Fabrication and characteristics of C_{84} fullerene field-effect transistors

Kana Shibata and Yoshihiro Kubozono\textsuperscript{a)}
Department of Chemistry, Okayama University, Okayama 700-8530, Japan and CREST, Japan Science and Technology Corporation, Kawaguchi, 322-0012, Japan

Takayoshi Kanbara
Department of Chemistry, Okayama University, Okayama 700-8530, Japan

Tomoko Hosokawa
Department of Chemistry, Okayama University, Okayama 700-8530, Japan and CREST, Japan Science and Technology Corporation, Kawaguchi, 322-0012, Japan

Akihiko Fujiiwara
Japan Institute of Science and Technology, Ishikawa 923-1292, Japan and CREST, Japan Science and Technology Corporation, Kawaguchi, 322-0012, Japan

Yasuhiro Ito and Hisanori Shinohara
Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan and CREST, Japan Science and Technology Corporation, Kawaguchi, 322-0012, Japan

(Received 25 November 2003; accepted 9 February 2004)

Fullerene field-effect transistors (FETs) were fabricated with thin films of C_{84}, which showed n-channel normally-on depletion-type FET characteristics. The C_{84} FET device exhibited the highest mobility, \( \mu \), of 2.1 \( \times \) 10^{-3} cm² V^{-1} s^{-1} among normally-on fullerene FETs. The carrier transport of this FET device can be interpreted as thermally activated hopping transport. Carrier type (n-channel) and transport mechanism (hopping) reflect the electronic properties of the C_{84} molecule. © 2004 American Institute of Physics. [DOI: 10.1063/1.1695193]

A large number of field-effect transistors (FETs) with thin films of organic molecules have been fabricated and their characteristics have been studied for next-generation electronics during the past decade.\(^1,2\) The field-effect mobilities \( \mu \) of organic FETs are lower by four orders of magnitude than those of conventional FETs with inorganic materials. Nevertheless, organic FETs are known to have many advantages such as large-area coverage, structural flexibility, and low-temperature and low-cost processing in comparison with inorganic FETs. In 1997 the mobility of a pentacene p-channel FET reached 1.5 cm² V^{-1} s^{-1}.\(^3\) Subsequently, a p-channel FET on single crystals of rubrene showed a mobility of 1.0 cm² V^{-1} s^{-1}.\(^4\)

The first fullerene FET was fabricated with thin films of C_{60} by Haddon \textit{et al.}\(^5\) This FET device showed a high mobility of 0.08–0.3 cm² V^{-1} s^{-1}. The high \( \mu \) value of this device implies that C_{60} FETs can play an important role in future applications such as identification tags, smart cards, and drivers for active-matrix displays based on the integration with organic light-emitting diodes. The mobility values of n-channel organic FETs except for the C_{60} FET are much lower than those of p-channel organic FETs.\(^1,2\) Furthermore, such high \( \mu \) value attracts interest in the physics and chemistry of C_{60} FETs. The improvement of properties of the C_{60} FET device has long been examined, and very recently the mobility reached 0.56 cm² V^{-1} s^{-1}, which is one of the highest mobilities among n-channel organic FETs.\(^6\) The highest \( \mu \) of 0.6 cm² V^{-1} s^{-1} was reported for \( N,N’ \)-dialkyl-3,4,9,10-perylene tetracalboxylic diimide derivative (PTCDI-C8H\textsubscript{2}) FET device.\(^7\)

Recently we reported the transport properties of C_{60} FET.\(^8\) Temperature dependence of the mobility suggested a hopping transport as a conduction mechanism for these FETs. Furthermore, a complementary metal–oxide–semiconductor logic gate circuit was fabricated with C_{60} and pentacene FETs,\(^8\) which leads us to realize various types of logic circuits such as NOR and NAND for computing and memory. The first FETs with metallofullerenes have been realized with Dy@C_{82} and La_{2}@C_{80}.\(^8,9\) These FETs operated as n-channel normally-on device, which is substantially different from enhancement-type FETs with C_{60} and C_{70}.\(^5,6,8,10\) The output characteristics of fullerene FETs, therefore, reflect intrinsic electronic structures of individual fullerene molecules. This letter reports on the fabrication of higher-fullerene FET devices with thin films of C_{84}, and the FET characteristics and their temperature dependence.

Schematic representation of C_{84} (D_{2d} isomer) and a cross-sectional view of the C_{84} FET device are shown in Fig. 1(a). Commercially available C_{84} (99%) was used for the fabrication of the thin film. Commercially available SiO_{2}/Si(100) wafers were used as substrates after cleaning with acetone, methanol, and H_{2}SO_{4}/H_{2}O_{2}. The thin film of C_{84} 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 75 and 4000 \( \mu \)m, respectively. The characteristics of the C_{84} FET device were measured under 10^{-6} Torr after annealing for 24 h at 120°C under 10^{-6} Torr.

The drain current \( I_{D} \) versus drain–source voltage \( V_{DS} \) plots for the C_{84} FET at 290 K are shown in Fig. 1(b). The
plots show output characteristics of \( n \)-channel normally-on depletion-type FET. Relatively large \( I_D \) is observed even at zero gate voltage \( V_G \). By varying \( V_G \) from \(-130 \) to \( 130 \) V, \( I_D \) increases as \( V_G \) increases as shown in Fig. 1~b. It can be seen that the channel conductance decreases by applying a negative \( V_G \), presumably due to the depletion of carriers in the channel. \( I_D \) remained constant below \( V_G < -70 \) V. This can be explained by assuming the existence of bulk current which cannot be reduced by applying the negative \( V_G \). The threshold voltage \( V_T \) was estimated to be \(-42 \) V from the \( I_D-V_G \) plot at \( V_{DS} = 10 \) V [Fig. 1(c)]. The negative \( V_T \) supports that the \( C_{84} \) FET is normally-on type. Very recently such a normally-on depletion-type property was observed in La\(_2@C_{80}\) FET.\(^9\)

The field-effect mobility for the \( C_{84} \) FET was estimated to be \( 1.1 \times 10^{-3} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) from the \( I_D-V_G \) plot [Fig. 1(c)]. This value is higher by one order of magnitude than those reported for Dy@C\(_{82}\) and La\(_2@C_{80}\) FETs.\(^8,9\) This implies that \( C_{84} \) is superior to metallofullerenes such as Dy@C\(_{82}\) and La\(_2@C_{80}\) as materials for an active layer in normally-on depletion-type FET. The \( \mu \) increases monotonically as temperature increases up to \( 320 \) K [Fig. 2(a)], the mobility reached \( 2.1 \times 10^{-3} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) at \( 320 \) K. FET behavior was not clearly observed below \( 180 \) K because of very small \( I_D \). The activation energy \( E_a \) was estimated to be \( 0.13 \) eV from the \( \ln \mu-T^{-1} \) plot shown in the inset of Fig. 2(a). These results show that the channel conduction of the \( C_{84} \) FET device follows a thermally activated hopping-transport model (\( \mu \sim \exp(-E_a/k_BT) \)). One of the origins of high \( \mu \) in the \( C_{84} \) FET may be attributed to the fact that the channel conduction occurs through a hopping between the delocalized lowest unoccupied molecular orbitals (LUMOs) in \( C_{84} \), which is different from that between the localized LUMOs dominated by encapsulated metal ions in metallofullerenes.\(^9\)

The threshold voltage \( V_T \) decreases monotonically with increasing temperature up to \( 320 \) K [Fig. 2(b)]. Such temperature dependence might be caused by an increase in bulk current. Actually the bulk current increased with increasing temperature,\(^11\) which results in an apparent variation in \( V_T \). The \( V_T \) values are positive at temperatures below \( 250 \) K, and the FET property apparently changes from the normally-on to a normally-off with decreasing temperature. As an ex-
ample of the normally-off like FET, the $I_D - V_{DS}$ plots at 230 K are shown in Fig. 2(c).

The high $I_D$ at $V_G = 0$ V in the high-temperature region can be explained by a small gap energy, $E_g$, of $\approx 0.55$ eV which was estimated from the temperature dependence of resistivity $\rho$ for the $C_{84}$ thin-film ($V_G = 0$ V).$^{11}$ The $E_g$ value of the $C_{84}$ thin film is much smaller than those determined for $C_{60}$ (1.8 or 2.1 eV) and $C_{70}$ (2.2 eV).$^{12,14}$ The $C_{60}$ and $C_{70}$ FETs showed enhancement-type normally-off properties.$^{5,6,8,10}$ Consequently, the normally-on type FET property in the $C_{84}$ FET device can be interpreted within the framework of high bulk current in the $C_{84}$ thin film. However, the origin of carriers of the high bulk current in the $C_{84}$ thin film remains to be clarified. The on–off ratio, $I_D (V_G = 130$ V)/$I_D (V_G = -130$ V), at $V_{DS} = 10$ V of the $C_{84}$ FET was $\approx 6$ at 290 K, as shown in Fig. 1(b). This low on–off ratio is owing to high bulk current of the $C_{84}$ thin film. On the other hand, the on–off ratio increases at low temperatures, and the value reached $\approx 37$ at 230 K [Fig. 2(c)]. This increment is caused by the reduction of bulk current at low temperature. This will open a way to fabricate practical devices with higher fullerene FETs for computing and memory.

Y.K. acknowledges Dr. Yoichi Nonogaki of the Institute for Molecular Science for his valuable discussion. The authors appreciate financial supports from CREST of Japan Science and Technology Corporation and from Mitsubishi foundation, and a Grant-in-Aid (15350089) of Ministry of Education, Culture, Sports, Science and Technology, Japan.

11. Unpublished data.