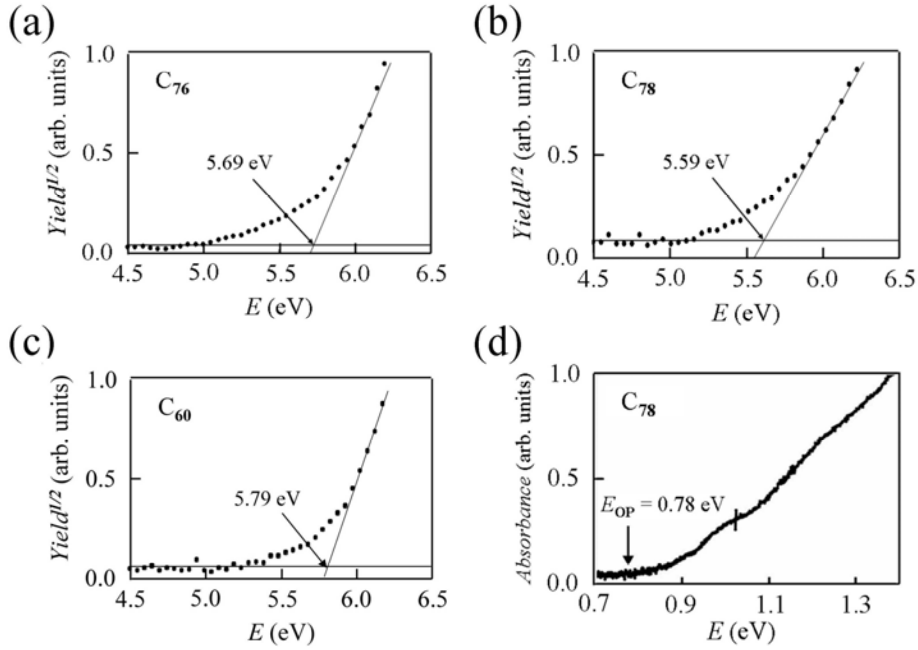

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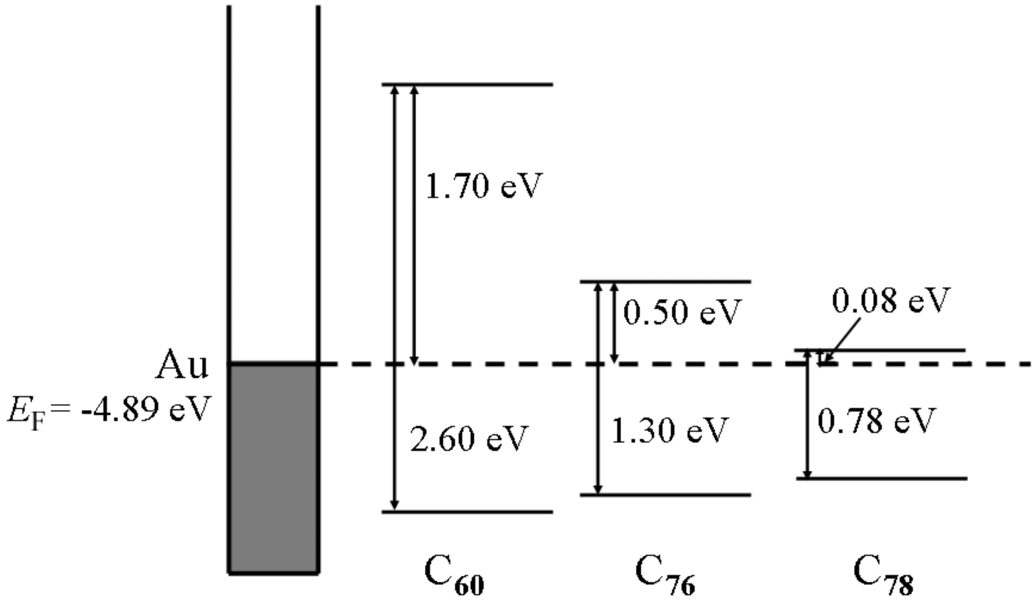

Fig.4. H. Sugiyama et al.