Fabrication and Characterization of an OTFT-Based Biosensor Using a Biotinylated F8T2 Polymer

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Solution-processable organic semiconductors have been investigated not only for flexible and large-area electronics but also in the field of biotechnology. In this paper, we report the design and fabrication of biosensors based on completely organic thin-film transistors (OTFTs). The active material of the OTFTs is poly(9,9-dioctylfluorene-co-bithiophene) (F8T2) polymer functionalized with biotin hydrazide. The relationship between the chemoresistive change and the binding of avidin-biotin moieties in the polymer is observed in the output and on/off characteristics of the OTFTs. The exposure of the OTFTs to avidin causes a lowering of ID at V_D = -40 V and V_G = -40 V of nearly five orders of magnitude.

Keywords: Organic semiconductor, OTFTs, polymer, F8T2, avidin, biotin, biosensor.

I. Introduction

Recently, organic semiconductors have received considerable attention due to their potential application in not only optoelectronic devices such as organic light-emitting diodes (OLEDs), organic thin-film transistors (OTFTs) [1], and photovoltaic devices, but also in the field of biotechnology [2]-[6]. Organic electronic devices have several advantages over conventional inorganic electronics including integration on both rigid and flexible substrates, ease of fabrication, and low-cost processing [7], [8]. Biosensors utilizing biomolecular interactions are widely used in biomedical diagnosis and environmental monitoring, and the majority of these interactions are based on measurement of changes in electrical or optical properties through antigen-antibody reactions [9]-[12]. To date, laboratory tools such as surface plasmon resonance (SPR) sensors have been developed extensively to study the processes of biological binding or adsorption; however, the commercialization of these tools has been limited to the fields of environmental monitoring, point of care (POC) diagnosis, and food safety testing [13]. The additional processes for the commercialization of ubiquitous biosensors require the devices to have a higher sensitivity, lower price, and smaller size with faster and easier measuring procedures. Because existing laboratory tools cannot suitably meet these requirements in terms of reducing the test reagents consumed and shortening experimental procedures, we propose a new biosensor with an organic semiconductor, leading to the realization of a simplified sensing system. This is essentially based on measuring changes in conductivity due to the binding of biomolecules. For this purpose, we synthesized an organic semiconducting copolymer composed of biotinylated fluorene

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and bithiophene though a palladium (0)-mediated Suzuki coupling polymerization [14], [15]. Organic thin film transistors were fabricated using the polymer as a p-type channel material. To test the device as a biosensor, the device characteristics were investigated in the presence of avidin antigen. The chemical structures and synthetic routes of the monomer and polymer are shown in Fig. 1(a) schemes 1 and 2.

II. Experimental Methods

The 9-position of 2, 7-dibromofluorene was alkylated with an *n*-hexylbromide and a 2-(2-bromoethoxy)tetrahydro-2H-pyran, and then 2, 7-positions of the molecule were borated with 2-isopropoxy-4, 4, 5, 5-tetramethyl-1,3,2-dioxaborolane. 10 mol% of hydropyranated fluorene diboronic ester, 40 mol% of dihexylfluorene diboronic ester, and 50 mol% of 5, 5'-dibromo-[2, 2']bithiophenyl were polymerized in presence of a palladium (0) catalyst. The end groups were capped with 2-bromothiophene. The hydropyrane groups in the precursor polymer were deprotected, and then biotin was introduced in the polymer side group by forming ester bonds. Each molecule and polymer was identified by ^{1}H-NMR, ^{13}C-NMR, FT-IR, elemental analysis, UV-visible absorption, and photoluminescence measurements. The synthetic details, identification results, and thermal and optical properties of the monomer and polymers will be reported in a separate paper.

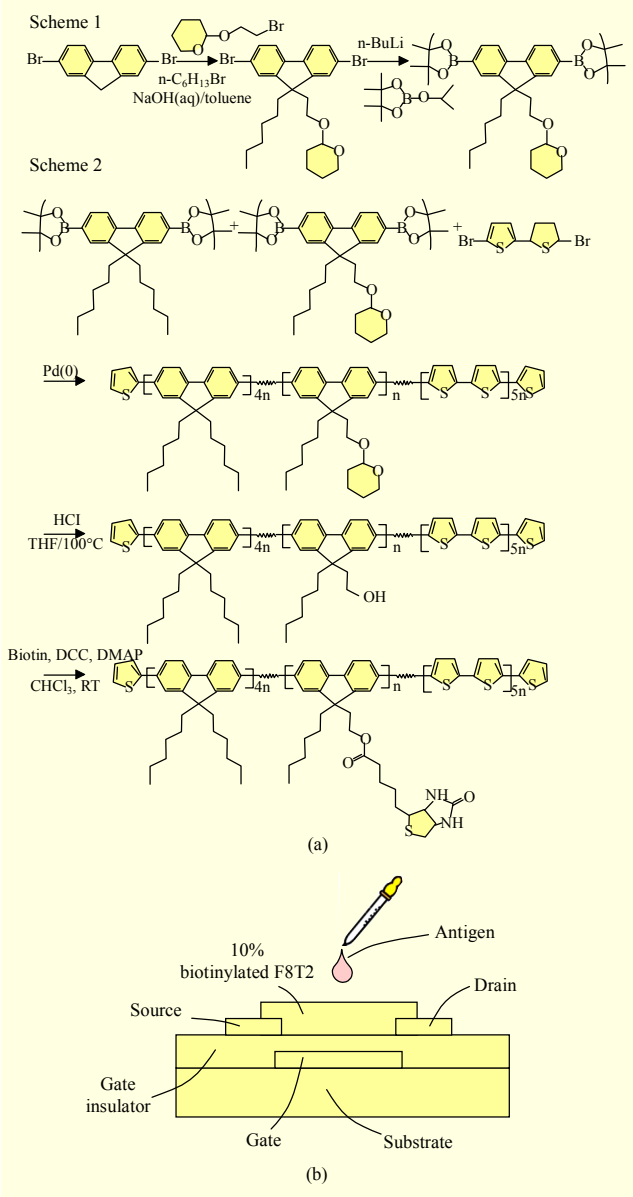

Fig. 1. (a) Synthetic of monomer and polymer schemes of a biotinylated F8T2 polymer and (b) schematic layout of a photolithographically defined bottom-gate OTFT structure.

A heavily doped Si-wafer (resistivity 5 Ωcm to 10 Ωcm) was used as a substrate. For the gate dielectric layer for all the devices, a 300 nm thick SiO_2 layer was thermally grown (capacitance per unit area C_0 = 10 nF/cm^2). Gate and source-drain electrodes were fabricated by means of a lift-off process. OTFT devices were fabricated in the bottom contact geometry. The source and drain electrodes, which consisted of a 10-nm thick Cr layer and an 80-nm thick Au layer were deposited by an e-beam evaporator apparatus. The source-drain width and length are 100 μm and 10 μm, respectively.

The synthesized biotinylated F8T2 polymer was dissolved in xylene, and a thin film was prepared on bottom-gated substrates using a conventional spin-coating method. After spin coating at 1,500 rpm for 30 s, the films were dried and subsequently annealed on a hot plate under N_2 gas in order to create a dense structure. The final annealing conditions were in a temperature range between 150°C and 280°C for 1 h. The thickness of the films was approximately 1,500 Å. A simplified cross-sectional diagram of a photolithographically defined bottom-gate OTFT is shown in Fig. 1(b).

To investigate the antigen-antibody reaction between avidin and biotin, two types of buffer solutions were prepared using avidin (Aldrich) and bovine-serium-albumin (BSA, Aldrich). After exposure to the buffer solutions for 1 min, the working areas of the OTFTs were rinsed several times with distilled water and allowed to dry under argon. The morphology and thickness of the films were observed using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

All of the electric measurements were carried out in a shielded container. The source electrode was grounded, and a DC voltage was then applied to the drain and gate electrodes, which were connected to external voltage sources.

The electric properties of the biotinylated F8T2 OTFTs before and after exposure to the solutions containing the antigen were measured at room temperature using a Hewlett-Packard 4145B semiconductor parameter analyzer.

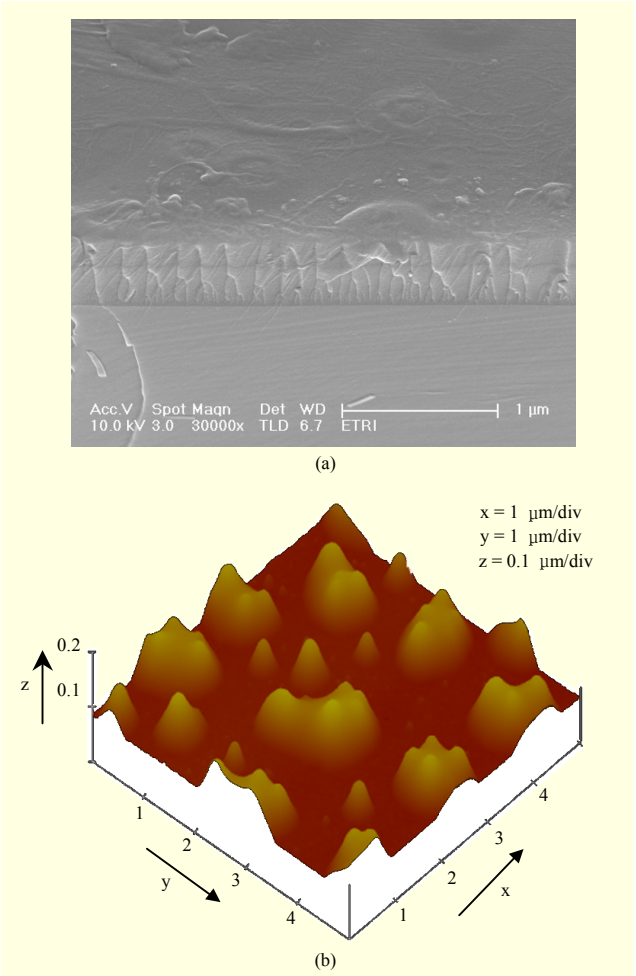

Fig. 2. (a) SEM and (b) AFM images of a biotinylated F8T2 polymer film coated onto an SiO_2/Si substrate.

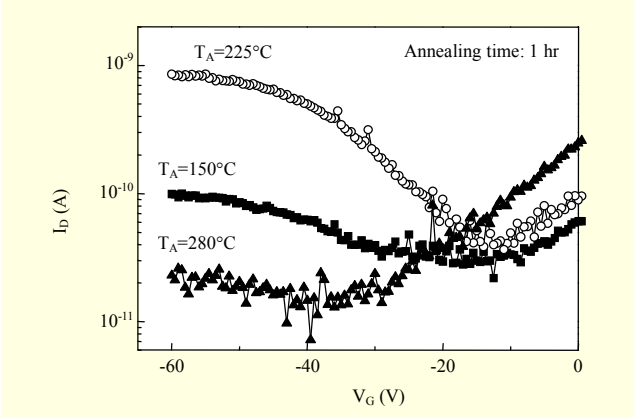

Fig. 3. Plot of drain current I_D versus gate voltage V_G at a drain voltage V_D of -60 V for biotinylated F8T2 OTFTs annealed within a temperature range of 150°C to 280°C.

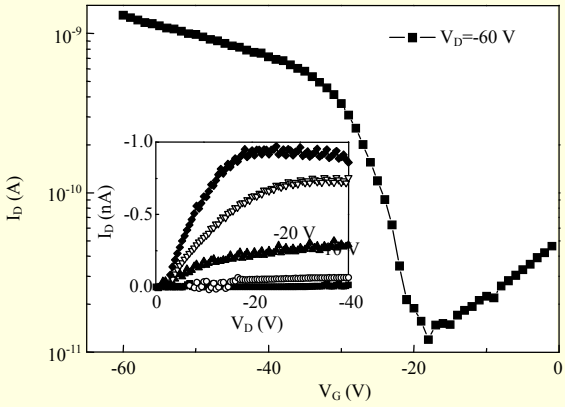

Fig. 4. Typical plot of drain current I_D versus gate voltage V_G at a drain voltage V_D of -60 V for biotinylated F8T2 OTFTs. Inset shows the I_D-V_D characteristics at various V_G between 0 and -40 V.

III. Results and Discussion

A cross section-view SEM image of a biotinylated F8T2 polymer film coating on an SiO_2/Si substrate is shown in Fig. 2(a). This image represents the surface after the final annealing process at 225°C for 1 h. The polymer film annealed below 150°C revealed a very poor surface morphology (not shown). As the annealing temperature increased, the number and density of the surface features decreased, and the smoothness of the surface improved. This result might indicate that an annealing temperature above 150°C is suitable for making a dense sample from a material comprised of both solvent and F8T2. From the cross-sectional SEM image, the thicknesses of the films were calculated to be approximately 4,300 Å. An AFM image of a biotinylated F8T2 polymer is shown in Fig. 2(b). This image represents the surface after the final annealing process at 225°C for 1 h. The image was captured over an area of 5 μm × 5 μm in non-contact mode at a scanning frequency of 0.5 Hz. The root-mean-square (RMS) roughness of this film was measured as approximately 21 nm. Compared to the samples annealed at higher temperatures, the surface morphology was only slightly changed, showing an RMS roughness of less than 20 nm.

Figure 3 shows a plot of drain current I_D versus gate voltage V_G at a drain voltage V_D of -60 V for biotinylated F8T2 OTFTs annealed within a temperature range between 150°C and 280°C. The length and width of the channel were 10 μm and 100 μm, respectively. From the dependence of the drain current I_D on the annealing temperature, the best electric property of an OTFT transistor was obtained. The I_D-V_G characteristics at T_A = 150°C show that the crystallization of the OTFTs did not seem to progress favorably, while at T_A = 280°C, the polymer seemed to be damaged thermally.

Figure 4 shows a typical plot of the drain current I_D versus the gate voltage V_G at a drain voltage V_D of -60 V for biotinylated F8T2 OTFTs fabricated with a channel length of

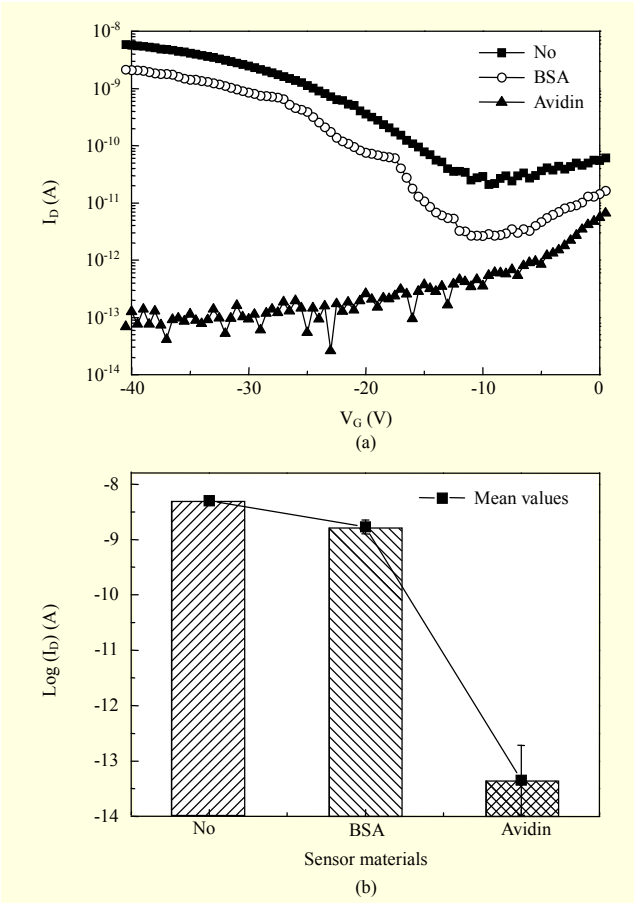

Fig. 5. (a) I_D-V_G characteristics of biotinylated F8T2 OTFTs before and after exposure to antigen containing solutions and (b) mean value and error bar of the I_D results at V_D = -40 V, V_G = -40 V obtained from ten independent measurements.

10 μm, channel width of 100 μm, and SiO_2 gate dielectric thickness of 300 nm. When the gate electrode was biased negatively with respect to the grounded source electrode, the OTFTs operated in accumulation mode, and the accumulated charges were holes. The inset of Fig. 4 shows the I_D-V_D characteristics at various values of V_G. The field-effect mobility and on/off ratio were approximately 2×10^{-4} $cm^2/V \cdot s$ and 10^2, respectively.

To investigate the performance of a biosensor fabricated using the biotinylated F8T2 OTFTs, a sample annealed at T_A = 225°C was used. Figure 5(a) shows the drain current I_D versus the gate voltage V_G curves of samples measured before and after exposure to the antigen-containing solutions. The preparation of the exposed samples proceeded by incubation in the solution for 10 min, which was followed by rinsing and drying. The avidin and reference solutions had concentrations of 8×10^{-10} mol of avidin and 6×10^{-10} mol of BSA in 1 cm^3 of aqueous buffer, respectively. The BSA solution was applied to confirm that the avidin was indeed interacting specifically with the biotin moieties in the biotinylated F8T2 polymer. While the exposure of the samples to BSA caused a very small change in the drain current and conductivity, the exposure of the samples to avidin caused a lowering of the drain current at V_D = -40 V and V_G = -40 V of nearly five orders of magnitude. Figure 5(b) shows the mean value and error bar of the I_D results at V_D = -40 V and V_G = -40 V as obtained from ten independent measurements. These results are applicable to the biosensor fabrication of OTFTs.

IV. Conclusion

This study investigated the electric and chemoresistive properties of biotinylated F8T2 OTFTs through the use of I_D-V_D and I_D-V_G measurements. To create a dense structure and find the optimum condition of the electric property, the OTFTs were annealed at various temperatures for 1 h under N_2 gas. In the I_D-V_G curves of OTFTs measured after exposure to the avidin-containing solution in comparison with a BSA-containing solution, lowering of the drain current was observed to be approximately five orders of magnitude, at V_D = -40 V and V_G = -40 V.

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