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Electrostatic high-density carrier doping into conjugated polymer semiconductors aligned by Langmuir-Blodgett methods

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Abstract

In this study, we investigate the electrostatic carrier doping into highly crystalline conjugated polymers. Generally, charge carriers in conjugated polymers are generated by chemical doping in which redox reactions and charge transfer occur between donor and acceptor molecules. In the chemical doping process, whole system including donor and acceptor molecules are reorganized, resulting in structural disorder and charge carrier localization[1]. In the present study, we demonstrate the electrostatic doping with electric double-layer transistor using conjugated polymer thin film fabricated by Langmuir-Blodgett methods.

1. Introduction of authors

Naotaka Kasuya: His specialized filed is solid states physics of small molecule semiconductors. In this study, he is responsible for fabricating electric double-layer transistor and investigation of all electrical measurements.

Masato Ito: His specialized filed is developments of fabrication process for polymer thin films. In this study, he is responsible for fabricating Langmuir-Blodgett thin film and investigation of crystallinity of the thin films.

2. Research background

A polymer semiconductor is an electronic material with a π-conjugated main chain. The structure is basically amorphous. However, polythiophene-based polymer semiconductors have a π-stack structure in which adjacent π-conjugated planes overlap, resulting in a highly crystalline region[2]. Recently, the Langmuir-Blodgett method (LB method), in which polymers are expanded on a liquid and external pressure is applied to promote self-assembly of the π-conjugated planes, makes it possible to fabricate highly oriented films with large crystalline regions[3]. It is reported that these aligned films have higher carrier mobility and electrical conductivity than amorphous films fabricated by the conventional spin-coating method because the band transport of carriers is dominated in the large crystalline regions created by the LB method[4].

Pi-conjugated polymer semiconductors are intrinsic semiconductors. Therefore, carrier doping is important to exhibit conductivity. Conventionally, carrier doping of polymer semiconductors is performed by introducing donor/acceptor molecules into the system and causing charge transfer through redox reactions. This is called chemical doping. In the chemical doping process, whole system including donor and acceptor molecules are reorganized, resulting in structural disorder and charge carrier localization[1]. Recently, electrostatic high-density carrier doping using an electric double-layer transistor has been developed for small molecule semiconductors that have the same problem of inducing structural disorder due to chemical doping as polymer semiconductors[5].

Here, we demonstrate electrostatic carrier doping using an electric double layer transistor on highly oriented polymer semiconductor film with crystalline regions fabricated by the LB method.

3. Methods

3-1. Fabrication of Langmuir-Blodgett thin film

In this work, we focus on the LB thin film of the well-studied thiophene-based conjugated polymer poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] (PBTTT-C14, Fig. 1(a)). It is reported that the orientation of conjugated main chain of PBTTT-C14 is promoted by alignment process in which PBTTT-C14 is in the liquid crystal states at more than 80 degC[3]. Therefore, in our work, thin film fabrication of PBTTT-C14 was performed on the surface of ionic liquid [EMIM][TFSI] heated to 140 degC. The solution of *o*-dichlorobenzene with 0.05 wt.% PBTTT-C14 was dropped and spread on the surface of heated ionic liquid. In 5 minutes for spreading the solution and evaporation of *o*-dichlorobenzene, compression of the polymer on the ionic liquid by using mechanical barriers was performed at a speed of 5 mm/min for orientation of the polymer (Fig. 1(b)). By the compression process, the area of thin film decreased and finally got 25% of the initial area. To prevent the deterioration of the polymer crystallinity due to rapid cooling after the compression process, aligned thin film on the ionic liquid was cooled down gradually and then transferred onto glass substrates at room temperature.

Figures 1(c) and (d) show the polarized optical microscopy images of LB thin film of PBTTT-C14. Switching between light and dark corresponding to direction of the polarizer and the orientation direction of thin film is observed, indicating that PBTTT-C14 thin film fabricated by LB methods has highly orientation and crystalline area along single direction. According to atomic force microscopy (AFM), the thickness of the LB thin film is 13 nm, corresponding to 5-6 molecular layer (Fig. 1(f)).

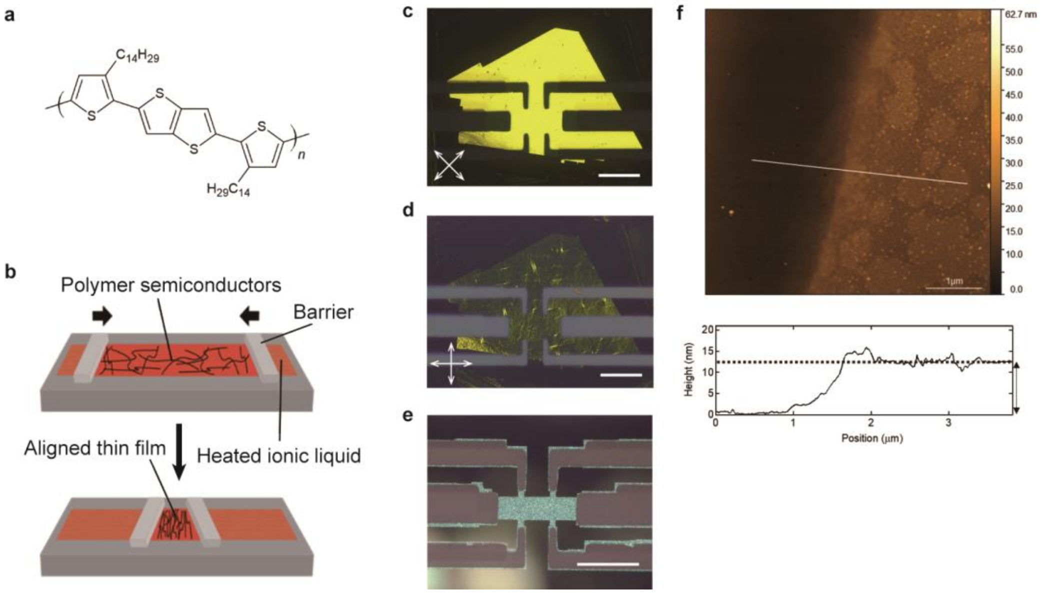

Figure 1. (a) The chemical structure of PBTTT-C14. (b) The schematic illustration of Langmuir-Blodgett method. (c) and (d) POM images of aligned PBTTT thin film. (e)POM image of spin-coated PBTTT thin film. The length of scale bar is 200 μm. (f) AFM image of aligned PBTTT thin film.

In this work, spin-coating thin film of PBTTT-C14, which is basically amorphous, was prepared to compare the transport properties between amorphous and highly crystalline thin films when carrier doping with EDLT is performed for them (Fig. 1(e)).

Figures. 2 (a) and (b) show the two-dimensional wide angle X-ray scattering (2DWAX) images of LB thin film of PBTTT-C14 to investigate the crystallinity of the thin film. The signal peaks (*h*00) derived from lamellar structure is observed along the direction perpendicular to the substrates (corresponding to q_z), and the peak 1.7 Å^{-1} derived from π-π stacking structure are observed along the direction parallel to the substrates (corresponding to q_{xy}), which indicate thiophene-based main chain construct edge-on structure (Fig. 2(c)). Furthermore, the peaks due to π-π stacking structure is observed only when incident direction of X-rays is parallel to the direction of barriers used in the LB methods and the peaks of π-π stacking structure is disappeared when X-rays is perpendicular to the direction of barriers. It indicates that LB thin film of PBTTT-C14 is aligned along the direction parallel to mechanical barriers.

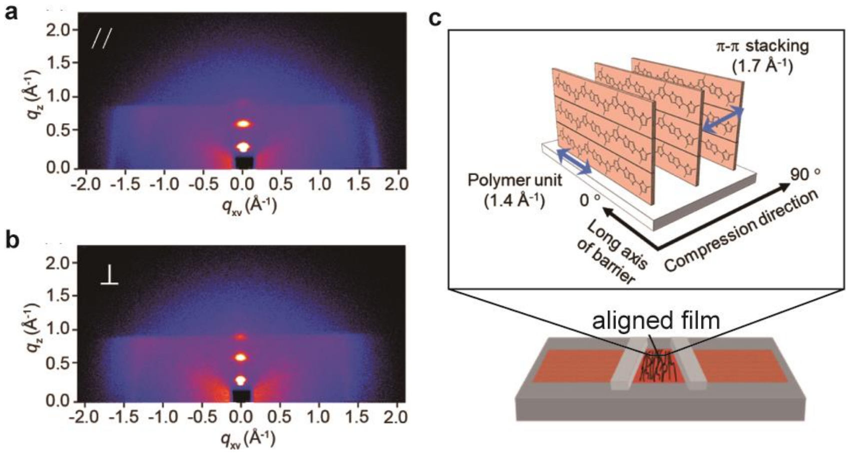

Figure 2. 2DGIWAX images of aligned PBTTT thin film along directions (a)parallel and (b) perpendicular to the long axis of the barrier. (c)schematic illustration of the edge-on lamellar structure and main chain alignment. [ref. 3]

3-2. Fabrication of EDLT

Au electrodes for source, drain, side-gate, and voltage probes were deposited on LB thin film via vacuum deposition. After making electrodes, the LB thin film was shaped into Hall-bar with YAG laser (wavelength is 266 nm). The samples were annealed at 180 degC in the Ar atmosphere for 30 minutes and then cooled down to room temperature gradually. The samples were set on the sample holder for electrical measurements and wired with Au wire. After wiring, the almost all area of a sample except for semiconductor channel and side-gate electrode was covered by fluorinated polymer CYTOP (AGC) to prevent unexpected electrochemical reaction between ionic liquid and electrodes. In this work, we used ionic gel, which is composed of ionic liquid and fluorinated polymer (p(VDF-HFP)), instead of ionic liquid. This ion gel makes handling easy during all measurements. EDLT was completed after lamination of ion gel onto the sample (Fig. 3).

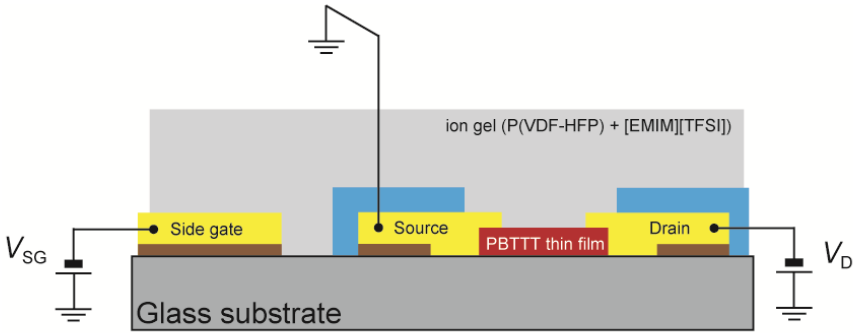

Figure 3. The schematic image of an electric double-layer transistor with PBTTT thin film as a conducting channel.

3-3. Investigation of transport properties

Electrical measurements of EDLT with LB thin film or spin-coated thin film of PBTTT-C14 were performed at room temperature in a glove box which was filled with Ar gas. Before measurements, vacuum dry of the samples was performed for at least three hours to remove water in the samples.

4. Results and discussion

Figures 4 shows the transport properties of EDLT with amorphous PBTTT-C14 thin film fabricated by spin-coated process. Figures 4(a) and (b) show the gate voltage dependence of drain current and gate current, respectively. Increasing drain current with negatively large gate voltage indicates typical p-type operation. At the first gate voltage sweep, electrical conductivity reaches 600 S cm^{-1} (Fig. 4(c)), which is as high as that of chemical doped amorphous PBTTT-C14[6]. However, since second gate voltage sweep, maximum electrical conductivity decreases monotonically. According to our previous research on carrier doping using EDLT with small molecular semiconductor[5], high electrical conductivity is obtained reproductively for multiple gate voltage sweep. Therefore, it is indicated that in the case of amorphous PBTTT-C14, carrier doping by EDLT induces irreversible damages to amorphous PBTTT-C14 structure, resulting in carrier localization. Based on the above discussion, in the hole carrier doping using EDLT with amorphous PBTTT-C14, intercalation of anion of ionic liquid occurs and electric double-layer between ionic liquid and PBTTT-C14 surface is not formed. The

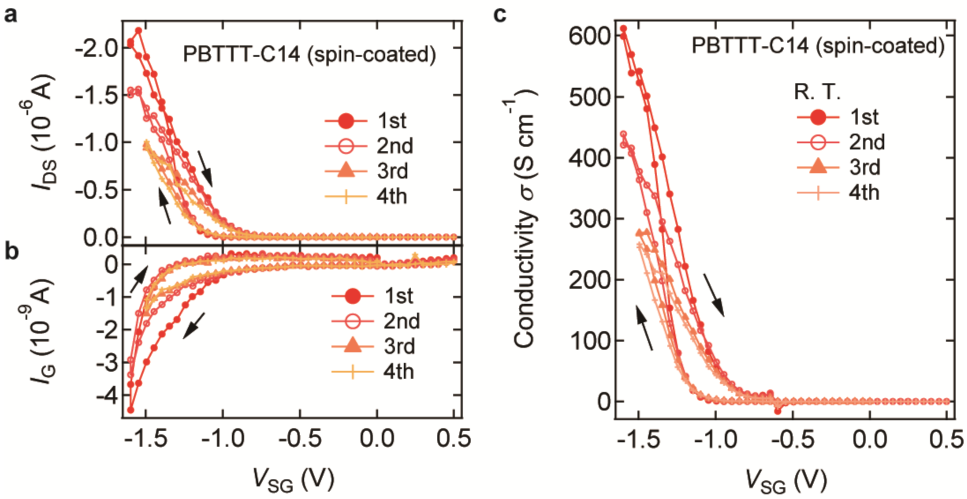

Figure 4. Transport properties of spin-coated PBTTT EDLT. Side-gate voltage dependence of drain current I_{DS} (a), gate current I_G (b), and four-probe conductivity σ (c).

structural disorder induced by anion intercalation results in decreasing charge carrier mobility and electrical conductivity.

Figures 5 shows the transport properties of EDLT with LB thin film of PBTTT-C14. Maximum electrical conductivity obtained at first gate voltage sweep is 630 S cm^{-1} as high as that of spin-coated amorphous PBTTT-C14 thin film. Note that whole thickness is considered for calculation of conductivity. As opposed to amorphous PBTTT-C14 film, electrical conductivity does not decrease even for multiple gate voltage sweep. It indicates that as for EDLT with LB thin film, electric double-layer forms properly at the interfaces between ionic liquid and PBTTT-C14 and charge carriers are induced electrostatically.

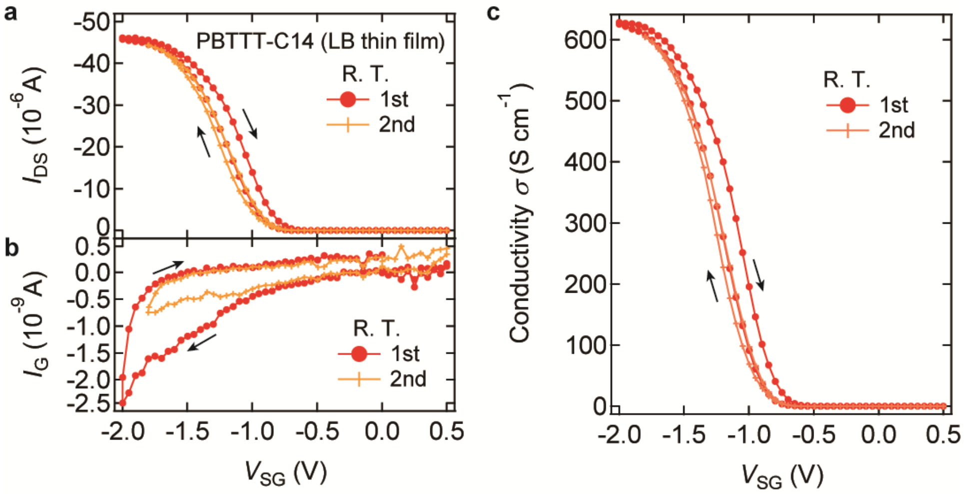

Figure 5. Transport properties of aligned PBTTT EDLT. Side-gate voltage dependence of drain current I_{DS} (a), gate current I_G (b), and four-probe conductivity σ (c).

PBTTT-C14 has two alkyl side chains per monomer unit, leading to enough void spaces to store dopant molecules when chemical doping is performed. In this work, to investigate the utility of electrostatic carrier doping using EDLT for various polymer semiconductors, we attempted the carrier doping into another polymer, poly(2,7-bis(3-alkylthiophen-2-yl)naphtho[1,2-*b*:5,6-*b′*]dithiophene (PNDTBT-4C16, Fig.6(b), (d)). PNDTB-4C16 has four alkyl side chains per monomer unit. Therefore, PNDTB-4C16 has little void spaces and cannot be doped chemically. Actually, comparing to the polymer PNDTB-C20 (Fig. 6(a), (c)) which has the same backbone as PNDTB-4C16 but has only two alkyl side chains per monomer unit, while PNDTB-C20 can be doped chemically and get good electrical conductivity 183 S cm^{-1}, PNDTB-4C16 cannot be doped chemically, resulting in low electrical conductivity 0.4 S cm^{-1} [7].

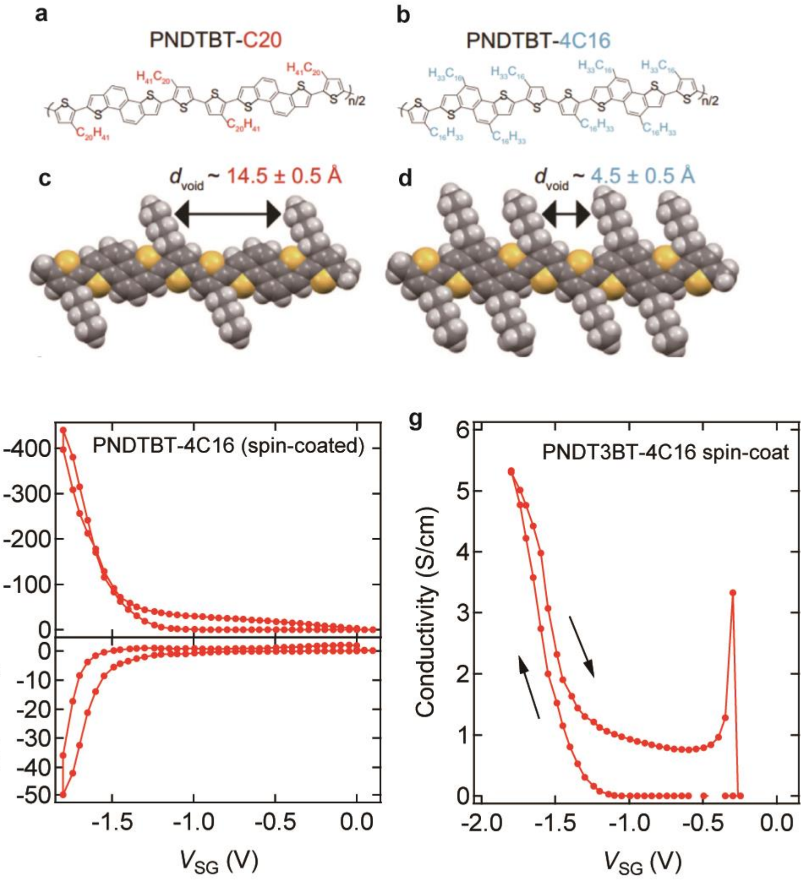

Figure 6. Chemical structure of (a), (c)PNDTBT-C20 and (b), (d)PNDTBT-4C16 quoted from ref. [7]. (e), (f) and (g) Transport properties of spin-coated PNDTBT-4C16. Side-gate voltage dependence of drain current I_{DS} (e), gate current I_G (f), and four-probe conductivity σ (g).

PNDTB-4C16 thin film was fabricated by spin-coating. So, PNDTB-4C16 thin film in this work is basically amorphous. Figures 6 (e)-(g) show the transport properties of EDLT with PNDTB-4C16 thin film. Maximum electrical conductivity reaches 5.3 S cm^{-1}, which is ten times higher than chemical doped PNDTB-4C16. Note that whole thickness is considered for calculation of conductivity. Considering that it is difficult to dope chemically into PNDTB-4C16, *i.e.*, PNDTB-4C16 does not have enough void spaces to store small molecules, charge carriers in the case using EDLT are induced electrostatically due to formation of electric double-layer at the interfaces between ionic liquid and PNDTB-4C16.

5. Conclusion

In conclusion, we fabricated electric double-layer transistors with spin-coated amorphous PBTTT-

C14 thin film, LB aligned PBTTT-C14 thin film and PNDTB-4C16 amorphous film respectively and tried to induce charge carriers electrostatically into each polymer semiconductors. The comparison between the spin-coated PBTTT films and the aligned films by the LB method shows that it is possible to induce carriers electrostatically when the proportion of coverage of crystalline area increases in polymer thin film. Experiments using PNDTBT-4C16, a polymer semiconductor with no void spaces for storing dopant molecules, yielded values of electrical conductivity ten times higher than those reported for chemical doping, suggesting that when dopants cannot be stored in the bulk, an electric double layer is formed on the semiconductor surface and carriers can be induced electrostatically. The results of PNDTBT-4C16 suggest that the formation of an electric double-layer on the semiconductor surface also occurs in the oriented film of PBTTT by the LB method. Once the electric double-layer is formed, the induced carriers are distributed on the surface and form a two-dimensional hole system. Since the LB film is not perfectly crystalline, the amorphous regions between adjacent crystalline regions enhance the localization of the carriers. So, it is expected that the transport phenomenon of the two-dimensional hole system will be observed by fabricating a larger crystalline region or reducing the channel size to the crystalline region size.

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