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Robust Hole Transport in a Thienothiophene Derivative toward Low-cost Electronics

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A new p-type organic semiconductor, bis(hexylthiophenyl)-thienothiophene, was synthesized and evaluated for its transport characteristics. A robust hole transport was observed even on bare SiO_2/Si and on flexible substrates under dark–air conditions. The discovered characteristics reduce the surface-preparation necessary for device fabrication for low-cost electronics.

Recently, organic semiconductors have been extensively studied for practical use in electronic devices. In particular organic thin-film transistor (OTFT) is a key device for the realization of plastic electronics. Stable flexible OTFT are required for flexible displays, radio frequency identification tags, and large-area sensors at low cost.[1]

One of the advantages in plastic electronics is providing low cost flexible circuits. A simple procedure to fabricate OTFT is very important for reducing cost. Besides this, the surface energy of gate-insulators commonly affect on the film morphology of organic semiconductor layer, in which the transport performance is drastically changed with the grain boundary population. Various SAM preparations therefore have been proposed to improve transport performance.[2] For realizing the plastic logic circuits, a thin uniform gate-insulator is indispensable to form the OTFT on a film. Control of the surface energy of the gate-insulator is also another requirement related to the surface energy control.

Air stability of organic semiconductor is another key factor for plastic electronics. Air-stable organic semiconductors will accelerate the development of plastic electronics by allowing use under ambient conditions. Related to this, several types of sophisticated air-stable organic semiconductors have been synthesized and evaluated in the recent past.[3] From a manufacturing point of view, a small number of synthesis step is highly favorable for chemical vendors. In particular, a simple π-conjugation system in the molecule providing a relative large band gap is highly desirable. Wide band-gap molecules are candidates to possess intrinsic air-stability due to the lower energy level of the highest occupied molecular orbital (HOMO).

Poly(2,5-bis(5-alkylthiophen-2-yl)thieno[3,2-*b*]thiophene) (pBTTT) is a well-known air-stable polymer showing relatively high hole transport performance.[4] Although the base unit of this polymer is a better candidate for an air-stable oligomer compared to quaterthiophene derivatives, there are no reports of the transport performance of this type of compound at the present stage.[5]

In this report, a p-type organic semiconductor, 2,5-bis(5-hexylthiophen-2-yl)thieno[3,2-*b*]thiophene (BHT-TT) was synthesized (Figure 1). It was revealed that the hole transport of BHT-TT is quite stable independent of the surface preparation of gate-insulator, by which the SAM process can skip from the fabrication procedure. Air-stability of the compound was also confirmed by the continuous measurement in dry air atmosphere in the dark.

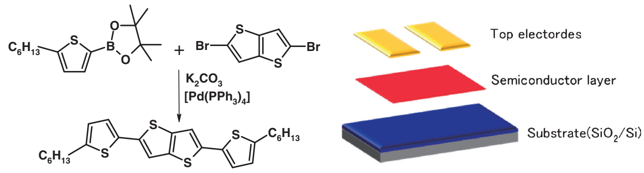

Figure 1. Reaction scheme and chemical structure of BHT-TT and the Si-based device structure.

BHT-TT was synthesized by the Suzuki–Miyaura coupling.[6] The detailed procedure is given as Supporting Information (SI).[7] A thermally grown 300 nm thick SiO_2 on highly p-doped Si wafer was used as SiO_2/Si substrate. SiO_2 surface was washed by ammonium hydroxide/hydrogen peroxide/water mixture, by which strong hydrophilic surface (hereafter referred as OH substrate) was prepared. The OH surface was transformed to a hydrophobic surface with silane coupling agents to provide ODTS or HMDS substrate.[2] Bare SiO_2/Si, and PMMA-coated Au/poly-(ethylene naphthalate) (PEN) film was also used as substrate. The detail preparation of the flexible device is described in SI.[7] An organic semiconductor layer was thermally deposited under 2×10^6 Torr. Au top-electrodes were deposited through a Ni shadow mask to form source and drain with 20 µm channel length (L) and 2 mm channel width (W).

Electronic characteristics were measured in vacuo. Then the device was moved into a vial half-filled with silica gel to investigate the stability in dry air under dark conditions. Another one was placed in ambient air by wrapping in Al foil to investigate the stability in the presence of ambient moisture. Transistor characteristics were measured with a system source meter (Keithley 2612). OTFT parameters were analyzed to compare the substrate effect on the transport performance of the resulting semiconductor. The transfer characteristics are analyzed by a conventional equation at saturated given by eq 1, here, μ, V_{th} and C_{ins} denote field-effect mobility, threshold voltage and capacitance of gate-insulator per unit area.

$$\sqrt{I_{DS}} = \sqrt{\frac{W}{2L}\mu C_{ins}}(V_{GS} - V_{th}) \qquad (1)$$

In this study, $10\,nF\,cm^{-2}$ was used for SiO_2/Si. For flexible devices, C_{ins} was directly measured by the capacitance of Au/

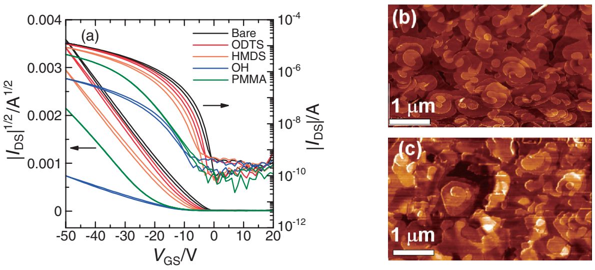

Figure 2. (a) Transfer characteristics of OTFTs with various surfaces and AFM images of BHT-TT on (b) bare and (c) OH substrates.

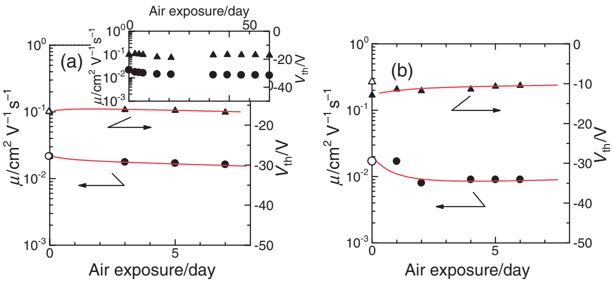

Figure 3. Duration of μ and V_{th} in (a) dried (RH 5%) and (b) ambient (RH 30%) dark–air conditions.

PMMA/Au fabricated on the same substrate,[8] being around 6 nF cm^{-2}.

Ionization potential was evaluated in a BHT-TT film. With photoelectron yield spectroscopy and absorption spectra, HOMO and LUMO levels of BHT-TT were estimated to be 5.2 and 2.5 eV, respectively. This HOMO level is suitable for hole injection from Au (5.1 eV).

Fine p-type output characteristics of OTFT with BHT-TT were found,[7] indicating that the BHT-TT is intrinsically a hole transport organic semiconductor. Figure 2 compares the transfer characteristics of OTFTs fabricated with various surface preparations of SiO_2/Si substrate. As shown in this Figure, all the hydrophobic substrates provide quite similar hole-transport characteristics. Although both the hole mobility (μ) and V_{th} decrease in the OTFT fabricated on OH substrate, hysteresis free characteristics were still observed consistently. The findings indicate the robust hole transport of BHT-TT in any surface preparation.

All the FET parameters of the OTFTs with various surfaces are essentially similar.[7] Even on the flexible substrate, μ is almost the same although a little increase of V_{th} was observed. In particular, transport performance found in the bare substrate device was rather superior to those on the hydrophobic substrates, indicating that the conventional SAM need not be prepared on the substrate for BHT-TT semiconductor layer.

Figures 2b and 2c show the AFM images of BHT-TT deposited on bare and OH substrates, respectively. BHT-TT films deposited on bare (RMS (root mean square): 1.7 nm) and on HMDS (RMS: 1.9 nm) substrates display quite similar morphologies in their grain size, grain shape, and roughness as shown in SI.[7] In particular, spiral-shape grains with similar size were observed for all the AFM images even on the OH substrate. On the contrary, a quite rough surface (RMS: 6.9 nm) was observed on the OH substrate. This indicates that the hydrophilic surface improves the vertical growth of the spiral grain, possibly due to the intrinsic hydrophobicity of BHT-TT. The difference of surface roughness on substrate corresponds to the decrease of hole transport on OH substrate.[7] The similar spiral-grain observed in AFM images is the most notable feature of BHT-TT with similar mobilities on various substrates except OH. However the similarity of the grains provides a limit of mobility by the grain boundary. It is one reason for the small mobility compared to that in pBTTT.[4] The findings indicate that bare SiO_2/Si substrate is sufficient for fabricating OTFT, as an advantage for reducing the number of preparation steps.

The transfer characteristics were well conserved with a small hysteresis even after 70 days exposure to dry air protected from light (less than RH 5%).[7] As shown in Figure 3a, quite a small change in both μ and V_{th} was found during the period of measurement. In ambient air in the dark (around RH 30%), a small decrease in μ was found as shown in Figure 3b. V_{th} was rather shifted to a lower voltage, possibly caused by a slight doping by ambient moisture. Even under the ambient air, the device shows a small hysteresis in the transport characteristics,[7] showing the robust hole transport characteristics of BHT-TT. This is also consistent with the hysteresis-free transport on OH substrate.

In summary, the hole transport characteristics of a newly synthesized BHT-TT were evaluated on SiO_2/Si substrate with various surface preparations and on flexible substrates. OTFT characteristics were preserved with bare SiO_2/Si substrate even after exposure to an air atmosphere in the dark, indicating the robust hole transport. This will be caused by the similar grain growth for any substrates observed in AFM images.

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