π-Conjugated Poly(1,10-phenanthroline)–$Ru^{II}(bpy)_2$ Complex as an n-Type Active Material for FET

Takakazu Yamamoto,*[1] **Yoshimasa Sakai,**[2]
and Shinji Aramaki[2]

[1]Chemical Resources Laboratory,
Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226-8503

[2]Optoelectronic Materials Laboratory,
Mitsubishi Chemical Corporation,
MCC Group Science and Technology Research Center,
1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502

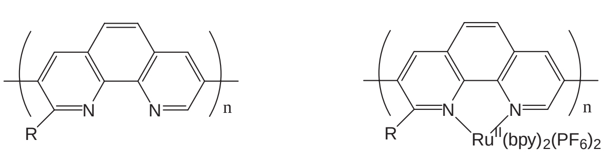
Received December 12, 2005; E-mail: tyamamot@res.titech.ac.jp

$Ru^{II}(bpy)_2$ complexes of poly(2-nonyl-1,10-phenanthroline-3,8-diyl) and poly(1,10-phenanthroline-3,8-diyl) acted as an n-channel in field-effect transistors (FETs), and showed electron mobility of 5.5×10^{-3} and 1.9×10^{-3} $cm^2\,V^{-1}\,s^{-1}$, respectively. Without the Ru^{2+} complexation, the original poly(1,10-phenanthroline-3,8-diyl) did not behave as the n-channel active material, suggesting the enhancement of electron-accepting and electron-conducting properties of the polymer by the metal complexation.

π-Conjugated polymers with electric and optical functionalities have been the subject of recent interest,[1,2] and investigation of field-effect transistors (FET) using the π-conjugated polymers as the active layer is being actively carried out.[3,4] Many π-conjugated polymers behave as a p-type active material in FETs, and examples of π-conjugated polymers working as an n-type active material are still limited.[4]

π-Conjugated polymer ligands constituted of electron-accepting imine (–C=N–) nitrogen-containing heterocyclic units, e.g., poly(1,10-phenanthroline-3,8-diyl)s[5] (Chart 1), may be candidates for the n-type active material in FETs.

When poly(1,10-phenanthroline-3,8-diyl)s form cationic transition-metal complexes, e.g., with $Ru^{II}(bpy)_2$,[5b] the electron-accepting feature of the polymer is considered to be enhanced by the presence of the cationic strongly electron-accepting metal unit. In addition, the coordinated cationic metal is expected to fix the lone-pair electrons at the nitrogen atom, which might cause competitive p-type conduction through formation of a cation radical of nitrogen,[6] and solubility of the rigid rod polymer is considered to increase according to the complex formation. However, the applicability of such cationic metal polymer complexes as the n-type active material in FETs has not been reported to our knowledge.



R = n-C_9H_{19}: pphen(2-Non)[5a]
R = H: pphen[5b]

$Ru^{II}(bpy)_2$ complex

Chart 1.

Herein, we report that the above shown $Ru^{II}(bpy)_2$ complexes of poly(1,10-phenanthroline-3,8-diyl)s actually act as the n-type active material in FETs.

Experimental

Materials. The polymers (pphen(2-Non)[5a] and pphen[5b]) and the 1:1 complex[5b] of the 1,10-phenanthroline unit of pphen with $Ru^{II}(bpy)_2$ were prepared according to the literature. The 1:1 $Ru^{II}(bpy)_2$ complex of the 2-nonyl-1,10-phenanthroline unit of pphen(2-Non) was prepared in a way similar to that applied for the preparation of the pphen–$Ru^{II}(bpy)_2$ complex: pphen(2-Non)-$[Ru(bpy)_2(PF_6)_2]_n$: Anal. Found: C, 47.76; H, 4.18; N, 8.18%. Calcd for $(C_{41}H_{40}F_{12}N_6P_2Ru\cdot1.7H_2O)_n$ or $(C_{21}H_{24}N_2\text{–}[Ru(bpy)_2](PF_6)_2\cdot1.7H_2O)_n$: C, 47.42; H, 4.21; N, 8.09%. n-Doped Si wafers (substrates) were purchased from Komatsu Silicon Corp.

FET. The FET device was fabricated by the following procedure.[4,7,8] The n-doped Si substrate having an oxide layer of 300 nm with capacitance per unit area of $11.5\,nF\,cm^{-2}$ was used as the gate of the FET. Two types of FET devices with and without trimethylsilyl functionalization were used. Trimethylsilyl functionalization of the Si/SiO_2 surface was carried out by exposing the Si wafer to hexamethyldisilazane (HMDS) vapor in a closed container overnight. An NMP solution of the pphen(2-Non)-$[Ru^{II}(bpy)_2(PF_6)_2]_n$ complex was passed through a 0.2 µm filter, and the filtrate was spread over the Si substrate by spin-coating to give a spin-coated film of the pphen(2-Non)$[Ru^{II}(bpy)_2(PF_6)_2]_n$ complex with a thickness of 100 nm. After drying for 72 h under 10^{-5} Torr, aluminum was vacuum evaporated through a shadow mask on the polymer layer at 10^{-6} Torr by using ULVAC EX-400 to give source and drain electrodes with a thickness of 1000 Å. The spin-coated film of the pphen$[Ru^{II}(bpy)_2(PF_6)_2]_n$ complex was prepared analogously. A pphen film was prepared by spin-coating using a CF_3COOH solution of pphen and dried analogously. For the top contact geometry, the source and drain electrodes had a channel width (W) of 1000 µm and a channel length (L) of 50 µm. Current–voltage characteristics were obtained with an Agilent 4155 C semiconductor parameter analyzer. To avoid the effects of ionic conduction on electric current, electric current at each data point was measured at a time longer (1.0 s) than usual (200 µs)[8] after setting the source–drain voltage, V_{SD}. The FET data were obtained at two measuring modes by increasing V_{SD} and by decreasing V_{SD}. The FET data were measured under the flow of nitrogen and under air.

Results and Discussion

The top-contact FET devices using the pphen(2-Non)$[Ru^{II}(bpy)_2]_n$ complex were fabricated on n-doped Si/SiO_2 substrates by the spin-coating technique. Details of the fabrication process are given in the Experimental Section. Figure 1 depicts source–drain current (I_{SD}) versus source–drain voltage (V_{SD}) plots of the pphen(2-Non)$[Ru^{II}(bpy)_2]_n$ complex-based FET with Al source- and drain-electrodes at different gate voltages (V_G's). Although the I_{SD} vs V_{SD} curve showed some hysteresis, the two curves obtained by increasing V_{SD} and decreasing V_{SD} essentially agreed. Such a small hysteresis is some-

Published on the web June 6, 2006; doi:10.1246/bcsj.79.959

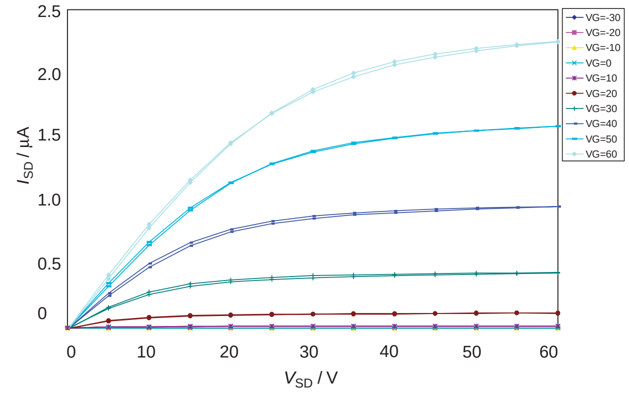


Fig. 1. I_{SD}–V_{SD} curve for the FET prepared using the pphen(2-Non)[Ru^{II}(bpy)$_2$]$_n$ complex (I_{SD} = source–drain current. V_{SD} = source–drain voltage). Channel length (L) = 50 μm. Channel width (W) = 1000 μm. Thickness of the film of the pphen(2-Non)[Ru^{II}(bpy)$_2$]$_n$ complex = 100 nm.

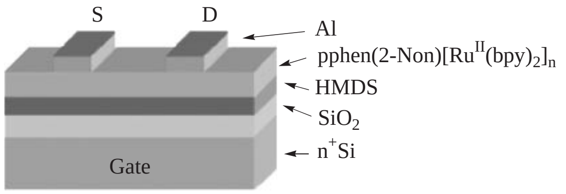


Fig. 2. Schematic structure of the top-contact pphen(2-Non)[Ru^{II}(bpy)$_2$]$_n$ complex-based FET used in the study. HMDS = hexamethyldisilazane.

times observed even with FETs using conventional semiconductors such as silicon. The present FET behaved similarly both under nitrogen and air. In all the I_{SD}–V_{SD} curves, the curve passes at the $I_{SD} = 0$ and $V_{SD} = 0$ point as depicted in Fig. 1. These data support obtaining of normal FET behavior and suggest the existence of only low trap density. Although the off-current at $V_G = 0$ was small, application of some negative voltage (e.g., V_G of -10 V) seemed to be necessary to attain I_{SD} of 0; such a phenomenon is sometimes observed with polymer FETs.

Characteristic transistor behavior was observed under positive biases onto the gate electrode confirming that the fabricated FET had n-channel characteristics. Application of negative V_G did not give a significant I_{SD}, revealing that the polymer complex was not bipolar. At a large V_{SD}, the current I_{SD} tends to saturate and is given by the following:[4,7]

$$I_{SD} = (W/2L)\cdot\mu C_i\cdot(V_G - V_T)^2, \tag{1}$$

where W is the channel width (1000 μm), L is the channel length (50 μm), μ is the FET carrier mobility, C_i is the capacitance per unit area of the SiO$_2$ layer (11.5 nF cm^{-2}), and V_T is the threshold voltage. Figure 2 exhibits the structure of the top-contact pphen(2-Non)[Ru^{II}(bpy)$_2$]$_n$ complex-based FET used in this study.

From Eq. 1, μ and V_T have been calculated from the slope and intercept of the linear part of the $I_{SD}{}^{1/2}$ versus V_G plots (at $V_{SD} = 60$ V) shown in Fig. 3. The μ and V_T thus calculated were 5.5×10^{-3} cm^2 V^{-1} s^{-1} and 6 V, respectively. The on/off ratio was evaluated as 3.3×10^4 from log i-V_G plots.[4,7,8] When the trimethylsilyl functionalization of the Si/SiO$_2$ surface with HMDS was not carried out, I_{SD} became somewhat smaller and the FET gave a smaller electron mobility of 4.2×10^{-3} cm^2 V^{-1} s^{-1}, suggesting that the trimethylsilyl functionalization brought about better contact between the pphen(2-Non)[Ru^{II}(bpy)$_2$]$_n$ complex with the Si/SiO$_2$ substrate. In the case of this FET, an on/off ratio of 150 was obtained. Use of the Ru^{II}(bpy)$_2$ complex of pphen also showed a similar n-channel behavior with a mobility of 1.9×10^{-3} cm^2 V^{-1} s^{-1} and an on/off ratio of 104. The data shown in Fig. 1 were obtained under N$_2$, and the FET also worked under air.

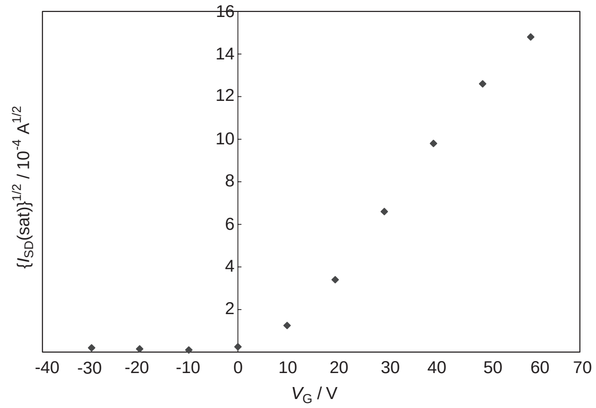


Fig. 3. Plots of $\{I_{SD}(\mathrm{sat})\}^{1/2}$ vs V_G. The plots are based on the data shown in Fig. 1.

Although the pphen(2-Non)[Ru^{II}(bpy)$_2$]$_n$ and pphen[Ru^{II}(bpy)$_2$]$_n$ complexes-based FETs gave the n-channel response, pphen itself did not respond to V_G in a range of $V_G = -30$ through 60 V (cf. the Supporting Information); this may have been due to difficulty in generating the carrier species in the polymer by the V_G, difficulty in pphen forming good contact with the SiO$_2$ gate layer and/or the aluminum electrode, or difficulty to form a well-organized structure within the channel area. The obtained results reveal the importance of the metal complexation of the 1,10-phenanthroline polymers for good FET performance.

As described above, the poly(1,10-phenanthroline)[Ru^{II}(bpy)$_2$]$_n$ complexes gave a good n-channel in the FET. Because various metal complexes of π-conjugated polymers have recently been reported,[9] the present findings are expected to expand the scope of polymer-based FETs.

Supporting Information

I_{SD}–V_{SD} curves obtained with the pphen-based FET. This material is available free of charge via the Internet at http://www.csj.jp/journals/bcsj/.

References

1 H. S. Nalwa, *Handbook of Organic Conductive Molecules and Polymers*, Wiley, Chichester, **1997**.

2 T. A. Skotheim, R. I. Elsenbaumer, J. R. Reynolds, *Handbook of Conducting Polymers*, 2nd ed., Dekker, New York, **1997**.

3 A. Babel, J. D. Wind, S. A. Jenekhe, *Adv. Funct. Mater.* **2004**, *14*, 891; A. Zen, M. Saphiannikova, D. Neher, U.

Asawapiron, U. Scherf, *Chem. Mater.* **2005**, *17*, 781; L.-L. Chua, P. K. H. Ho, H. Sirringhaus, R. H. Friend, *Adv. Mater.* **2004**, *16*, 1609; H. G. O. Sandberg, T. G. Bucklund, R. Osterbacka, H. Stubb, *Adv. Mater.* **2004**, *16*, 1112; T. Yamamoto, T. Kanbara, C. Mori, H. Wakayama, T. Fukuda, T. Inoue, S. Sasaki, *J. Phys. Chem.* **1996**, *100*, 12631; T. Yamamoto, H. Wakayama, T. Kanbara, K. Sasaki, K. Tsutsui, S. Furukawa, *Denki Kagaku oyobi Kogyo Butsuri Kagaku* **1994**, *62*, 84; *Chem. Abstr.* **1994**, *120*, 179375.

4 L.-L. Chua, J. Zaumsell, J.-F. Chang, E. C.-W. Ou, P. K.-H. Ho, H. Sirringhaus, R. H. Friend, *Nature* **2005**, *434*, 194; A. Babel, S. A. Jenekhe, *J. Phys. Chem. B* **2002**, *106*, 6129; A. Babel, S. A. Jenekhe, *J. Am. Chem. Soc.* **2003**, *125*, 13656.

5 a) T. Yamamoto, K. Anzai, T. Iijima, H. Fukumoto, *Macromolecules* **2004**, *37*, 3064. b) T. Yamamoto, Y. Saito, K. Anzai, H. Fukumoto, T. Yasuda, Y. Fujiwara, B.-K. Choi, K. Kubota, T. Miyamae, *Macromolecules* **2003**, *36*, 6722.

6 S. Doi, Y. Tsubata, M. Ueda, T. Noguchi, T. Ohnishi, *J. Photopolym. Sci. Technol.* **2003**, *16*, 303; T. Fukuda, K. Suruga, K. Ishikawa, H. Takezoe, A. Fukuda, T. Kanbara, T. Yamamoto, *Synth. Met.* **1995**, *74*, 43.

7 G. Horowitz, *Adv. Mater.* **1998**, *10*, 365; Z. Bao, A. Dodabalapur, A. J. Lovinger, *Appl. Phys. Lett.* **1996**, *69*, 4108; C. Videlot, J. Ackermann, P. Blanchard, J. M. Raimundo, P. Frere, M. Allain, R. de Battingnies, E. Levillain, J. Roncali, *Adv. Mater.* **2003**, *15*, 306.

8 T. Yamamoto, H. Kokubo, M. Kobashi, Y. Sakai, *Chem. Mater.* **2004**, *16*, 4616.

9 T. Pautzsch, E. Klemm, *Macromolecules* **2002**, *35*, 1569; Q. Wang, L. Yu, *J. Am. Chem. Soc.* **2000**, *122*, 11806; R. P. Kingsborough, T. M. Swager, *Prog. Inorg. Chem.* **1999**, *48*, 123; T. Yamamoto, T. Maruyama, Z.-H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda, K. Kubota, *J. Am. Chem. Soc.* **1994**, *116*, 4832; T. Yamamoto, Y. Yoneda, T. Maruyama, *J. Chem. Soc., Chem. Commum.* **1992**, 1652.