Transactions of the Materials Research Society of Japan 32[2] 345-348 (2007)

Electrical Properties of $M(dmit)_2$ –Alkylammonium LB films in the FET Structure

Yoko Tatewaki[1], Hitoshi Ohnuki[2] and Keiichi Ikegami[1]
[1]Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST),
1-1-1 Umezono, Tsukuba, 305-8568, Japan,
Fax: +81-(0)29-861-5375, *e-mail : y-tatewaki@aist.go.jp.
[2]Dept. of Marine Technology, Tokyo University of Marine Science and Technology, 2-1-6 Etchujima, Koto-ku,
Tokyo 135-8533, Japan

We have produced LB films composed of $[M(dmit)_2]$-$[N(C_mH_{2m+1})_n(CH_3)_{4-n}]$ 1 : r ($[M\text{-}(nC_m)_r]$) complexes set in the bottom-contact-type Field-Effect transistor (FET) structure, where M = Au, Ni or Pd, m = 8, 10, 12, 14, 16, 18 or 22, n = 2, 3 or 4, and r = 1 or 2. We have measured the I_{ds}-V_{ds} characteristics of these LB films. The FET characteristics were observed in some cases. But the transconductivity of the devices has been found to be quite low. Moreover, an anomalous hysteric behavior of I_{ds}-V_{ds} characteristics has been detected for some complexes.

Key words: Langmuir-Blodgett film (LB film), $M(dmit)_2$, Field-Effect transistor, Electrical properties, Alkylammonium

1. INTRODUCTION

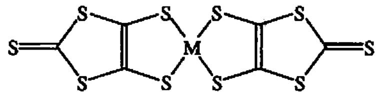
The $[M(dmit)_2]_1$ $[N(C_mH_{2m+1})_n(CH_3)_{4-n}]_r$ ($[M\text{-}(nC_m)_r]$) complexes show a variety of electrical properties ranging from dielectric to superconducting[1]. The Langmuir-Blodgett (LB) films of $Au(dmit)_2$-dialkylammonium salts exhibited a high lateral conductivity of 40 - 100 S/cm at room temperature after electrochemical oxidation or I_2 doping, and had metallic temperature dependence of the conductivity[2,3]. Furthermore, the ac magnetic susceptibility and resistance suggested the existence of a super conducting phase below 4 K[4].

It was clarified that the field effect doping (FE doping) was one of effective carrier dope methods for the organic semiconductors. An important factor for realizing optimum transport characteristics was building a well ordered conducting path for charge carriers, where oriented π-conjugated molecular system interact with each other in face-to-face direction to form a stacking structures[5,6]. The LB technique is useful to control the molecular arrangements, and to contact conducting path for charge carriers [7,8].

In this work, we are aiming at the improvement of the conductivities of the LB film composed of $[M\text{-}(nC_m)_r]$ complexes by using the FE doping method. If the mechanism of conduction composed of $[M\text{-}(nC_m)_r]$ is clarified, we will obtain the clue of the new devices.

2. EXPERIMENTAL

The $[M\text{-}(nC_m)_r]$ salts were synthesized following the procedure of Steimecke *et al*[9]. Scheme 1 and 2 show the structure of $[M(dmit)_2]$(M = Pd, Au, Ni) and $[N(C_mH_{2m+1})_n(CH_3)_{4-n}]$, respectively. Here, M is the center metal (Pd, Au or Ni), m is the number of carbons (m = 8-22) and n is the number of long alkylchains of $[N(C_mH_{2m+1})_n(CH_3)_{4-n}]$. The ratio of $[M(dmit)_2]$: $[N(C_mH_{2m+1})_n(CH_3)_{4-n}]$ is 1 : 1 or 1 : 2.



Scheme 1. Molecular structure of $M(dmit)_2$.

$N(C_mH_{2m+1})_n(CH_3)_{4-n}$

Scheme 2. Molecular structure of alkylammonium.

The prepared FET devices were in the bottom-gate and bottom-contact configuration (Fig. 1(a)). As the substrates, which act as the gate electrode, n-doped silicon plates (10 mm^2, 0.02 Ωcm, 500 µm thick) were used. The surface of the substrate was oxidized to form the gate insulator layer (300 nm thick). Hexamethyldisilazane (HMDS) self-assembled-monolayers were formed on the substrate surface to reduce the effects of the carrier trapping sites in the SiO_2 layer by immersing substrates in a chloroform solution (10 %) of HMDS at 50 °C for 4 h. The Cr and Au electrodes were vacuum-deposited on the HMDS-covered substrate surface, and the $[M\text{-}(nC_m)_r]$ LB films of 12 layers, which is expected to serve as a semiconductor layers, were deposited on the substrate. The thicknesses of the Cr and Au layers were 5 and 40 nm, respectively. Fig. 1 (b) and (c) show the picture of a prepared FET sample and the Magnification between Au electrodes.

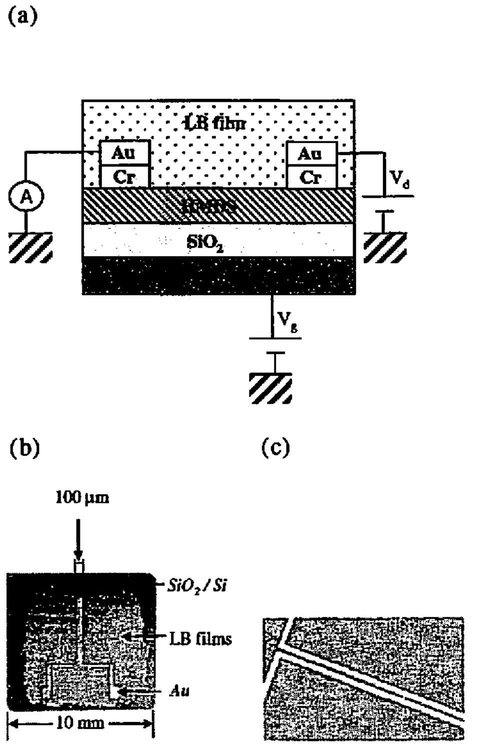


Fig. 1. (a) Schematic diagram of the FET structure used in this work, (b) Photograph of a FET sample, (c) Magnification around the gap in (b).

The LB films were prepared by the method described below. Pure water with a resistivity greater than 1.8 x 10^7 Ωcm, which was used as the subphase, was prepared by using a Millipore Milli-Q system. A Langmuir trough of Lauda film waage was used. The [M-(nC$_m$)$_r$] complexes were solved in the 1 : 1 mixture of benzene and acetonitrile (1 mM). The solution was spread on the water surface to form floating monolayers. The monolayers were left for 5 minutes after spreading of the solutions, then, compressed until the surface pressure reached to 25 mN/m. The LB deposition was started 5 minutes after the compression of the film. LB films were deposited by the horizontal lifting method.

The prepared FET devices were dried for more than 24 h in air and 15 minutes in vacuum (< 5 x 10^{-3} Torr). Electrical characterization was carried out by sweeping the source-drain voltage (V_{ds}) at a constant gate voltage (V_g) or sweeping V_g at a constant V_{ds} while monitoring the source-drain current (I_{ds}). These measurements were performed

Table I. The list of the tasted [M-(nC$_m$)$_r$] FET samples. Here, "a" and "n.a" mean "FET active" and "not FET active", respectively.

m	8	10			12		14		16		18	22
n	3	2	3	4	2	3	2	3	2	3	2	2
Au (1:1)	n.a.	a	n.a.	-	-	n.a.	a	n.a.	-	n.a.	a	n.a.
Ni (1:1)	-	a	n.a.	n.a.	n.a.	-	n.a.	-	n.a.	-	n.a.	n.a.
(1:2)	-	n.a.	-	-	n.a.	-	-	-	n.a.	-	n.a.	-
Pd (1:1)	-	-	-	-	-	-	-	-	-	-	n.a.	-
(1:2)	-	-	-	-	-	-	-	-	-	-	n.a.	-

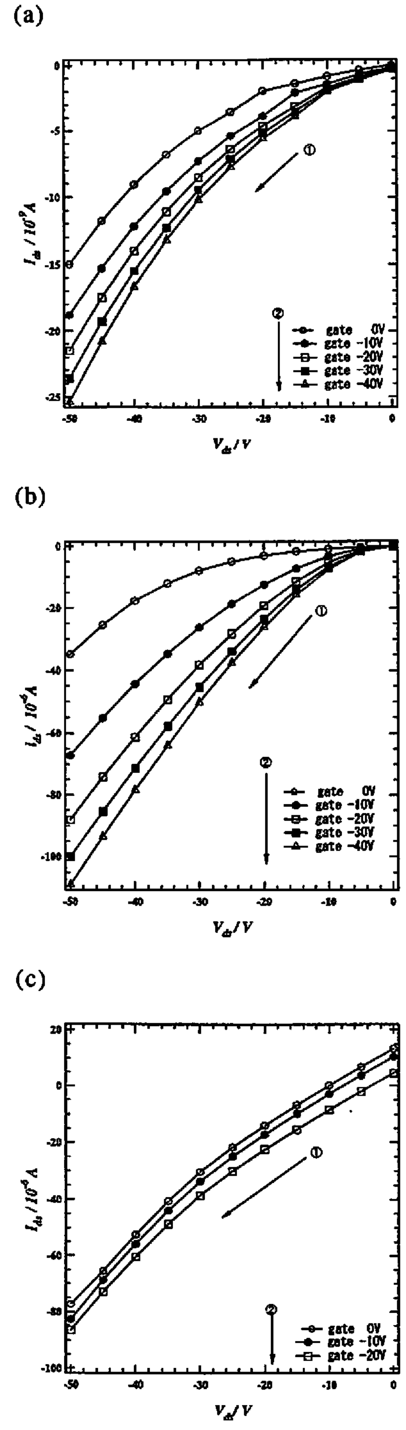


Fig. 2. I_{ds}-V_{ds} characteristics of FET samples composed of [M-(nC$_m$)$_r$] LB films. The gate voltage was changed from 0 V to -40 V. The source-drain voltage was changed from 0 V to -50 V. (a)[Ni-(2C$_{10}$)], (b)[Au-(2C$_{10}$)], (c) [Pd-(2C$_{18}$)].

Table II. The list of samples composed of [M-(nC_m)$_r$] (M = Au and Ni, m = 10, 14 and 18). To clarify the effects the center metal and the alkyl-chain length, I_{ds} at V_{ds} = -50 V and V_g = -40 V and the magnification when V_g were changed from V_g = 0 V to -40 V.

m M	10	14	18
Au	110 x 10^{-6} (A) 3 times	1.4 x 10^{-6} (A) 4 times	0.017 x 10^{-6} (A) 1.3 times
Ni	0.025 x 10^{-6} (A) 2 times	-	-

in a vacuum chamber under darkness by using source-measure units (Keithley 6157A, Keithley 487).

3. RESULTS AND DISCUSSION

We have measured the I_{ds}-V_{ds} and I_{ds}-V_g characteristics of the LB films of a wide variety of [M-(nC_m)$_r$] complexes in the FET structure (Table. I). The I_{ds}-V_{ds} characteristics of representative samples are shown in Fig. 2; (a) [Ni-($2C_{10}$)$_1$], (b) [Au-($2C_{10}$)$_1$], (c) [Pd-($2C_{18}$)$_1$].

In the n = 3 and 4 cases, no clear V_g dependence of the I_{ds}-V_{ds} characteristics was observed. In the M = Pd and r = 2 cases, no clear V_g dependence of the I_{ds}-V_{ds} characteristics was observed either. These samples exhibited I_{ds}-V_{ds} characteristics similar to that indicated in Fig. 2(c).

The samples with [Ni-($2C_{10}$)$_1$], [Au-($2C_{10}$)$_1$], [Au-($2C_{14}$)$_1$] and [Au-($2C_{18}$)$_1$] show V_g dependent I_{ds}-V_{ds} characteristics. They show the n-type characteristic when the gate voltages were changed from 0 V to -40 V (see Fig. 2(b) and (c), for example).

To clarify the effects the center metal and the alkyl-chain length, I_{ds} at V_{ds} = -50 V and V_g = -40 V and the magnification when the gate voltage were changed from V_g = 0 V to -40 V of these FET-active samples are listed in Table II. Both of the current and the current-magnification of the sample composed of [Au-($2C_{10}$)$_1$] were found to be larger than those in the [Ni-($2C_{10}$)$_1$] case.

Similarly, the current of the sample in the n = 10 case was larger than those in the n = 14 and 18 cases. The current-magnifications of the samples in the n = 10 and 14 cases were the same, and that of the sample in the n = 18 case was smallest.

Fig. 3 (a) and (b) show the I_{ds}-V_g characteristics of the samples composed of [Ni-($2C_{10}$)$_1$] and [Au-($2C_{10}$)$_1$] after the measurements of I_{ds}-V_{ds} characteristics indicated by Fig. 2. I_{ds} of [Ni-($2C_{10}$)$_1$] and [Au-($2C_{10}$)$_1$] samples observed when $|V_g|$ was increased to 80 V were 2-3times larger than there initial values at V_g = 0. Here, V_{ds} was fixed at -50 V and -30 V, respectively for the [Ni-($2C_{10}$)$_1$] and [Au-($2C_{10}$)$_1$]. This change in I_{ds} was found to be irreversible. That is, when V_g was changed from -80 V to 0 V, $|I_{ds}|$ of these samples remains large. The changes in I_{ds} of [Au-($2C_{14}$)$_1$] and [Au-($2C_{18}$)$_1$] samples were same.

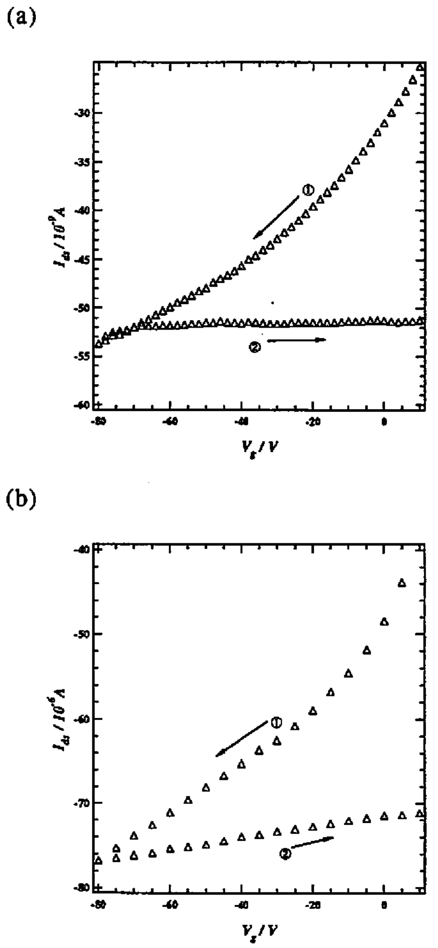


Fig. 3. I_{ds}-V_g characteristics of FET samples composed of [M-(nC_m)$_r$]LB films. The gate voltage was changed from 0 V to -80 V, and then, returned to 0 V. The source-drain voltage of (a) and (b) were -50 V and -30 V. (a) [Ni-($2C_{10}$)$_1$], (b) [Au-($2C_{10}$)$_1$].

Reversible behaviors should be observed for normal FETs in this kind of experiments. In other words, our FET samples are not normal. The followings can be the cause of this a normal irreversible behavior. 1) Chemical change in complex due to large V_g, 2) Structural change in the LB films due to V_g, 3) Changes in the LB films due to I_{ds}. But, further experiments are clearly needed for elucidating the mechanism of the observed phenomenon.

4. CONCLUSION

We have reported that the FE doping in FET structure of LB film composed of [M-(nC_m)$_r$]. As the gate voltage increased, increases in I_{ds} were observed for the FET samples composed of [Ni-($2C_{10}$)$_1$], [Au-($2C_{10}$)$_1$], [Au-($2C_{14}$)$_1$] and [Au-($2C_{18}$)$_1$]. I_{ds}-V_{ds} characteristics of these samples were irreversible. We detected the characteristic behaviors. If the conduction mechanism of samples becomes clear, a new memory device based on [M-(nC_m)$_r$] complexes can be proposed.

5. REFERENCES

[1] "Organic Superconductors", Ed. By T. Ishiguro, K. Yamaji and G Saito, Springer Series in Solid-State Sciences, Springer, Berlin (1977).

[2] Y. F. Miura, Y. Okuma, H. Ohnishi, T. Kawasaki and M. Sugi, *Jpn. J. Appl. Phys.*, 37, L1481-L1483 (1998).

[3]T. Nakamura, K. Kojima, M. Matsumoto, H. Tachibana, M. Tanaka, E. Maeda and Y. Kawabata, *Chem. Lett.*, 367-368 (1988).

[4]Y. F. Miura, M. Horikiri, S. Tajima, T. Wakaita, S. -H. Saito and M. Sugi, *Synth Met.*, **133-134**, 663-664(2003).

[5]H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki and H. Inokuchi, *Mol. Cryst. Liq. Cryst.*, **107**, 33-43 (1984).

[6] P. Delhaes, "Low-Dimensional systems and molecular electronics", Ed. By R. M. Metzger, Plenum Press, New York (1990) pp.43.

[7]G. Roberts, "Langmuir-Blodgett Films", Plenum Press, New York, 1990.

[8]M. R. Bryce and M. C. Petty, *Nature*, **374**, 771-776 (1995).

[9]G. Steimecke, H. J. Sielder, P. Kirmse and E. Hoyer. Phosphorus Sulfur, **7**, 49-55, (1979).

(Received January 16, 2007;Accepted February 17, 2007)