Fabrication and electrical characteristics of organic thin film transistor using π-conjugated dendrimer

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Abstract

We fabricated organic thin film transistors (OTFTs) by using soluble π-conjugated dendrimers of 4(HPBT)-benzene, 4(HPTT)-benzene, and 4(HPDTT)-benzene. Electrical characteristics such as current–voltage characteristic curves and their temperature dependence were measured for the dendrimer-based OTFT devices. The active layer using planar π-conjugated dendrimers was spin-coated, and thermally grown silicon dioxide layer was used as a dielectric layer. Through the measurements of source–drain currents with varying gate voltages, we obtained charge carrier mobility (μ), on/off current ratio (I_{on/off}), and threshold voltage (V_{th}). The 4(HPBT)-benzene and 4(HPTT)-benzene-based OTFT devices showed that the μ’s were \( \sim 6.2 \times 10^{-3} \text{ cm}^2/\text{V s} \) and \( \sim 1.9 \times 10^{-3} \text{ cm}^2/\text{V s} \), respectively. We measured temperature-dependent mobility and activation energy (E_a) of the dendrimer-based OTFTs by using Arrhenius fitting. The E_a’s of 4(HPTT)-benzene and 4(HPDTT)-benzene-based OTFTs were estimated to be \( \sim 0.39 \text{ eV} \) and \( \sim 0.13 \text{ eV} \), respectively. In case of 4(HPBT)-benzene-based OTFT, two trap levels were measured and the E_a’s were estimated to be \( \sim 0.027 \text{ eV} \) and \( \sim 0.22 \text{ eV} \).

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1. Introduction

π-Conjugated organic material-based electronics has been rapidly grown in the past decade. The organic molecules and polymers have advantages for the applications to optoelectronics, because of large area coverage, structural flexibility, and low-temperature and low-cost processing. Organic light-emitting diodes (OLEDs) have been already commercialized, and organic photovoltaic cells for low-cost solar energy generation have been actively studied [1–3]. Organic thin film transistors (OTFTs) using π-conjugated molecules and polymers have been recently studied for the use of electric drivers of flat panel displays.

The charge carrier mobility for OTFTs was reported to be \( \sim 1.5 \text{ cm}^2/\text{V s} \) in the case of vacuum-deposited pentacene molecules [4], and \( \sim 0.1 \text{ cm}^2/\text{V s} \) for spin-coated poly(3-hexylthiophene) [5]. The structure of π-conjugated organic materials used for OTFTs had been limited in linear shape as pentacene molecule. Most recently, a few reports have been focused on star-shaped organic molecules, so called dendrimers [6–8]. π-Conjugated organic dendrimers can be adopted to fabricate the OTFTs, because of their solubility. Ponomarenko et al. reported that three-armed conjugated dendrimer-based OTFTs had a charge carrier mobility of \( \sim 2 \times 10^{-4} \text{ cm}^2/\text{V s} \) [7]. In general, the charge carrier mobility of the OTFTs using soluble organic materials as an active layer is lower than that using vacuum-deposited organic molecules, because of poor molecular ordering. However, the solution process using soluble organic materials can introduce to easy patterning and low-temperature processing.

In this paper, we report on the fabrication and electrical characteristics of OTFTs using soluble four-armed conjugated dendrimers with a planar star shape. The OTFT devices using 4(HPBT)-benzene as an active layer showed a charge carrier mobility as high as \( \sim 6.2 \times 10^{-3} \text{ cm}^2/\text{V s} \). From temperature-dependence of the mobility, the activation energy of 4(HPTT)-benzene and 4(HPDTT)-benzene was estimated to be \( \sim 0.39 \text{ eV} \) and \( \sim 0.13 \text{ eV} \), respectively. Especially for the 4(HPBT)-benzene-based OTFT, two activation energies were estimated to be \( \sim 0.027 \text{ eV} \) and \( \sim 0.22 \text{ eV} \).
2. Experiment

We synthesized four-armed crystalline dendrimers containing 5′-hexyl-[2,2′]-bithiophenyl-5-carbaldehyde prepared by Vilsmeier reaction of 5-hexyl-[2,2′]-bithiophenyl. 5-Hexyl-5′-vinyl-[2,2′]-bithiophenyl was synthesized by the Wittig reaction between 5′-hexyl-[2,2′]-bithiophenyl-5-carbaldehyde and methyltriphenylphosphonium iodide. Same methods were utilized for synthesizing the intermediates for 4(HPTT)-benzene and 4(HPDTT)-benzene. Three dendrimers were synthesized by a Pd(0)-catalyzed Heck coupling reaction of the 1,2,4,5-tetrabromo-benzene and the 5-hexyl-5-propenyl-[2,2′]-bithiophenyl [4(HPBT)-benzene], 2-hexyl-5-propenyl-thieno[3,2-b]thiophene [4(HPTT)-benzene] or 6-hexyl-2-propenyl-dithieno[3,2-b;2′,3′-d]thiophene [4(HPDTT)-benzene] peripheral group in a yield of 30–40%. The chemical structures of the dendrimers are shown in Fig. 1 (a)–(c). The core parts of the dendrimers exhibit two-dimensional planar geometry. The organic thin film transistors (OTFTs) using these three dendrimers, 4(HPBT)-benzene, 4(HPTT)-benzene, and 4(HPDTT)-benzene, were fabricated. Highly doped p-type Si wafer and thermally grown SiO_2 layer were used as a gate electrode and dielectric layer, respectively. The thickness and dielectric constant (\(\varepsilon_r\)) of the SiO_2 layer were \(\sim 200\) nm and \(\sim 3.9\), respectively. Using conventional lithography, gold (Au) source and drain electrodes were patterned with the length and width on the active region as 5 \(\mu\)m and 1500 \(\mu\)m, respectively. The dendrimers dissolved in chlorobenzene solvent were spin-coated at 1000–1500 rpm for 5 min, and annealed at 140–150°C for 30 min, for the formation of active layer. The schematic diagram of the OTFT device fabricated in the study is shown in Fig. 1(d).

The current–voltage (\(I–V\)) characteristics of the four-armed dendrimer-based OTFTs were measured under vacuum condition below \(10^{-3}\) Torr by using a Keithley 237 SMU. The wire bonder (Kunche & Sona 4524) was used for electrical contact from Au electrodes to a chip carrier for the OTFTs. The CTI-Cryogenic cryostat system was used to measure temperature dependence of the \(I–V\) characteristics for the dendrimer-based OTFTs.

3. Results and discussion

Fig. 2(a)–(c) shows typical source–drain current (\(I_{ds}\)) characteristic curves with various gate voltages (\(V_g\)’s) for the dendrimer-based OTFTs. As the \(V_g\) negatively increased, the \(I_{ds}\) negatively increased for all OTFT devices, implying p-type characteristics. The 4(HPBT)-benzene-based OTFTs have the \(I_{ds}–V_d\) curves with a decay of the current in the saturation region as shown in Fig. 2(a), which implies trapping of free holes during the measurements [9]. That is, 4(HPBT)-benzene-based OTFTs had more traps compared with 4(HPTT) or 4(HPDTT)-benzene-based devices.

Fig. 3(a) shows \(-I_{ds}\) characteristics as a function of \(V_g\) for the OTFT devices using 4(HPBT)-benzene. The on/off current ratio (\(I_{on/off}\)) and threshold voltage (\(-V_{th}\)) were ~10^3 and ~30 V, respectively. For the 4(HPTT)-benzene and 4(HPDTT)-benzene-based OTFTs, \(I_{on/off}\) and \(-V_{th}\) were \(10^2–10^3\) and <5 V, respectively, as shown in Fig. 3(b) and (c). The charge carrier mobility \(\mu\) of the OTFT can be estimated by using the following equation in the saturation region of current:

\[
I_{ds} = \frac{W \mu C_d}{2L} (V_g - V_{th})^2.
\]

where \(W\) is the channel width, \(L\) the channel length, \(\mu\) the charge carrier mobility, and \(C_d\) is the capacitance per unit area of the dielectric layer. The \(\mu\) was \(\sim 6.2 \times 10^{-3}\) cm²/V s calcu-
lated from the slope of the plot of \((-I_{ds})^{1/2}\) versus \(-V_g\) for the OTFT using 4(HPBT)-benzene, as shown in Fig. 3(a). The \(\mu\)'s of 4(HPTT)-benzene and 4(HPDTT)-benzene-based OTFTs were estimated to be \(\sim 1.9 \times 10^{-3}\) cm\(^2\)/V s and \(\sim 2.2 \times 10^{-4}\) cm\(^2\)/V s, respectively. The important factor of determining on/off current ratio and charge carrier mobility of the devices is chemical structure related to \(\pi\)-conjugation length of active organic molecules. Because \(\pi\)-conjugation paths of four-armed dendrimers were well-formed and core parts of the dendrimers exhibited two-dimensional planar geometry, the charge carrier mobility of the devices was relatively higher than that of the previous report using soluble dendrimers bearing three conjugated arms [7]. The slight differences of the charge carrier mobility and on/off current ratio of the devices might originate from different planar structure, \(\pi\)-conjugation length, band gap, and solubility.

The charge carrier mobility \(\mu\) of an OTFT can vary with temperature. The variation of the \(\mu\) as a function of temperature can be occurred when the injected charges from the electrodes to \(\pi\)-conjugated molecules are captured by the shallow or deep traps, and they can be thermally activated. Temperature dependence of the \(\mu\) is described by the multitrap and release (MTR) model as follows:

\[
\mu = \mu_0 \exp \left( -\frac{E_a}{k_B T} \right).
\]  

(2)

Here \(\mu_0\) is the free carrier mobility, \(E_a\) the activation energy to escape from trap states to delocalized states, and \(k_B\) is the Boltzmann constant [9–11]. Fig. 4(a) and (b) shows temperature dependence of the \(\mu\) of the 4(HPTT)-benzene, 4(HPDTT)-benzene, and 4(HPBT)-benzene-based OTFTs in the saturation region of the \(I-V\) characteristic curves, based upon the Arrhenius relation. The \(\mu\)'s of OTFT devices decreased as temperature decreased from 300 K to 100 K, implying the localization of charges due to the traps. The temperature dependence of the \(\mu\) was fitted to the MTR model, as shown in Fig. 4(a) and (b). Using the slope of the plot of \(\mu\) versus 1000/T, we estimated the value of \(E_a\). For the OTFT using 4(HPTT)-benzene and 4(HPDTT)-benzene, the \(E_a\)'s were \(-0.39\) eV and \(-0.13\) eV, respectively. The higher value of the \(E_a\) of 4(HPTT)-benzene-based OTFT devices implies that the OTFT devices using 4(HPTT)-benzene have more and/or deeper trap states than that using 4(HPDTT)-
benzene. In case of the 4(HPBT)-benzene-based OTFT, two slopes were measured, as shown in Fig. 4(b), implying two trap levels. The $E_a$'s of shallow and deep traps were estimated to be $\sim 0.027$ eV and $\sim 0.22$ eV, respectively. Unlike structure of 4(HPTT) or 4(HPDTT)-benzene, the area of core part of 4(HPBT)-benzene having planar geometry is relatively small and the outer thiophene rings are tilted with core part as shown in Fig. 1(a)–(c). It could be explained that the tilted structure of the 4(HPBT)-benzene molecules caused the shallow traps.

4. Conclusion

Soluble $\pi$-conjugated dendrimers have been used for the fabrication of organic thin film transistors. Four-armed dendrimers such as 4(HPBT)-benzene, 4(HPTT)-benzene, and 4(HPDTT)-benzene with a planar structure were spin-coated as an active layer. Through the measurements of source–drain current with varying gate voltages, we obtained that the on/off current ratios and threshold voltages were measured to be $10^2$–$10^3$ and 5–30 V, respectively. The charge carrier mobilities of OTFT devices using 4(HPBT)-benzene, 4(HPTT)-benzene, and 4(HPDTT)-benzene as an active layer were measured to be $\sim 6.2 \times 10^{-3}$ cm$^2$/V s, $\sim 1.9 \times 10^{-3}$ cm$^2$/V s, and $\sim 2.2 \times 10^{-4}$ cm$^2$/V s, respectively. From the temperature-dependent mobility and the MTR model, we estimated that the activation energies of 4(HPTT)-benzene and 4(HPDTT)-benzene-based OTFTs were $\sim 0.39$ eV and $\sim 0.13$ eV, respectively, in the saturation region. The higher activation energy of the 4(HPTT)-benzene-based OTFTs represents the existence of the deeper trap sites to resist charge transport. For the 4(HPBT)-benzene-based OTFTs, the activation energies were $\sim 0.027$ eV and $\sim 0.22$ eV, shallow and deep traps, respectively.

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References