Transport properties of field-effect transistor with Langmuir-Blodgett films of C_{60} dendrimer and estimation of impurity levels

Naoko Kawasaki, Takayuki Nagano, and Yoshihiro Kubozono[a)]
Research Laboratory for Surface Science, Okayama University, Okayama 700-8530, Japan

Yuuki Sako, Yu Morimoto, and Yutaka Takaguchi
Graduate School of Environmental Science, Okayama University, Okayama 700-8530, Japan

Akihiko Fujiwara
Japan Advance Institute of Science and Technology, Ishikawa 923-1292, Japan

Chih-Chien Chu and Toyoko Imae
Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan

(Received 9 October 2007; accepted 23 November 2007; published online 14 December 2007)

Field-effect transistor (FET) device has been fabricated with Langmuir-Blodgett films of C_{60} dendrimer. The device showed *n*-channel normally off characteristics with the field-effect mobility of 2.7×10^{-3} cm^2 V^{-1} s^{-1} at 300 K, whose value is twice as high as that (1.4×10^{-3} cm^2 V^{-1} s^{-1}) for the FET with spin-coated films of C_{60} dendrimer. This originates from the formation of ordered π-conduction network of C_{60} moieties. From the temperature dependence of field-effect mobility, a structural phase transition has been observed at around 300 K. Furthermore, the density of states for impurity levels was estimated in the Langmuir-Blodgett films. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2824818]

Various types of thin film field-effect transistor (FET) devices were fabricated with spin-coated films of [6,6]-phenyl C61-butyric acid methyl ester and C60-fused *N*-methylpyrrolidine-*meta*-C12 phenyl (C60MC12).[1,2] The FET device with C60MC12 showed the relatively high μ value ($\sim$0.6 cm^2 V^{-1} s^{-1}) because this fullerene related material could result in the self-assembled films which take 2.32 nm period bilayer structures with interdigitated dodecyl chains.[2] Recently, we have fabricated the FET devices with the spin-coated films of C_{60} dendrimer [Fig. 1(a)] developed by Takaguchi and co-workers,[3,4] and the μ value was 1.4×10^{-3} cm^2 V^{-1} s^{-1} at 300 K[5]. The channel conduction is based on π network through the C_{60} moieties. Further, the Langmuir-Blodgett (LB) films can be formed with the C_{60} dendrimer, as shown in Fig. 1(b),[4] and the LB films are expected to form more ordered arrangement of C_{60} moieties than in the spin-coated films. In the present study, we have fabricated the FET devices with the LB films of C_{60} dendrimer and investigated their FET properties.

The structure (top-contact type) of the FET device with the LB films of C_{60} dendrimer is shown in Fig. 1(c). The LB films composed of five layers of C_{60} dendrimer were used as the active layers of the FET device. The thickness can be estimated to be $\sim$15 nm. The procedure of the formation of LB films is described elsewhere.[4] The channel length L and channel width W were 5 μm and 6 mm, respectively. The thickness of Au source/drain electrodes was 50 nm. The capacitance per area C_0 was 8.63×10^{-9} F cm^{-2} for SiO_2. The FET properties were measured under high vacuum of 10^{-6} Torr. The atomic force microscope (AFM) image of the LB films is shown in Fig. 1(d); the AFM image of LB films containing a defect is positively shown so that the LB is clearly recognized to be formed on Si/SiO_2 substrate from the contrast. The Si/SiO_2 surface was found to be covered with LB films of C_{60} dendrimer without defects over several square micrometers on the basis of the AFM images measured for some Si/SiO_2/LB substrates.

Figure 2(a) shows the drain current I_D versus drain-source voltage V_{DS} plots for the FET with the LB films of C_{60} dendrimer at 300 K; the annealing was carried out at 60 °C for 12 h under vacuum of 10^{-6} Torr before the FET measurement. The plots show typical *n*-channel normally off output characteristics. The value of μ was determined to be 2.1×10^{-4} cm^2 V^{-1} s^{-1} at 300 K from the $I_D^{1/2}$-V_G plot [Fig. 2(b)] at saturation regime of $V_{DS}=100$ V with general formula for FET analysis;[6] the μ reached the value of 2.7×10^{-3} cm^2 V^{-1} s^{-1} at 300 K by a repetition of annealing, as shown in Fig. 2(c). The μ value is twice as high as that obtained for the FET with spin-coated films of C_{60} dendrimer (1.4×10^{-3} cm^2 V^{-1} s^{-1} at 300 K). The higher performance in the FET with the LB films than in the spin-coated film FET can be attributed to the formation of well-ordered π-conduction path. The value of threshold voltage V_{TH} was 36 V [Fig. 2(b)]. No FET properties were observed in the FET device with the L of 30 μm, suggesting that the ordered region in the LB films is still smaller than 30 μm, while the FET properties with spin-coated films could be observed at $L=30$ μm.[5] In the spin-coated films, the conduction path was easily formed even at the L of 30 μm because of the thicker films ($\sim$1 μm) than the LB films ($\sim$15 nm). The on-off ratio reached 10^7 in the LB film FET.

The temperature (T) dependence of μ value in the FET device with the LB films is shown in Fig. 2(c). The μ value increases with an increase in T up to 300 K, and the μ value decreased rapidly above 300 K; the maximum μ value was 2.7×10^{-3} cm^2 V^{-1} s^{-1} at 300 K, as described above. The drastic decrease is also observed in that reported for the FET device with the spin-coated films.[5] As the drastic decrease above 300 K recovers when cooling the T, this transition cannot be ascribed to neither the degradation of the

[a)]Electronic mail: kubozono@cc.okayama-u.ac.jp

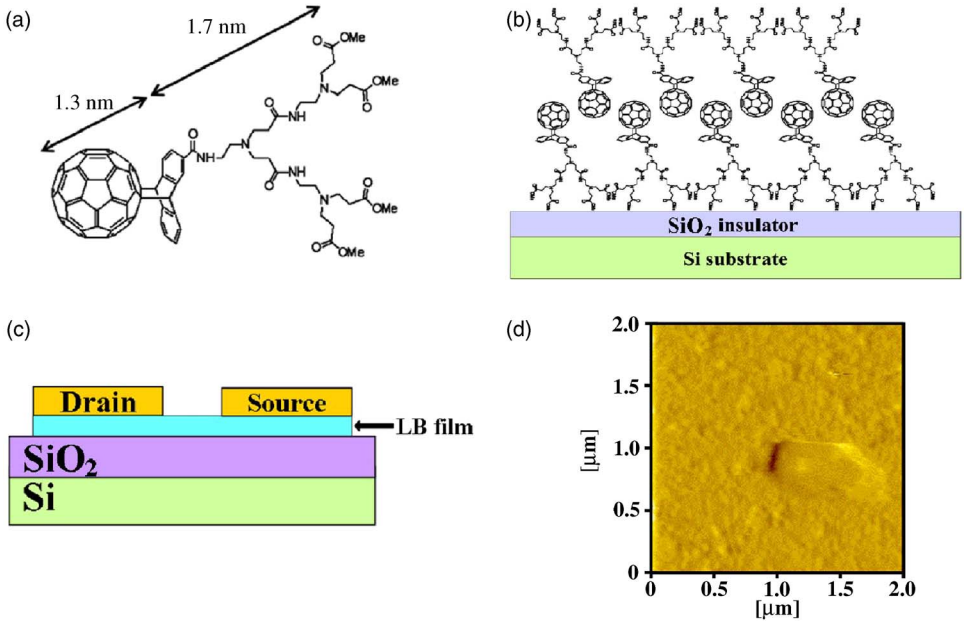

FIG. 1. (Color online) (a) Molecular structure of C_{60}-dendrimer molecule used in this study, (b) structure of LB films of C_{60} dendrimer, (c) the device structure of the LB film FET, and (d) AFM image of LB films used for the FET device. This AFM image contains a defect in which the surface is not covered with the LB films.

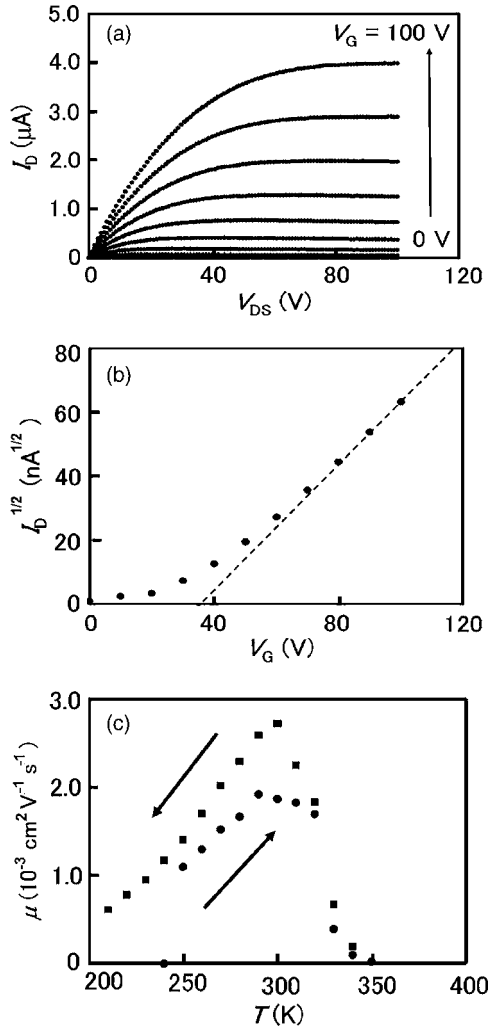

FIG. 2. (a) Output and (b) transfer characteristics for the LB film FET. In (b), the $I_D^{1/2}$-V_G plot at V_{DS}=100 V is drawn together with the fitting line with general formula for FET analyses (Ref. 9). (c) μ-T plots for the LB film FET. The symbols ● and ■ refer to the μ values obtained in increasing and decreasing T, respectively.

C_{60}-dendrimer molecule nor the evaporation of the solvents incorporated into the LB films. Furthermore, the reversible transition of the powder sample of C_{60} dendrimer was found at around 300 K by the differential scanning calorimetry. Consequently, this transition probably corresponds to the structural order-disorder of C_{60}-dendrimer LB films.

The μ value for the LB film FET increased by a factor of 2 in comparison with that for the spin-coated film FET. This result is inconsistent with the first expectation that the highly ordered π-conduction network in the LB film FET should remarkably increase the μ value in comparison with that in the spin-coated film FET. From the expectation of the well-ordered C_{60}-moiety network in the LB films, which was supported by the x-ray reflection,[4] we assumed that the characteristics of the LB film FET are not still governed by the formation of well-ordered π-conduction network between the C_{60} moieties but by the impurity levels formed into the LB films. In order to evidence this assumption, we have estimated the density of states $N(\varepsilon)$ for the impurity levels which exists in the LB films and compared the $N(\varepsilon)$ with that for C_{60} thin film FET formed by the thermal deposition. Here, ε is the energy measured from the lowest unoccupied molecular orbital (LUMO) level.

As seen from the schematic energy band diagram in the LB film FET shown in Fig. 3(a), the LUMO level which is associated with n-channel conduction is lowered by applying the V_G (>0), and the activation energy E_a, i.e., the energy difference between the impurity levels matching the Fermi level of electrodes and the LUMO level, should decrease gradually. The E_a values were determined by a least-squares fitting with $I_D \sim \exp(-E_a/k_BT)$ to the I_D-T plot in the T region of 260–310 K at each V_G of 40–100 V (in 1 V step) and at the fixed V_{DS} of 100 V; k_B is Boltzmann constant. The E_a-V_G plot is shown in Fig. 3(b), and the E_a decreases monotonously with an increase in V_G, which is consistent with the behavior expected from the energy band diagram [Fig. 3(a)]. The $N(\varepsilon)$ for the impurity levels is given by $N(\varepsilon) = C_0/e[1/(dE_a/dV_G)]$, where e is the electronic charge;[7] ε is approximately equal to E_a as expected from the energy diagram [Fig. 3(a)]. The $N(\varepsilon)$ for the C_{60}-dendrimer LB film FET is shown as a function of ε in Fig. 3(c) together with

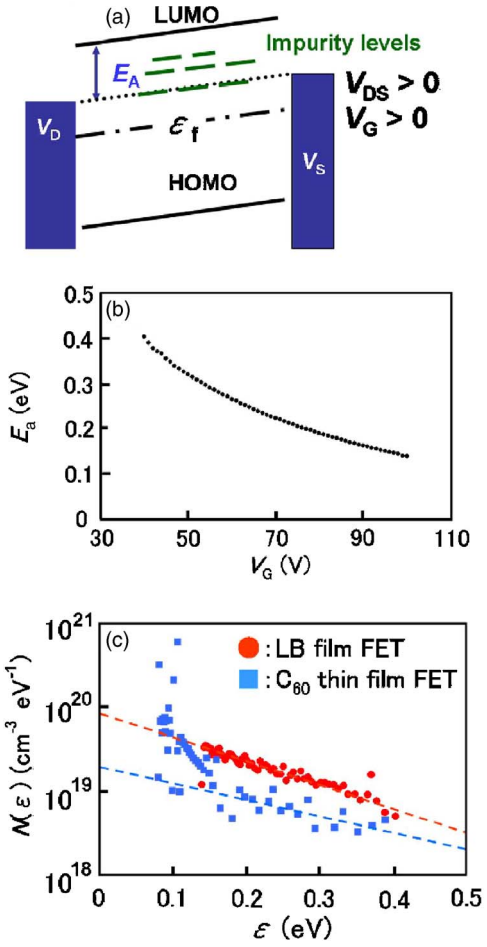

FIG. 3. (Color online) (a) Schematic energy diagram for the LB film FET. ε_F is the Fermi level for the C_{60}-dendrimer LB films, and at $V_G=0$ V, the Fermi level of electrodes matches with the ε_F. (b) E_a-V_G plot for the LB FET. (c) $N(\varepsilon)$-ε plots for the LB and C_{60} FET.

$N(\varepsilon)$-ε plot for the C_{60} FET; the $N(\varepsilon)$ is given by a logarithmic scale. Since the $N(\varepsilon)$ values in low ε region below 0.15 eV are scattered in the C_{60} FET, the scattered $N(\varepsilon)$ values are ruled out in the analyses described in the subsequent paragraph.

The $N(\varepsilon)$ was $10^{19}-10^{20}$ cm^{-3} eV^{-1} for both LB film and C_{60} FETs. The trapped carriers are assumed to exist within 5–10 nm of the interface between active layers and gate dielectric on the basis of the results reported so far,[7,8] and actually, the trapping depth of 7.5 nm was used for the $N(\varepsilon)$ estimation. As seen from Fig. 3(c), the $N(\varepsilon)$ for the LB film FET in the ε region of 0.15–0.4 eV is approximately four times as high as that for the C_{60} thin film FET which exhibits the μ value of 0.14 cm^2 V^{-1} s^{-1}. This result suggests that the lower μ value (2.7×10^{-3} cm^2 V^{-1} s^{-1}) in the LB film FET than that (0.14 cm^2 V^{-1} s^{-1}) in the C_{60} FET can be closely related to the $N(\varepsilon)$ for the impurity levels. The $N(\varepsilon)$-ε plots were well fitted by $N(\varepsilon)=N_0\exp(-\beta\varepsilon)$, and the N_0 and β were determined to be 8.1×10^{19} cm^{-3} eV^{-1} and 6.4 eV^{-1} for the LB FET, respectively, and 2.0×10^{19} cm^{-3} eV^{-1} and 5 eV^{-1} for the C_{60} FET. Consequently, the $N(\varepsilon)$ for the C_{60}-dendrimer LB film FET showed only an exponential decay with an increase in ε. The structureless behavior is different from the $N(\varepsilon)$ for the single crystal pentacene FET, which exhibits a peak ascribable to the impurity levels produced from the bias-stressed defects of pentacene as well as an exponential decay.[7] Therefore, the LB film FET is scarcely affected by the bias stress.

Finally, we have calculated the values of subthreshold swing S for the C_{60}-dendrimer LB film and C_{60} thin film FETs from the $N(\varepsilon)$ of the impurity levels with $S=(k_BT/e)(\ln 10)[1+eN(\varepsilon)/C_0]$,[9] where $N(\varepsilon)$ is given in unit (cm^{-2} eV^{-1}). In this estimation, the $N(\varepsilon)$ values were used at the same V_G ($<V_{TH}$) as those used in the determination of experimental S values from I_D-V_G plots, i.e., $N(\varepsilon)=1.91\times10^{12}$ cm^{-2} eV^{-1} at $\varepsilon=0.54$ eV and $V_G=25$ V for the LB FET and $N(\varepsilon)=1.61\times10^{12}$ cm^{-2} eV^{-1} at $\varepsilon=0.50$ eV and $V_G=55$ V for the C_{60} FET. The S values were estimated to be 2.2 V/decade for the LB FET and 1.8 V/decade for C_{60} FET from the $N(\varepsilon)$ and the above equation. These values were 1/5 times the experimental S values, 10.2 V/decade for the LB FET and 7.9 V/decade for the C_{60} FET, determined from I_D-V_G plots. Nevertheless, the increase in experimental S values from 7.9 V/decade (C_{60} FET) to 10.2 V/decade (LB FET) can be completely correlated with the increase in S from 1.8 V/decade (C_{60} FET) to 2.2 V/decade (LB FET) estimated from the $N(\varepsilon)$ values, i.e., the ratio of the increase is the same for both S values from the I_D-V_G and from the $N(\varepsilon)$, suggesting that a relative relation of $N(\varepsilon)$ between LB and C_{60} films is reliable. The deviation of the absolute S value estimated with $N(\varepsilon)$ from that with I_D-V_G plot may be ascribed to the factors other than $N(\varepsilon)$ such as the increase in off current produced by the measurements under light condition.

The authors are grateful to Mr. Yohei Ohta and Mrs. Michie Sasaki for their kind assistance through this work. This work was partly supported by NEDO and by a Grant-in-Aid (No. 18340104) from MEXT, Japan.

[1] Th. B. Singh, N. Marjanovic, G. J. Matt, N. S. Sariciftci, R. Schwödiauer, and S. Bauer, Appl. Phys. Lett. **85**, 5409 (2004).
[2] M. Chikamatsu, S. Nagamatsu, Y. Yoshida, K. Saito, K. Yase, and K. Kikuchi, Appl. Phys. Lett. **87**, 203504 (2005).
[3] Y. Takaguchi, Y. Sako, Y. Yanagimoto, S. Tsuboi, J. Motoyoshiya, H. Aoyama, T. Wakahara, and T. Akasaka, Tetrahedron Lett. **44**, 5777 (2003).
[4] C. Hirano, T. Imae, S. Fujima, Y. Yanagimoto, and Y. Takaguchi, Langmuir **21**, 272 (2005).
[5] H. Kusai, T. Nagano, K. Imai, Y. Kubozono, Y. Sako, Y. Takaguchi, A. Fujiwara, N. Akima, Y. Iwasa, and S. Hino, Appl. Phys. Lett. **88**, 173509 (2006).
[6] S. M. Sze, *Semiconductor Devices: Physics and Technology* (Wiley, New York, 2002).
[7] D. V. Lang, X. Chi, T. Siegrist, A. M. Sergent, and A. P. Ramirez, Phys. Rev. Lett. **93**, 086802 (2004).
[8] A. R. Völkel, R. A. Street, and D. Knipp, Phys. Rev. B **66**, 195336 (2002).
[9] J.-P. Colinge and C. A. Colinge, *Physics of Semiconductor Devices* (Kluwer, Boston, 2002).