Organic Thin Film Transistors with Substituted Polyacetylenes Containing a Hetero Atom∗

Tetsuya Imamura  
Department of Electrical and Electronic Engineering, Muroran Institute of Technology,  
27-1 Mizumoto-cho, Muroran, Hokkaido 050-8585, Japan

Yasuteru Mawatari  
Division of Science for Composite Functions, Muroran Institute of Technology,  
27-1 Mizumoto-cho, Muroran, Hokkaido 050-8585, Japan

Hisashi Fukuda†  
Department of Electrical and Electronic Engineering, Muroran Institute of Technology,  
27-1 Mizumoto-cho, Muroran, Hokkaido 050-8585, Japan

Masayoshi Tabata  
Division of Science for Composite Functions, Muroran Institute of Technology,  
27-1 Mizumoto-cho, Muroran, Hokkaido 050-8585, Japan

(Received 9 October 2008; Accepted 6 May 2009; Published 11 July 2009)

Organic thin film transistors (OTFTs) using substituted polyacetylenes which have a helical form were fabricated. Substituted polyacetylenes soluble to various organic solvents were obtained using a rhodium complex as the stereoregular polymerization catalyst of the substituted acetylenes. The polymer thin films were formed by spin coating method. Poly(2-ethynylthiophene) and poly(3-ethynylthiophene) bearing a thiophene ring as the side-chain is operated at p-type semiconductor and the maximum field-effect mobility of the P2ET and P3ET OTFT is estimated at 4.3 × 10⁻³ and 6.7 × 10⁻³ cm²/Vs respectively. [DOI: 10.1380/ejssnt.2009.767]

Keywords: Electrical transport measurement; Metal-semiconductor interfaces; Transistor; Organic thin film; Substituted polyacetylene; Rhodium complex catalyst

I. INTRODUCTION

The research of organic semiconductor materials was started in the 1950’s, and the researchers in the world have interested. In recent years, Dr. Hideki Shirakawa was awarded the Nobel Prize for chemistry in a study of the conductive polyacetylene. A study of organic thin film transistor (OTFT) using polythiophene was started in 1986. In recent years, the field-effect mobility of OTFTs which are close in amorphous silicon and poly silicon has been reported all over the world [1]. OTFTs have been not only interested because of their flexibility, lightness, and shock resistance but also expected as the third semiconductor material following silicon and compound semiconductor [2]. Above all, poly(3-hexylthiophene) (P3HT) is the most popular polymer at present so that we have reported a relationship between the molecular orientations and electrical properties of P3HT OTFT [3–5].

On the other hand, we have shown a new type of the stereoregular polymerization of substituted acetylenes (SA) initiated by a rhodium complex catalyst, [Rh(nbd)Cl]₂ (nbd = norbornadiene). In the substituted polyacetylene (SPA), the chemical and physical properties such as solubility to organic solvent, oxidation stability, and so on can be controlled by molecular design of the monomer structure. In this report, we show syntheses of SPA containing a hetero atom and fabrication of the OTFT using SPA polymers together with their electrical and physical properties.

II. EXPERIMENTAL

We synthesized two kinds of substituted acetylene monomers, i.e., 2-ethynylthiophene (2ET) and 3-ethynylthiophene (3ET). The synthetic routes are shown in Fig. 1.

The 2ET and 3ET monomers were polymerized using the rhodium complex catalyst, [Rh(nbd)Cl]₂(Fig. 2) and triethylamine (NEt₃) as the cocatalyst [6]. Figure 3 shows the polymerization of their monomers. The reaction was stopped using excess amount of methanol, the resulting polymers, i.e., poly(2-ethynylthiophene): (P2ET)

* This paper was presented at International Symposium on Surface Science and Nanotechnology (ISSS-5), Waseda University, Japan, 9-13 November, 2008.
†Corresponding author: fukuda@mmm.muroran-it.ac.jp
FIG. 2: A rhodium complex catalyst, \([\text{Rh(nbd)Cl}]_2\).

FIG. 3: Rhodium-catalyzed polymerization of 2- and 3-ethynylthiophene monomers.

and poly(3-ethynylthiophene); (P3ET) were dried in desiccator under reduced pressure of \(10^{-3}\) Torr at the room temperature.

The OTFT was fabricated as follows: The starting materials were Sb-doped n-type (<0.1 Ω·cm), Czochralski(CZ)-grown 1-inch Si(100) wafers, which were then cut into 1.5 cm×1.5 cm square chips. These chips were rinsed in deionized water, ethyl alcohol, acetone, and methyl alcohol, and were cleaned by a standard RCA method. Then, the samples were treated by dry oxygen ambient at 1100° for 120 min to form 200 nm-thick SiO2 film. After that, Au electrode on SiO2 as a source/drain was formed by vacuum deposition and photolithography methods. Finally, the polymer thin films were prepared by dropping the CH₂Cl₂ solution of the polymers on the spinning substrate. Figure 4 shows the structure of the fabricated OTFT. Figure 5 shows the pattern of source/drain electrode, which defined channel length \(L = 20 \mu m\) and channel width \(W = 20 \mu m\), respectively.

III. RESULTS AND DISCUSSION

A. Polymerization

Rhodium complex catalyst, \([\text{Rh(nbd)Cl}]_2\) is stable in air and the preferred catalyst to selectively yield the corresponding cis-transoid polymers even at room temperature.

Both P2ET and P3ET obtained by the rhodium-catalyzed polymerizations (Fig. 3) were fine powder, the color of P2ET was brown and the color of P3ET was ocher. These polymers were soluble to chloroform, dichloromethane (CH₂Cl₂), tetrahydrofuran (THF), and chlorobenzene. The number average molecular weight: \(M_n\) of polymers was measured with Gel Permeation Chromatography (GPC) using chloroform solvent; \(M_n(\text{P2ET}) = 21200\) and \(M_n(\text{P3ET}) = 9800\). The thin film was prepared by a cast coating method.

B. XRD patterns of powdery polymers

X-Ray Diffraction (XRD) pattern was obtained to estimate the crystallinity of these powdery polymers at room temperature. Figure 6 shows the XRD patterns of the powdery P2ET and P3ET. Based on these XRD patterns and Molecular Mechanics calculation of the similar polymers which were prepared with the rhodium-catalyst these polymers were concluded to have a helical form and were composed of pseudohexagonal structures called \(\pi\)-conjugated columnar (Fig. 7) [8]. Two broad peaks were observed at \(d = 9.73\) Å and 4.59 Å (P2ET), \(d = 10.28\) Å and 4.43 Å (P3ET), respectively. These peaks show (100) diffraction and halo peak, respectively. The diameters of the columnar (P2ET) and
Diameter of columnar (100) (P3ET) calculated from the (100) diffraction peaks were $D = 10.97$ Å (P2ET) and $D = 12.01$ Å (P3ET), respectively.

However, their half peak widths of the (100) diffraction peaks are very wide and halo peak intensities are relatively strong. Therefore, these polymers are assumed to be fairly amorphous having pseudohexagonal structures partially.

### C. XRD patterns of thin films

The XRD patterns of the P2ET and P3ET films were also measured to estimate their crystallinities. Figure 8 shows the XRD patterns of P2ET and P3ET films. The two broad and sharp peaks were observed at $d = 8.61$ Å and 2.73 Å (P2ET), $d = 8.59$ Å and 2.72 Å (P3ET) respectively. These peaks show (100) diffraction and Si substrate peaks. The half peak width of the (100) diffraction peaks was very wide as well as the XRD patterns of the powdery P2ET and P3ET. The halo peak intensities of the films were lower than those of the powder polymers.

The surface morphology of the P2ET and P3ET was investigated using atomic force microscope. The result indicates grain structure with diameter of 0.05 to 0.1 µm and surface roughness of 3.2 to 5.5 nm. Therefore, we may suppose that these films are almost amorphous and polymer chains are parallel to the substrate to some extent.

### D. Current-voltage characteristics of the OTFTs

We measured current-voltage characteristics of the OTFTs. The typical drain voltage ($V_{ds}$) and drain current ($I_d$) characteristics of the OTFTs at negative gate bias were measured, and the field-effect mobility of the OTFTs was calculated. Figures 9 and 10 show the current-voltage characteristics of P2ET OTFT and P3ET OTFT, respectively.

The drain current ($I_d$) was found to be controlled by negative gate bias. Therefore, we suppose that these polymers are considered as a p-type organic semiconductor material and the OTFTs can be operated in the accumulation mode. Gal et al. reported that the P2ET showed n-type behavior after doping iodine, bromine and ferric chloride, respectively [9]. In contrast, we synthesized p-type P2ET without doping materials. The field-effect mobility was calculated using the results of the current-voltage characteristics. The mobility values in the saturation region can be calculated using Eq. (1).
is two order lower than that of P3HT OTFT. However, reproducibility of the OTFT was still low in order to show the typical transistor characteristics. We supposed that noise caused in drain current shown in Figs. 8 and 9 because there was the spatial injection barrier in the interface between the Au electrode and the organic thin film [11].

E. Contact of interface between Au electrode and organic thin film

To evaluate contact of interface between Au electrode and organic thin film, we measured work function of the Au and the ionization potential of organic thin film by using Photo-Electron Spectroscopy in Air (PESA). Figure 11 shows the photoelectron spectrum of the Au film.

Threshold energy of the photoelectron spectrum corresponds to the work function in metal and ionization potential in organic material [12]. From the result of photoelectron spectrum shown in Fig. 12, work function of the Au ($\Phi_M$) is estimated as 5.10 eV, ionization potential of the P2ET film is 5.54 eV and ionization potential of the P3ET film is 5.62 eV. Therefore, we suppose there is energy barrier against the hole corresponding to remaining between work function of the Au and the ionization potential in the interface between the Au electrode and the organic thin film. The hole injection is not performed smoothly because there is energy barrier against the hole so that we suppose gradient of the linear region in the current-voltage characteristics is gradual.

\[
\mu = \frac{2LI_d}{WC(V_g - V_t)^2},
\]

where $C$ is capacitance per unit area of the insulating layer, $V_t$ is the threshold voltage. $C$ is 15.7 nF/cm$^2$, $V_t$ is −4.0V (P2ET OTFT) and $V_t$ is −10.2V (P3ET OTFT). The field-effect mobility value of P2ET is $4.3 \times 10^{-3}$ cm$^2$/Vs and the field-effect mobility value of P3ET is $6.7 \times 10^{-3}$ cm$^2$/Vs with the error of ±1.0 $\times$ 10$^{-3}$ due to gate leakage and drain current fluctuation as shown in Figs. 9 and 10. The threshold voltage derived from subthreshold characteristics deviates owing to the above behavior. The gate leakage may originates from a current transport through defects in the oxide films. In fact, the leakage increases with increasing the vertical electric field and the channel conductance also fluctuates owing to carrier trap behavior via the defects in the oxide.

In the case of the regioregular P3HT, about 0.1 cm$^2$/Vs is reported [10]. Therefore, the mobility of these OTFTs is two order lower than that of P3HT OTFT. However, reproducibility of the OTFT was still low in order to show the typical transistor characteristics. We supposed that noise caused in drain current shown in Figs. 8 and 9 because there was the spatial injection barrier in the interface between the Au electrode and the organic thin film [11].

IV. CONCLUSION

In this report our aim is to apply organic semiconductor material to electronic device. Therefore, we synthesized two kinds of substituted acetylene monomers and polymerized using these monomers. Then, we fabricated the OTFT with the synthesized polymers and estimated their electrical and physical properties.

In the synthesis of polymers, P2ET and P3ET which are soluble to various organic solvent were yielded by rhodium-catalyzed polymerizations. Therefore, we confirmed what these polymers are able to form thin film by a cast coating method.

From the current-voltage characteristics of the OTFTs, the OTFTs are operated at negative gate bias and shows p-channel enhancement behavior. In addition, the field-effect mobility of the P2ET and P3ET OTFT was estimated at $4.3 \times 10^{-3}$ and $6.7 \times 10^{-3}$ cm$^2$/Vs respectively. These values are two order lower than that of the regioregular P3HT OTFT. To improve the output characteristics and the field-effect mobility of the P2ET and P3ET OTFT, we should improve the fabrication process of the OTFT and analyze the basic properties of these polymers. Concretely, the improvement of the fabrication process is the optimization of condition to form thin film and choice of electrode material, and analysis of the basic properties is measurement of energy bandgap and so on.
[1] E. Hasegawa, *Organic Electronics* (Kogyo Chosakai Publishing, Tokyo, 2005).

[2] H. Fukuda, T. Kojima, and K. Uesugi, IEICE Technical Report **106**, 39 (2006).

[3] H. Fukuda, M. Ise, T. Kogure, and N. Takano, Thin Solid Films, **464-465**, 441 (2004).

[4] H. Fukuda, Y. Yamagishi, M. Ise, and N. Takano, Sensors and Actuators B **108**, 414 (2005).

[5] K. Sugiyama, T. Kojima, H. Fukuda, H. Yashiro, T. Matsura, and Y. Shimoyama, Thin Solid Films **516**, 2691 (2008).

[6] M. Nakamura, M. Tabata, T. Sone, Y. Mawatari, and A. Miyasaka, Macromol. Chem. Phys. **35**, 2000 (2002).

[7] M. Tabata and Y. Mawatari, Koubunshi (Polymers) **55**, 938 (2006) (in Japanese).

[8] M. Tabata, T. Sone, Y. Mawatari, D. Yonemoto, A. Miyasaka, T. Fukushima, and Y. Sadahiro, *Electronic and Optical Properties of Conjugated Molecular Systems in Condensed Phases*, S. Hotta (Ed.) (Research Signpost, Kerala, 2003), pp. 99-121.

[9] Y. S. Gal, B. Jung, and S. K. Choi, J. Appl. Polymer Sci. **42**, 1793 (1991).

[10] T. R. Hebner, C. C. Wu, D. March, M. H. Lu, and J. C. Sturm, Appl. Phys. Lett. **72**, 519 (1998).

[11] M. Nakamura, *Evaluation and Application of Organic Transistor Material* (CMC Publishing Co., Ltd, Tokyo, 2005).

[12] C. Adachi, T. Oyamada, and Y. Nakajima, *Data Book on Work Function of Organic Thin Films*, 2nd edition (CMC Publishing Co., Ltd, Tokyo, 2006).

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)